Carbon–Carbon Bond-Forming Reactions Promoted by Trivalent Manganese

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1. Introduction

In the past decade, major advances in radical chemistry have been made by the use of transition metals. This field has witnessed impressive accomplishments, and tremendous potential lies ahead. There are many transition metal-mediated methods for producing radicals, including (a) oxidation of C—H bonds or unsaturated fragments by transition metals in higher oxidation states, (b) reduction of C—X bonds or unsaturated moieties by transition metals in lower oxidation states, and (c) homolysis of metal–carbon σ bonds. Redox methods for generating radicals are well elaborated and utilize transition metals in different oxidation states, (1-6) such as Mn(III), Ti(IV), Co(III), Cu(II), Fe(II), Ag(II), Pb(IV), Ce(IV), Mn(IV), V(V), Ag(I), Cu(I), Co(II), Fe(II), V(II), Cr(II), Nb(IV), and Ru(II). In the vast majority of these reactions, transient organometallic species have not been either isolated or identified. Their tentative structures have been proposed, in some cases based solely on chemical logic. Accordingly, the mechanisms of these multistep interactions have not been fully established. Particularly lacking is a clear recognition of those elementary steps that occur inside the ligand sphere of the transition metal.

In comparison with traditional methods of radical generation, (5-8) redox initiators demonstrate remarkable regioselectivity and are especially efficient in polyfunctional organic compounds. Furthermore, new types of radicals, inaccessible by traditional approaches, can be successfully generated. The main difference lies in the multiple roles that metal oxidants play during the reaction, namely, one-electron transfer between proradical and transition metal to produce radical species, followed by redox interaction with intermediate adduct radicals. For this reason, metal-mediated reactions differ significantly from those of peroxide- or light-initiated processes.

Trivalent manganese occupies a rather unusual place among metal oxidants in higher oxidation states and is particularly useful in this field. Numerous novel regio-, chemo-, and stereoselective synthetic methods have been developed in both inter- and intramolecular reactions, and their applicability to the construction of complex natural and biologically active compounds has been demonstrated. Despite its growing significance for synthetic chemistry, manganese(III)-mediated reactions have not been comprehensively reviewed in recent years. Reviews by de Klein, (9) Snider, (10) and Melikyan (11) have discussed selected aspects of Mn(III) chemistry; limited coverage is also available in other papers as part of larger topics. (3-6)

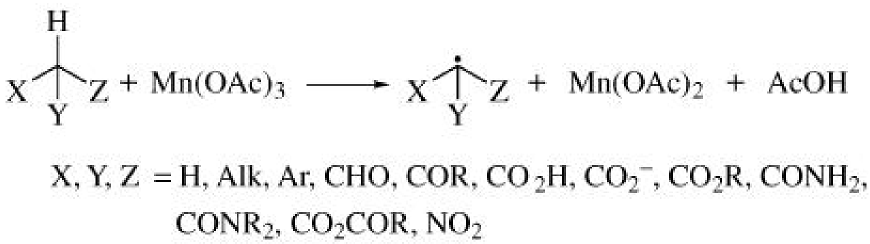
The subject of this chapter is the radical carbon–carbon bond-forming reaction induced by trivalent manganese derivatives such as $Mn(OAc)_3$,$Mn(acac)_3$, and $Mn(pic)_3$. It includes the oxidative generation of α - or α , α -dioxoalkyl or alkyl radicals and their subsequent addition to unsaturated moieties. Both inter- and intramolecular processes are discussed, with special emphasis on the regio-, chemo-, and stereoselectivity issues, as well as natural products syntheses. A comprehensive representation of experimental data is accompanied by critical analyses to give a reader adequate ideas of the current status of this field, of what and can be achieved, of what can be anticipated in any new reaction or in any new application of a known process, and of predictions that can be made based on the collective accumulated knowledge. Discussions of oxidations of unsaturated compounds (9, 12, 13) such as arenes and alkenes, of the α -acetoxylation (14, 15) and α -chlorination (16, 17) of ketones, and of chlorination of alkenes (18, 19) are beyond the scope of this review.

Throughout the chapter the following abbreviations are used: LTR–ligand transfer reaction, (20, 21) transfer of an atom or group to a radical center of an adduct radical, presumed to be proceeding in the transition metal ligand sphere; ETR–electron transfer reaction, (20, 21) transfer of an electron from a radical center to a transition metal ion; HAA–hydrogen atom abstraction, (7) a propagation step in traditionally initiated radical reactions.

2. Mechanism

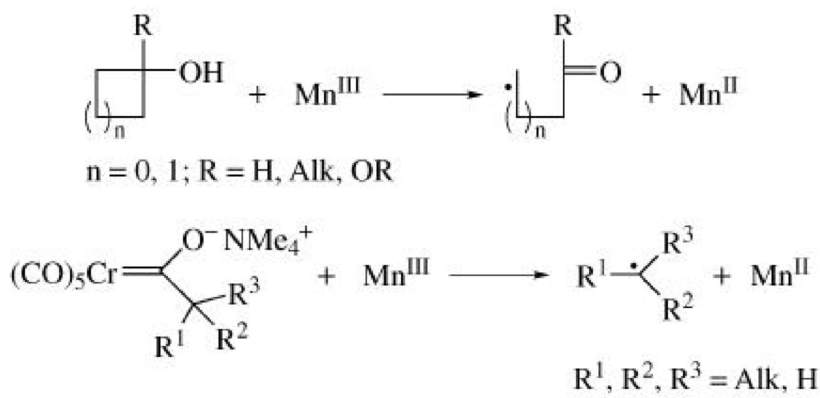
2.1. Generation of Radicals

The initial step of a radical bond-forming reaction is considered to be generation of a carbon-centered radical by one-electron oxidation of the carbonyl component (Eq. 1). The stoichiometry of the process requires an equimolar amount



(1)

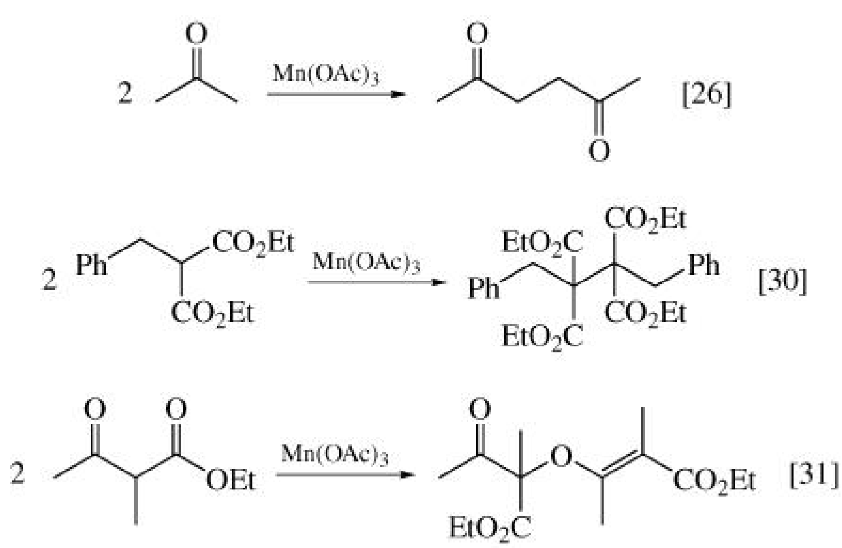
of metal oxidant. The ease of oxidation depends upon the nature of the substituents X, Y, and Z, and is greatly facilitated by carbonyl or nitro groups in the α position. Radicals with one activating group (aldehydes, ketones, monocarboxylic acids, carboxylic acid anhydrides, and nitroalkanes), two activating groups (β -diketones, β -ketoesters, β -ketocarboxylic acids, malonic acid and its half- and diesters and diamides, cyanoacetic acid, cyanoacetamide, α -acyl- γ -lactones, β -ketophosphonates, β -ketosulfoxides, and β -ketosulfones) or three activating groups (ortho esters) are generated efficiently from the corresponding C - H precursor. The greater the number of activating groups, the faster is the radical generation process. For example, the generation of radicals from β -diketones and β -ketoesters occurs smoothly at room temperature, whereas monoketones and monocarboxylic acids require temperatures up to 120–140°. (11) The mechanism of radical generation is not well understood. (9, 11) In recent years, novel methods for generating alkyl radicals with Mn(III) have been developed, utilizing as radical precursors cyclopropanols (22, 23) and cyclobutanols (24) or Cr(0) complexes (Eq. 2). (25)



(2)

Direct experimental proof for the formation of radicals in Mn(III)-induced oxidations of carbonyl compounds is lacking. Indirect evidence for radical intermediates is the formation of dimers and the regioselectivity of aromatic substitution.

Dimers from mono- and dicarbonyl compounds attributable to radical couplings have been isolated in several cases. Ketones (26) and carboxylic acids (27, 28) tend to produce C - C dimers, whereas with dicarbonyl compounds both C - C (29-31) and C - O (31) dimers have been isolated (Eq. 3).

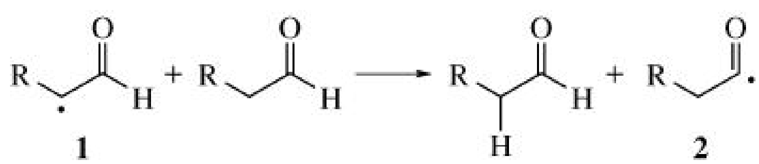


(3)

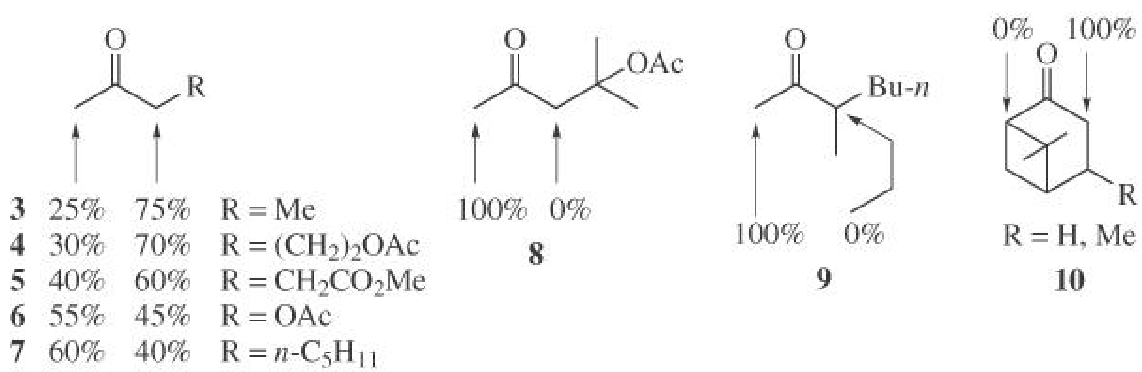
The regioselectivity of aromatic substitution reactions, (i.e., the high level of *ortho*-substituted products), is consistent with the formation of free radicals. (32) In particular, carboxymethylation of chlorobenzene and toluene affords substitution products containing 30–46% and 39–58% of *ortho* isomers, respectively. (27) In the analogous reaction, anisole produces 78% of the *ortho*-substituted product. (33) Acetonylation of monosubstituted benzenes (34, 35) and nitromethylation reactions (36) show a similar pattern. For steric reasons, this is not the case with di- and tricarbonyl compounds. (37-40)

The regioselectivity of radical generation is crucial with unsymmetrical carbonyl compounds. One of the major advantages of transition metals, in particular trivalent manganese, is the highly selective formation of radicals that are not accessible under "traditional" conditions, for example, with peroxides. (7, 8)

Oxidation of aldehydes with $Mn(OAc)_3$ under homogeneous conditions generates α -formyl alkyl radicals **1**, which can add to olefins (vide infra). In the absence of solvent in a heterogeneous process, acyl radicals **2** are produced from α -formyl alkyl radicals by intermolecular H-atom transfer. (41-43)



Unsymmetrical ketones can generate isomeric α -oxoalkyl radicals by competing oxidation of the primary, secondary, or tertiary C - H bonds. Ketones **3–7**, containing methyl and methylene groups, react with alkenes with low selectivity. (44-47) The exclusive reaction of the methyl group in ketone **8** may reflect the steric inaccessibility of the methylene group. (45) The unreactivity of the methyne group in ketone **9** toward the metal oxidant may also be due to steric hindrance. (46) The highly regioselective oxidation of the methylene group in ketone **10** might be due to the relative instability of the isomeric bridgehead radical. (46a)



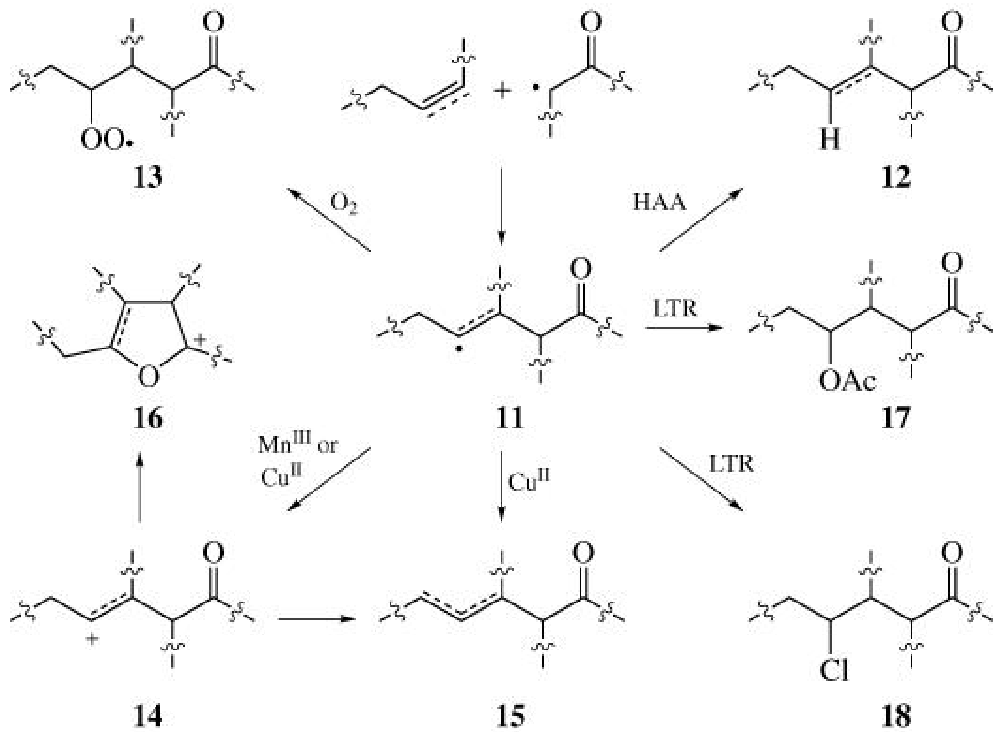
It is important to note that the ratio of addition products is not necessarily the same as the relative rates of generation of isomeric radicals, since the rates of their addition to substrates may be different for different radicals. For example, the oxidation of 2-butanone with $Mn(OAc)_3$ in the absence of alkenes produces 1- and 3-acetoxybutan-2-ones in a ratio of 2.5:1, indicating preferential oxidation of the methyl group, (48) as opposed to the 1:3 ratio of addition of isomeric radicals to an olefin. (44)

Oxidation of β -dicarbonyl compounds and their analogues occurs regioselectively at internal methylene or methyne groups because of their higher acidity and enolizability compared with competing methyl groups.

2.2. Adduct Radicals: Formation and Reactivity Patterns

Educt radicals generated in the presence of “matching” unsaturated substrates may attack across multiple bonds to produce adduct radicals **11**. (11) These are short-lived transient intermediates in radical (cyclo)addition reactions, and their direct detection and spectral characterization still remain a challenge for “radical” chemists. The synthetic result and selectivity of the process depend upon the reactivity patterns of adduct radicals; their transition to stable organic products can occur in several ways (Eq. 4). The normal pathway (7, 8) is represented by H-atom abstraction, which results in the formation of the more saturated derivatives **12**. For both alkenes (Tables I and II) and alkynes (Table XII), the corresponding HAA-products **12** have been isolated, resulting from atom transfer to alkyl and vinyl adduct radicals, respectively. (44, 49, 50)

Adduct radicals **11** can be trapped with molecular and redox radical scavengers, enhancing the synthetic potential of the reaction as well as providing experimental proof for the existence of free adduct radicals. Trapping experiments have been accomplished with molecular oxygen as a scavenger and β -dicarbonyl compounds as reagents. (51-56) In most cases, peroxy radicals **13** attack acetyl groups intramolecularly to produce cyclic peroxides (Eq. 5). In the absence of



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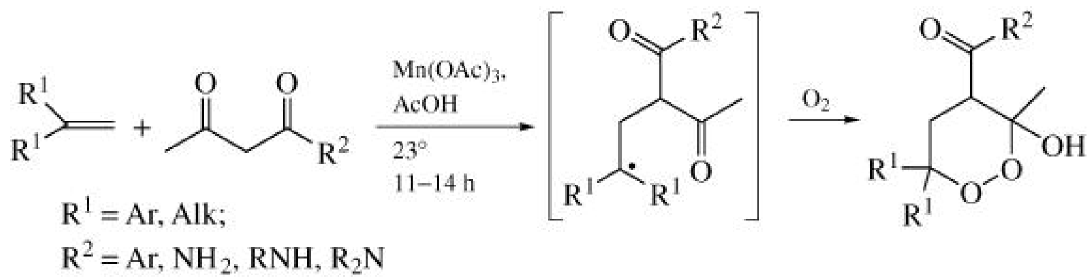


(5)

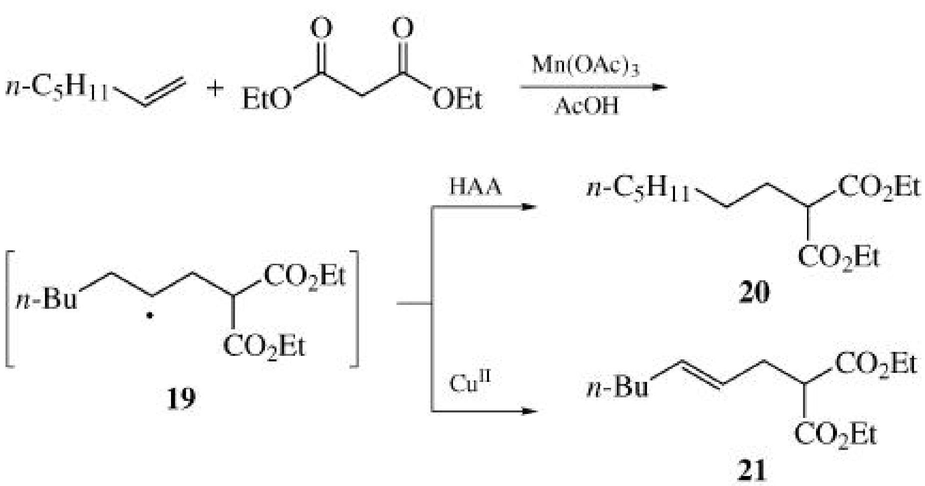
acetyl groups, the corresponding hydroperoxides have been isolated. (54) An alternative radical trap is carbon monoxide, which is highly efficient in both inter- and intramolecular processes (Table XXXIX).

Adduct radicals **11** can be oxidized by Mn(III) or Cu(II) ions to the corresponding carbocations **14**. The ease of oxidation depends dramatically upon the nature of substituents and functional groups α to the radical center. Carbocations **14** undergo β elimination to produce β , γ - and/or γ , δ -unsaturated derivatives **15**, or intramolecular cyclizations to carbonyl-containing groups such as acyl, carboxy, alkoxycarbonyl, or unsaturated fragments like double bonds. The cyclization produces cyclic carbocation **16**, which forms β -elimination products (dihydrofurans, furans, or γ -lactones), undergoes tandem (poly)cyclizations, or reacts with nucleophiles. (57)

Alternative pathways for adduct radicals **11** involve ligand transfer from the Mn(III) complex to alkyl or vinylic radical centers. Numerous examples of AcO group (48, 58-62) and Cl atom (50, 63, 64) transfers have been reported; the formation of LTR products **17** and **18** might occur via carbocations **14**.

Cyclizations on multiple bonds and aromatic rings represent an additional and synthetically useful pattern for adduct radicals **11**. This pattern has been demonstrated by numerous intramolecular (Tables XXIV–XXXI) and tandem cyclizations (Tables XXXII–XXXVIII), as well as by addition–cyclization processes (Table XXXIII).

One of the most crucial points in the design of Mn(III)-mediated reactions is the choice of metal oxidant, in particular, the use of either Mn(III) complexes alone or in combination with catalytic or equimolar amounts of $Cu(OAc)_2$. The latter is widely utilized in intermolecular functionalization of unsaturated substrates with aldehydes, (65) ketones, (44, 45, 49, 59, 66, 67) carboxylic acids, (68) β -dicarbonyl compounds, (45, 57, 69-78) dicarboxylic acid derivatives, (64) and nitroalkanes, (79) as well as in addition–cyclization reactions, (80-82) intramolecular (83-97) and tandem cyclizations, (56, 86-88, 91, 94, 96, 98-103) and polycyclizations. (104) The major incentive for using a Cu(II) salt as a cooxidant is to improve the selectivity of the reaction or to redirect it toward the formation of new products. This approach is exemplified by the interaction of 1-heptene with diethyl malonate. (64) In the absence of $Cu(OAc)_2$, addition of the bis(ethoxycarbonyl)methyl radical to the double bond produces adduct radical **19**, which undergoes H-atom abstraction to afford saturated diester **20**. To the contrary, Cu(II) ions efficiently trap transient radicals **19** by oxidation to γ , δ -unsaturated derivative **21**.

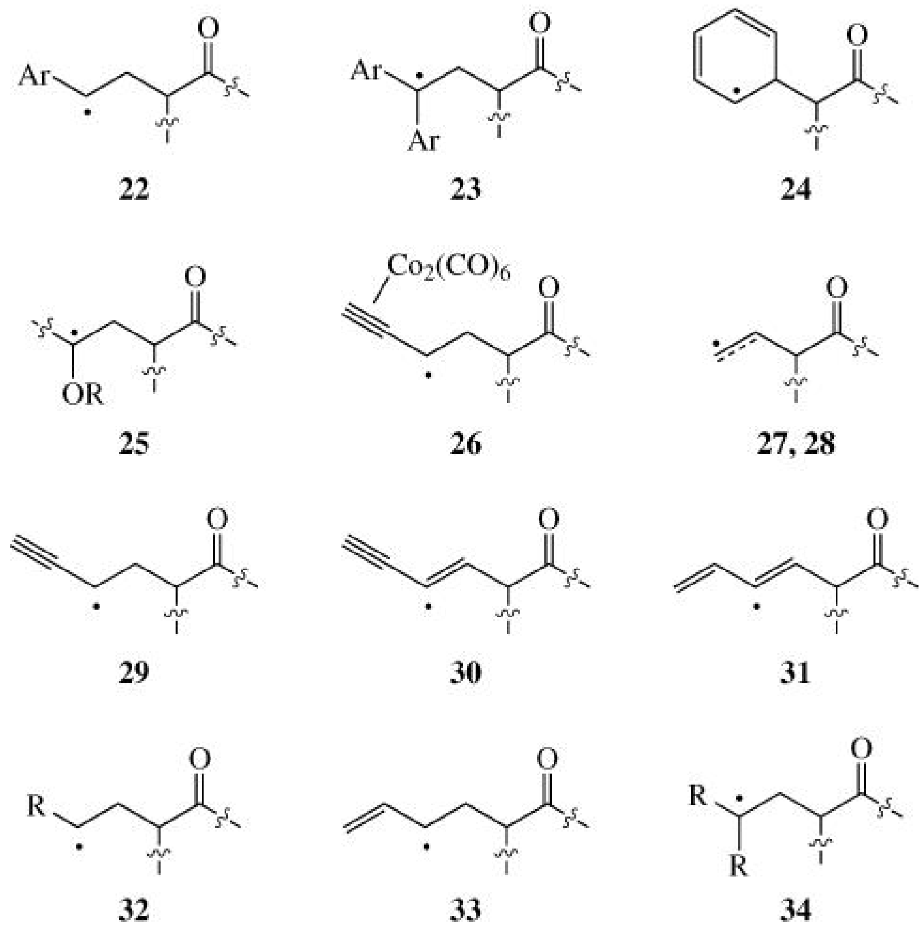


In combination with trapping experiments utilizing molecular oxygen, (51-56) Cu(II)-modified reactions provide sound experimental evidence for the existence of free adduct radicals that break away from the manganese cluster prior to conversion to final products. The striking effect of Cu(II) acetate is caused by its ability to oxidize alkyl radicals to carbocations; (21, 58) the rate of this oxidation is 350 times greater than that with $Mn(OAc)_3$. (58) This is the reason that $Cu(OAc)_2$ is used in reactions where Mn(III) ions are not sufficiently powerful to oxidize intermediate radicals. In some cases, catalytic amounts of Cu(II) ions are sufficient to achieve the desired result, but the rate of oxidation with $Cu(OAc)_2$ also changes, depending on the structures of adduct radicals. In these cases, the use of equimolar amounts of cooxidant, or even a several-fold excess, might be necessary to obtain good yields.

The choice of metal oxidant still remains empirical, although a large number of examples allow one to draw some conclusions from the structures of adduct radicals as to which might or might not require the use of an oxidant stronger than $Mn(OAc)_3$. Such generalizations are useful for the design of new reactions.

The most common types of adduct radicals are shown in Eq. 6. Intermediates **22–26** constitute a first group of adduct radicals that are oxidized by $Mn(OAc)_3$. Synthetically this means that in the presence of $Mn(OAc)_3$ an oxidative cyclization, elimination, or ligand-transfer reaction can occur, but not H-atom abstraction. Another distinctive feature of these reactions is that the addition of $Cu(OAc)_2$ does not change the distribution of products or appreciably affect yields. The common structural feature of adduct radicals **22–26** is the effective stabilization of their corresponding carbocations by conjugation with unsaturated moieties (**22–24**), by interaction with unshared electron pairs of an α -substituent (**25**), or with a π -bonded metal cluster (**26**). This stabilization decreases the ionization potential of the radicals, thus enabling Mn(III) ion oxidation to carbocations.

The second group of adduct radicals (**27–31**) are oxidized by $Cu(OAc)_2$ but not by $Mn(OAc)_3$. These intermediates are stabilized less than those in the first group. In the absence of Cu(II) ions, they produce either H-atom abstraction products (**27**, **28**) or undergo polymerization (**29–31**). The introduction of a more powerful metal oxidant into the reaction results in the formation of oxidative elimination, ligand transfer, or cyclization products.



(6)

Most secondary alkyl (**32**) and allylic (**33**) radicals require the use of $Cu(OAc)_2$, although there are some reports on their partial (58, 105, 106) or even complete (107-109) oxidation with trivalent manganese. Tertiary alkyl radicals **34** are on the borderline between more- and less-stabilized adduct radicals, although they are closer to the first group. There are several reports of their effective oxidation by Mn(III) ions alone, (31, 65, 70, 82, 106, 110, 111) as well as single reports on either partial oxidation (110) or the formation of H-atom abstraction products. (49)

The large number of intermolecular reactions, including the composition of metal oxidants used and product distribution, can be found in Tables I–XXIII. Additional examples are provided by mono- and tandem cyclizations, where $Cu(OAc)_2$ is widely and effectively used to improve the selectivity of the reactions (Tables XXIV–XXXVIII).

A word of warning is relevant here. Although experimental data on the formation of free radicals and free-adduct radicals are well documented, any generalizations should be made with extreme caution. First, whatever is shown for a certain type of unsaturated substrate and carbonyl compound might be incorrect for even a closely related type of interaction. Second, the formation of free educt radicals in the absence of unsaturated substrates does not necessarily mean that this is the case when a substrate is present in the reaction mixture, since C - C bond formation can still occur within the metal–ion ligand sphere. (12, 31) Third, dimerization or trapping reactions indicate only that there is a certain fraction of scavengable radicals, but they do not prove that all products are formed via radicals.

2.3. Kinetics

Kinetic studies of Mn(III)-mediated reactions are directed toward acquiring in-depth understanding of the process and resolution of the most crucial issues in the multistep mechanism. Among the latter are the following. Are keto or enol forms oxidized by metal oxidant? Does the interaction of educt radicals with unsaturated substrates occur within the ligand sphere of the metal? What is the rate-determining step—enolization, formation of the metal-complexed (or metal free) educt radical, or C - C bond formation? Are products derived from metal-complexed or kinetically free adduct radicals? The available kinetic data shed light on only a few of these issues.

The oxidation of aldehydes with $Mn(OAc)_3$ produces α -formyl alkyl radicals, which may be converted into acyl radicals by intermolecular H-atom transfer. (42, 43) The rate-determining step in the oxidation is homolysis of a C - H bond, as established by the high isotopic effect obtained with CD_3CHO . (43) Free radicals are in equilibrium with oxallylic complexes of the metal, thus affecting the regioselectivity of the process. (112) In particular, the formation of α -alkyl substituted aldehydes is attributed to the reaction proceeding in the coordination sphere of the metal. Enolization is believed not to precede the oxidation, since oxidation occurs for nonenolizable aldehydes.

The oxidation of ketones by $Mn(OAc)_3$ occurs via the keto form since its rate is a factor of 10 higher than racemization (43, 113) or isotope exchange. (114) The kinetic isotopic effect for CD_3COCD_3 is 5.8, indicating that α -C - H bond cleavage is the slowest step. (114) Somewhat contradictory results have been obtained in the oxidation of cyclohexanone, where enolization is proposed to precede the oxidation step. (115) The rate-determining step in the interaction of ketones with mono- and binuclear aromatic compounds is complexation of the Mn(III) enolate with the arene and subsequent C - C bond formation within the coordination sphere of the metal. (116)

The oxidation of carboxylic acids is independent of alkene concentration and is directly proportional to their acidity over a range of 16 pK_a units. (117) The rate-determining step is the abstraction of a proton from the bridged acetate followed by electron transfer from the enolate ion to the Mn(III) atom. (12, 117)

This mechanism explains the accelerating effect of acetate anions on the rate of alkene annulation. Control experiments indicate that if the oxidation of acetic acid with $Mn(OAc)_3$ is performed in the absence of alkenes, no succinic acid is formed. (12) The authors concluded that no free carboxymethyl radicals are released and that the formation of the C - C bond occurs within the metal–oxidant ligand sphere. (12) The issue of whether radical dissociation from the metal occurs prior to cyclization is not resolved.

Lactonization of alkenes does not require cooxidant to produce γ -lactones in good to high yields. (11) This observation can be rationalized in terms of an intramolecular cyclization taking place within the Mn(III)–ligand sphere, since free adduct radicals (e.g., **27–29**), and most secondary alkyl (**32**) and allylic (**33**) radicals are not oxidized by Mn(III) ions and thus cannot cyclize on a carboxy group. Although both *cis*- and *trans*-4-octene produce the same ratio of the isomeric γ -lactones (*trans*:*cis* = 3.3:1), (117) this result does not resolve the issue of metal binding to the adduct radicals, since stereomutation could also occur with a Mn(III)-bound adduct radical.

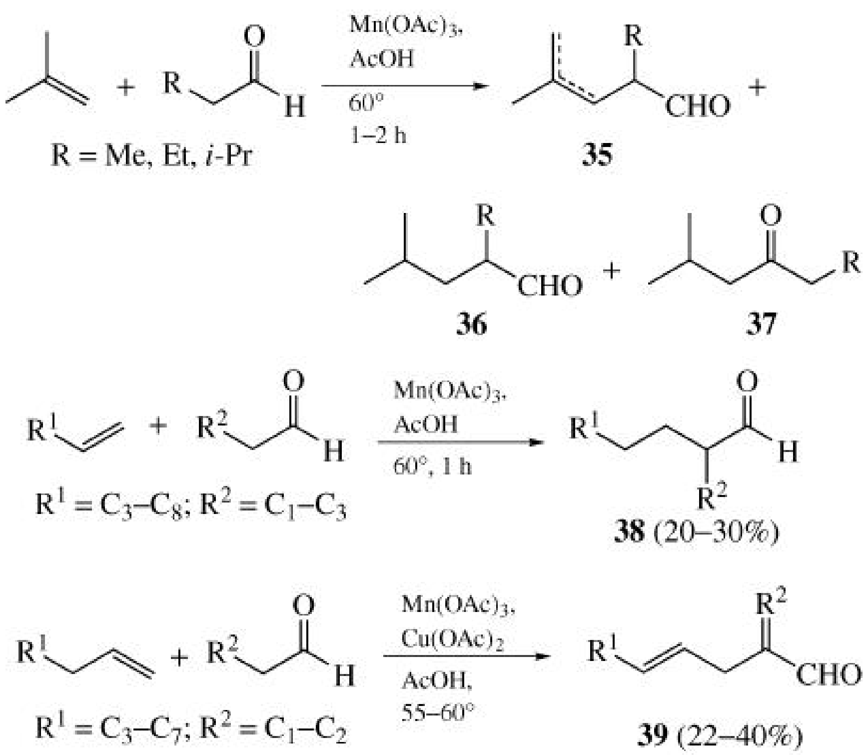
The oxidation of β -ketoesters with $Mn(OAc)_3$ is dramatically accelerated in the presence of unsaturated substrates, (31, 72, 118) indicating that the generation of radicals and C - C bond formation occur within the ligand sphere of the metal. Recent investigation suggests that there is a substantial difference in the behavior of unsubstituted and 2-methyl-substituted acetoacetates. (31) For the former, C - C bond formation within the Mn(III)–ligand sphere is proposed to be the rate-determining step, whereas for the latter the Mn(III) enolate may be produced in the slowest step. In a recent and well-designed comparative study, it has been demonstrated that the nature of the radicals generated by either Mn(III)-mediated oxidation or TBTH-induced atom transfer is the same, (119) thus supporting the existence of free radicals.

3. Scope and Limitations

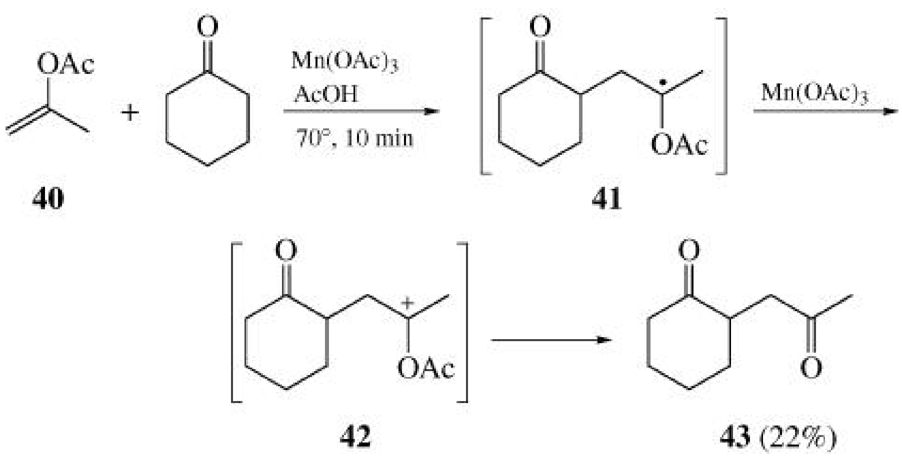
3.1. Intermolecular Reactions

3.1.1. Compounds with One Multiple Bond—Regio- and Stereoselectivity

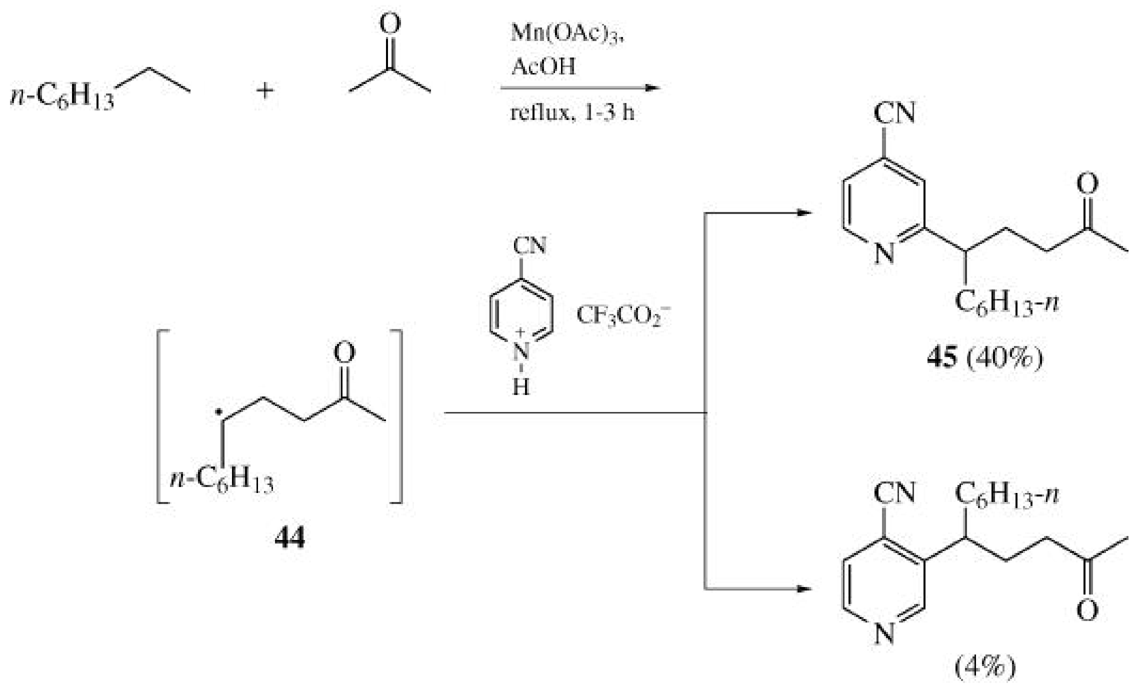
Manganese(III)-mediated reactions of alkenes with aldehydes suffer from low selectivity, separation problems, and moderate yields. The initial step gives rise to two types of adduct radicals formed by the addition of α -formyl alkyl and acyl radicals across the double bond. Their conversion to products occurs by different pathways, that is, oxidative β -deprotonation, H-atom transfer, or AcO-group transfer, depending on the alkene structure. (43) Isobutene-derived tertiary adduct radicals tend more toward elimination, producing β , γ - and γ , δ -alkenals **35**. Their proportion in the product mixture is 50–70%, in addition to the saturated aldehyde **36** and ketone **37**. (110) The introduction of $Cu(OAc)_2$ into the reaction mixture as cooxidant (21, 58, 120) improves both the yield (up to 46%) and selectivity of the process (up to 93% **35**). (110) In contrast to the more easily oxidizable tertiary adduct radicals, secondary radicals favor H-atom abstraction, producing saturated aldehydes and ketones. (41, 42, 121) This method has been made synthetically attractive by optimization to selectively produce α -alkylated aldehydes **38**. (41) In the presence of $Cu(OAc)_2$, secondary adduct radicals undergo regioselective β elimination yielding γ , δ -alkenals **39** on a preparative scale. (122)



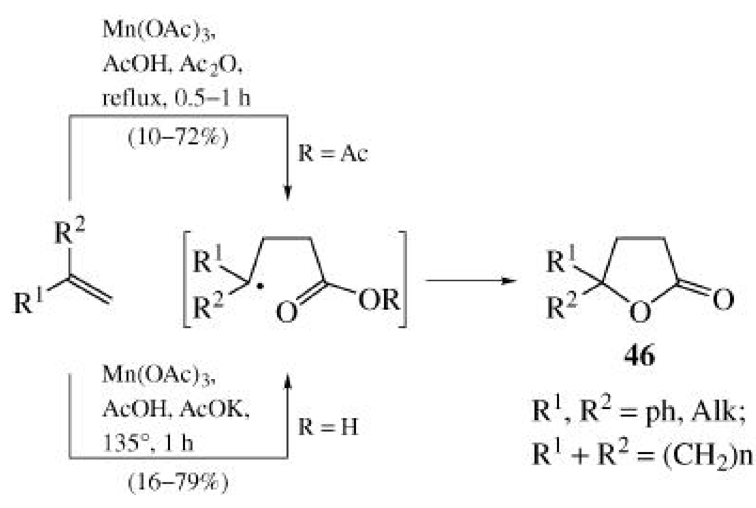
The reactions of alkenes with ketones are mechanistically analogous to those of aldehydes, and include generation of α -oxoalkyl radicals, their regioselective addition to the terminal double bond of alkenes, and subsequent transformation of adduct radicals to afford H-atom abstraction products, isomeric alkenones, and γ -acetoxy ketones (Table II). Both acyclic and cyclic ketones have been used as reagents; terminal alkenes are the most investigated substrates, along with single reports on cycloalkenes. Of practical importance is the telomerization of ethylene when used as an unsaturated substrate. (66, 67, 123) The chain length and terminal functionality depend on the reaction conditions and the presence of Cu(II) additives, producing either saturated (123) or unsaturated (66, 67) telomeric ketones. The nature of the products reflects the reactivity patterns of primary adduct radicals, that is, H-atom abstraction in the presence of $Mn(OAc)_3$ and β elimination or AcO-group transfer mediated by $Cu(OAc)_2$. (120) From the synthetic viewpoint, one of the major achievements of this area is a novel approach to 1,4-diketones using enol acetates as substrates. (46a) The generality of the reaction has been well demonstrated by using acyclic, cyclic, and terpenoid ketones. As shown in the specific example, the addition of an educt radical to the double bond of enol acetate **40** produces adduct radical **41**; the latter is easily oxidized by Mn(III) ions owing to effective stabilization of secondary carbocation **42** by the α -oxygen atom. Subsequent release of the acetyl group yields 1,4-diketone **43**. (46)



The interaction of alkenes with ketones can be converted into conjugated addition by using protonated pyridines as nucleophilic radical traps. (124) Adduct radicals **44** alkylate electron-deficient aromatic rings with high positional α selectivity (9:1), producing pyridine **45** as a major isomer. In a similar manner, but in higher yield, the reaction proceeds with protonated isoquinoline as a radical trap. (124) Although limited success has been achieved with cyclohexene, overall this reaction looks promising and deserves more attention to define further the scope, synthetic utility, and stereoselectivity.



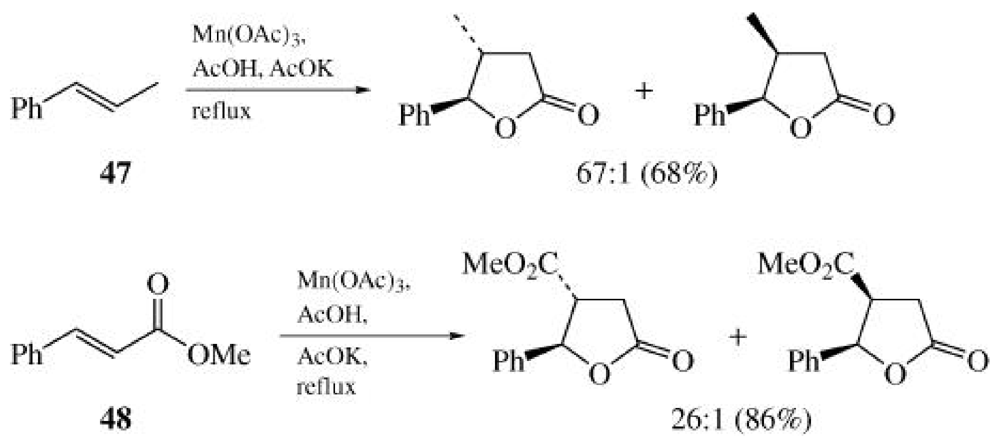
Carboxylic acids, in particular acetic acid, react with alkenes to produce γ-lactones **46** as the major products (Eq. 7). (28, 125) Alternative procedures include the



(7)

use of acetic anhydride (28) and potassium acetate. (125) A good level of understanding has been achieved concerning separate steps of the mechanism (see also Kinetics section). (12, 117) In particular, potassium acetate acts as a base, facilitating the rate-determining deprotonation of bridging acetate ligands, and acetic anhydride is oxidized prior to acetic acid because of its higher acidity (pK_a 18 vs. 25). Yields of γ -lactones are systematically higher with potassium acetate because of the formation of unsaturated and γ -acetoxy carboxylic acids in the presence of acetic anhydride. (117) In some cases, allylic acetates are formed as byproducts, (28, 125) although the selectivity for lactonization is usually very high, that is, the ratio γ -lactone:allylic acetate is 30:1 and 50:1 with methylstyrene and 1-octene, respectively. (125)

The regioselectivity of lactonization is high with terminal alkenes, which are attacked by carboxymethyl radicals at the C_1 carbon atom (Table III). Regioselectivity becomes a critical issue with unsymmetrical di- and trisubstituted alkenes, being governed by the relative stabilities of adduct radicals as well as by steric factors. β -Methylstyrene (**47**) reacts regioselectively, demonstrating the higher stability of the benzylic radical compared to the secondary radical (Eq. 8). (117)



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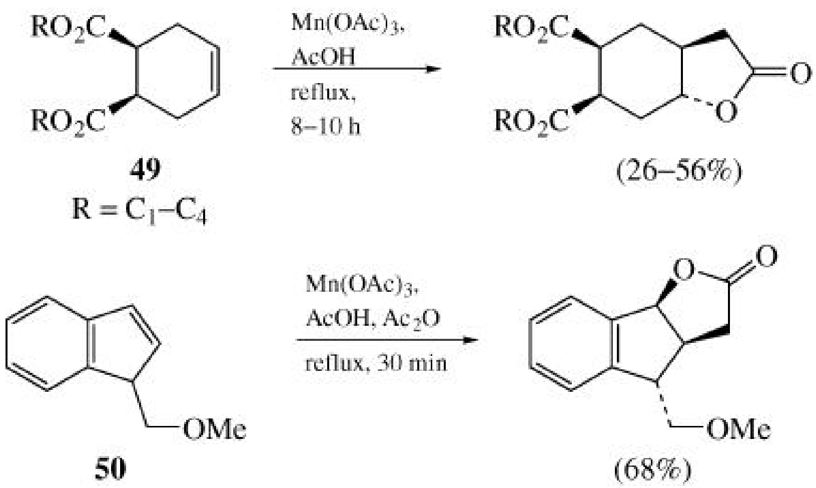
(8)

Analogously, the greater stability of tertiary versus secondary alkyl radicals determines the regioselectivity with 2-methyl-2-pentene (126) and 3-ethyl-2-pentene. (117) Remote differences in the alkyl chains do not substantially affect the addition of educt radicals. (127) In α , β -unsaturated esters, the regioselectivity depends upon the nature of the β substituent. The relative stability of the adduct radicals with α -methyl and α -*tert*-butoxycarbonyl groups appears to be close, resulting in low regioselectivity in the lactonization of *tert*-butyl crotonate. (117) To the contrary, the powerful stabilizing effect of a phenyl group directs the addition of both acetic (117, 128) and chloroacetic (129) acids to ester **48** (Eq. 8). Analogous regioselectivity has been observed with coumarins, although the products are α -acetoxymethyl and α -diacetoxymethyl derivatives. (130)

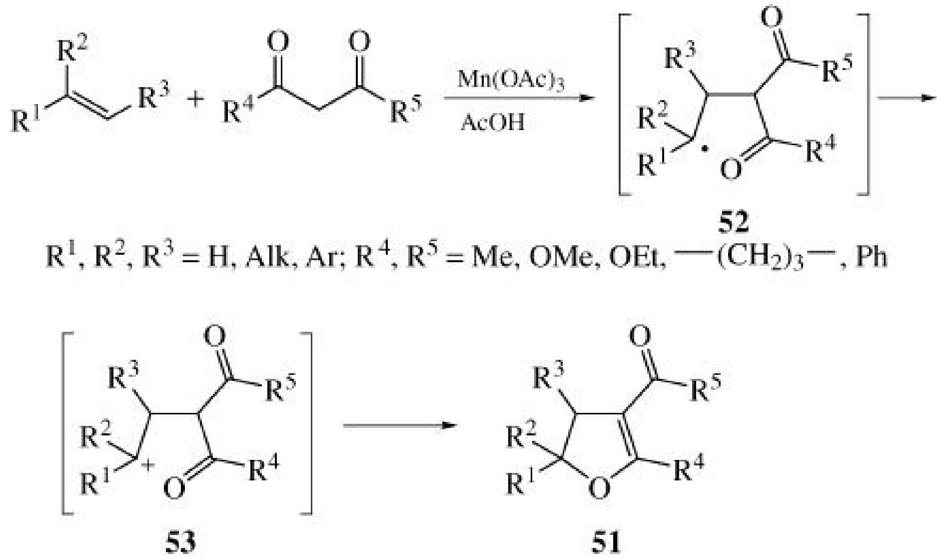
Stereoselectivity is one of the most critical aspects of the annulation reaction. It includes, first, the relative configuration of the "double-bond" carbons, and second, the stereochemical relationship of the latter to the α substituent of the lactone ring. Alkenes and cycloalkenes produce *cis*- and *trans*- γ -lactones in different ratios (Tables III and IV). In particular, substrates **47** and **48** (Eq. 8) represent two examples of highly stereoselective formation of *trans*- γ -lactones (up to 98.5%). (117) *Trans* stereoselectivity might be even higher in the reactions of *cis*-4,5-disubstituted cyclohexene **49** (Eq. 9) and norbornene. (131) It is noteworthy that unsubstituted



(9)

cyclohexene undergoes lactonization with preponderant formation of the *cis* isomer. (117) Exclusive *cis* annulation has been observed with benzofuran, (132) bornene, (133) and indenes, (117, 134) (e.g., **50**). (134) One of the critical points in stereochemical studies is the stereomutation observed in lactonization of *cis*- and *trans*-4-octenes, which results in the formation of the same mixture of isomeric γ -lactones (*trans*:*cis* = 3.3:1). (117) This result excludes a "concerted" mechanism as an option, although it does not address the issue of in- or out-of-ligand-sphere formation of products. Substituted acetic acids and their homologues produce γ -lactones with two (α , γ) or three (α , β , γ) stereocenters. (126, 128, 129) In all cases where stereochemistry is established, the reactions are nonstereoselective, producing mixtures of two or four stereoisomers in similar amounts; (129) the only exception is the lactonization of methyl cinnamate with chloroacetic acid, which forms a single stereoisomer. (129)

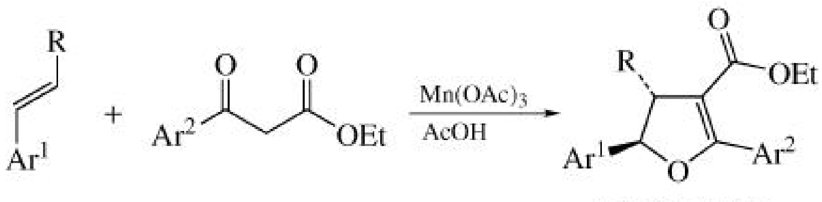
Reactions of alkenes with β -dicarbonyl compounds represent a general method for the synthesis of polysubstituted dihydrofurans **51** (Eq. 10, Table VII).



(10)

Regioselective generation of the α , α -dioxoalkyl radicals in the presence of alkenes produces adduct radicals **52**, which undergo intramolecular cyclization with acyl or benzoyl groups to form dihydrofurans **51**. The reaction is especially facile with aromatic substituents at the double bond, since benzylic radicals are easily oxidized by Mn(III) ions to carbocations **53**. The latter have not been directly observed, but their formation along the reaction coordinate has been proposed based on overwhelming indirect evidence (see Adduct Radicals section). With alkyl adduct radicals, $Cu(OAc)_2$ is used to effect fast oxidation. Selectivity drops with $Mn(OAc)_3$ alone, since the reactivity patterns of alkyl radicals include H-atom transfer, (70, 105) β -elimination, (31, 70) and acetoxy group transfer. (31) Most of the reactions are mediated by equimolar amounts of $Mn(OAc)_3$, but there has been occasional use of $Mn(acac)_3$. (45, 55, 135) Both Mn(III) and Mn(II) acetates have been used in combination with molecular oxygen, which acts as both a regenerating and oxidizing agent. (51, 53, 54) A synthetically useful modification is the introduction of lithium chloride into the reaction mixture, whereby chlorine ligand transfer becomes a new reaction pathway for adduct radicals. (63) Besides commonly used β -diketones and β -ketoesters, new types of carbonyl components such as β -keto phosphates, β -keto sulfoxides, and β -keto sulfones have recently been used to produce dihydrofurans. (53)

Reactions of terminal and 1,1-disubstituted alkenes are highly regioselective, with the attack of electrophilic educt radicals occurring at the double-bond terminus (Table VII). 1,2-Disubstituted substrates like β -alkyl- and β -alkoxycarbonylstyrenes also react regioselectively owing to the effective stabilization of radical intermediates by α -aryl groups. (136) The scope of the reaction has been further expanded by involving a large number of styrene derivatives and β -aroyl esters (Eq. 11). Nonconjugated alkadienes (Table XV) can be either bis- (109) or monofunctionalized, (72) with faster reaction at the electron-rich double bond. (82)

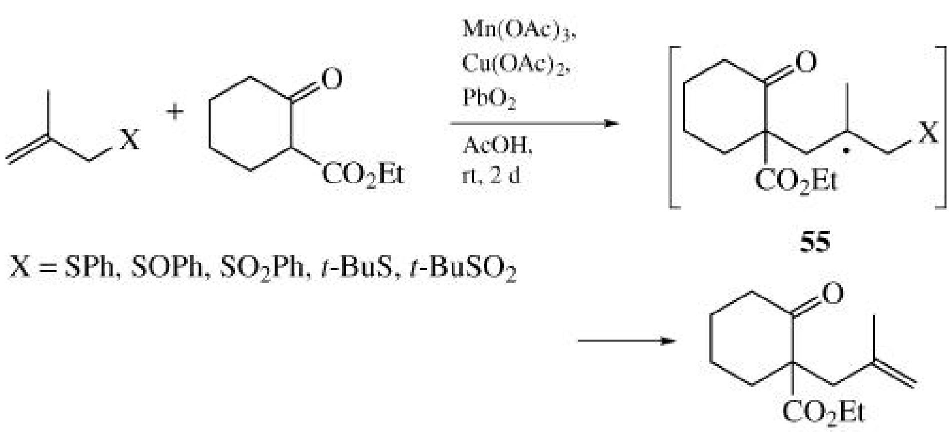


54 (27–71%) (11)

R = H, Me, CH_2OAc, CO_2Et;
Ar^1, Ar^2 = Ph, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$

The stereochemistry of the process remains mostly unknown because cycloalkenes and 1,2-disubstituted alkenes have not been investigated in detail (Table VII). Only in the reaction of styrenes with β -aroyl esters has the stereochemistry of dihydrofurans **54** been established to be *trans*. (136)

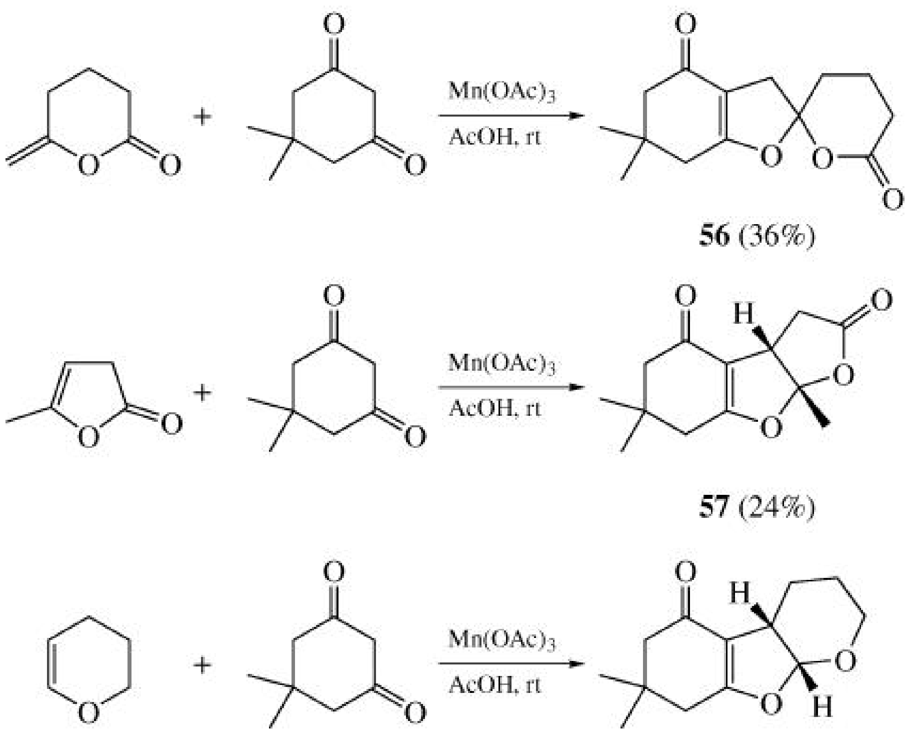
A novel method of isoprenylation of mono- and β -dicarbonyl compounds has been developed by using allyl sulfides, sulfoxides, and sulfones as unsaturated substrates (Table VII). (71) Adduct radicals **55** undergo homolytic β scission to release sulfur-centered radicals. The generality of the method is demonstrated by the use of a large number of acyclic and cyclic β -dicarbonyl compounds, although use of the strong oxidant PbO_2 severely limits the types of prospective substrates. (71)



55

X = SPh, SOPh, SO_2Ph, *t*-BuS, *t*-$BuSO_2$

Dihydrofuran synthesis by reaction of alkenes with β -dicarbonyl compounds has been brought to a new level by involving endo- and exocyclic enol ethers and enol lactones as substrates (Table XI). An extensive exploration of these reactions has led to the synthesis of a large number of oxaspirolactones and *cis*-fused di- and tricyclic systems. (137-143) Selected examples shown in Eq. 12 feature regioselective addition of α , α -dioxoalkyl radicals to a β carbon producing α -oxygen-substituted adduct radicals. Their oxidation by $Mn(OAc)_3$ is greatly facilitated by the oxygen atom and leads to spiro and fused systems **56–58**. The attractive feature of these reactions is their high *cis* stereoselectivity, exemplified by polycyclic fused systems **57** and **58**. From the standpoint of synthetic chemistry, these reactions are very attractive for constructing complex polycyclic compounds in one step from readily available starting materials.



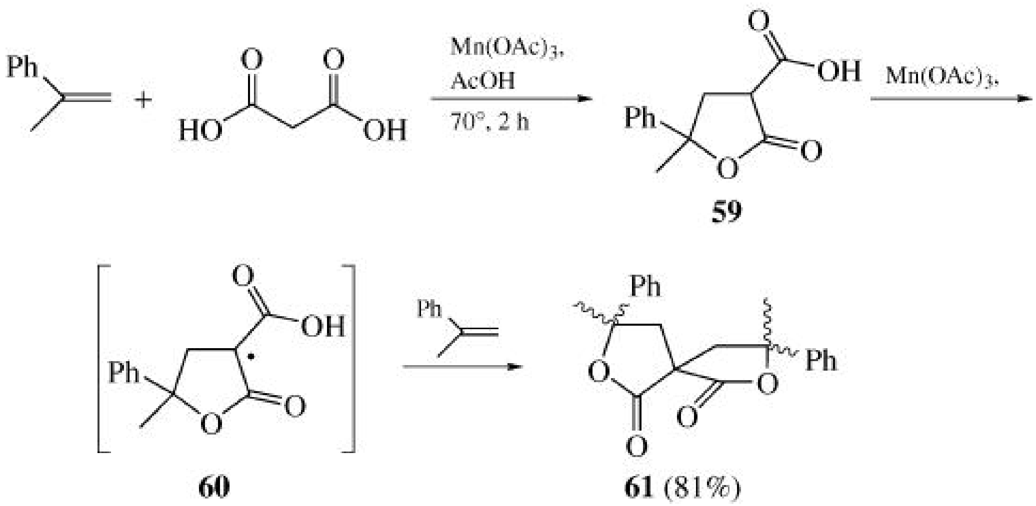
56 (36%)

57 (24%)

58 (43%)

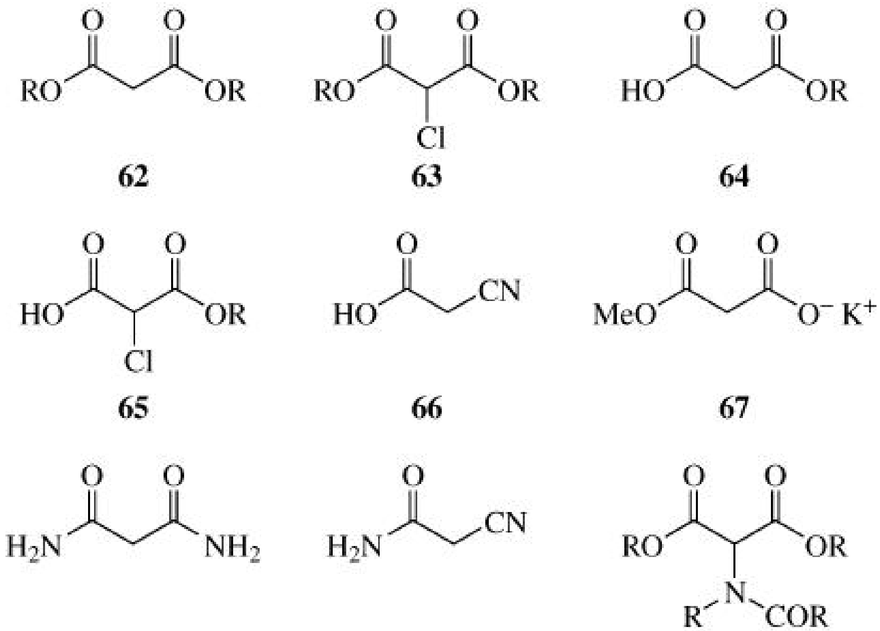
(12)

Malonic acid, with *gem*-carboxylate moieties, provides a new dimension in Mn(III)-mediated reactions: sequential lactonization with the participation of two molecules of alkene (Table IX). (144, 145) Thus, initially formed γ -lactone **59** is oxidized again to generate educt radical **60**, which reacts with a second molecule of substrate to produce spiro compound **61**. A number of alkenes and cycloalkenes



have been bis-annulated with malonic acid, demonstrating the generality of the reaction and providing facile access to the synthetically useful 2,7-dioxa[4.4]nonane-1,6-diones. (144, 145) The lack of stereoselectivity seems to be a major drawback since mixtures of unsymmetrical and symmetrical *syn* and *anti* stereoisomers are usually formed. The highest selectivity is observed in the reaction of cyclopentene (92% of the unsymmetrical isomer). (145) Synthetic utility of the reaction has been enhanced by the use of nonconjugated alkadienes such as 1,5-hexadienes as unsaturated substrates. (145) Although yields are low to moderate, topologically unusual bridged tricyclic systems have been successfully constructed in one step (Table XV). Overall, reactions of malonic acid with alkenes have not received the attention they deserve; major advances would be complete control of the stereoselectivity as well as further expansion of scope. Halide and methyl-substituted malonic acids produce monoannulated products such as saturated and α , β -unsaturated γ -lactones. (146)

Dicarboxylic acid derivatives **62–70** have been widely used as carbonyl components (Eq. 13, Table X). The synthetic outcome of the reaction depends upon



62 63 64 65 66 67 68 69 70

(13)

the nature of the functional groups in the carbonyl components and on their ability to interact with radical/cationic centers in the adduct radicals. Malonic diesters **62** and α -chloro diesters **63** produce linear products, (50, 63, 64, 111) since cyclization on the alkoxycarbonyl group is a slow process compared with that of acyl and carboxy groups. Major reactivity patterns of adduct radicals appear to be H-atom abstraction, (64) regioselective β -deprotonation, (64, 111) and Cl-atom transfer if lithium chloride is used as an additive. (50, 63) Malonic acid derivatives that contain carboxy (**64**, (146, 147) **65**, (147) **66** (128, 129, 147)) or carboxylate (**67** (129, 148, 149)) groups all produce corresponding γ -lactones analogous to those from monocarboxylic acids (Eq. 7, Tables III–V). Malonic diamides **68** undergo partial hydrolysis to generate carboxy groups and thereby α -aminocarbonyl- γ -lactones. (150) A novel cyclization pathway for aminocarbonyl fragmentation has been observed that gives rise to α , β -unsaturated γ -lactams. (150) This is a new reactivity pattern for benzylic adduct radicals, and although only two examples have been reported, both utilizing heavily substituted alkenes, this reaction might be of general use. Cyanoacetamide **69** produces a variety of structures arising from acetoxy group transfer, cyclizations on carboxy and aminocarbonyl groups, and secondary transformations of γ -lactams. (151) *N*-Acyl substituted malonic diester **70** is an exotic type of carbonyl compound, the chemistry of which does not include participation of the pendant *N*-fragment. (107)

The reactions of malonic acid derivatives with unsymmetrical alkenes are highly regioselective (Table X). Educt radicals attack double bonds to generate more stable intermediates; phenyl groups have a strong directing effect in β

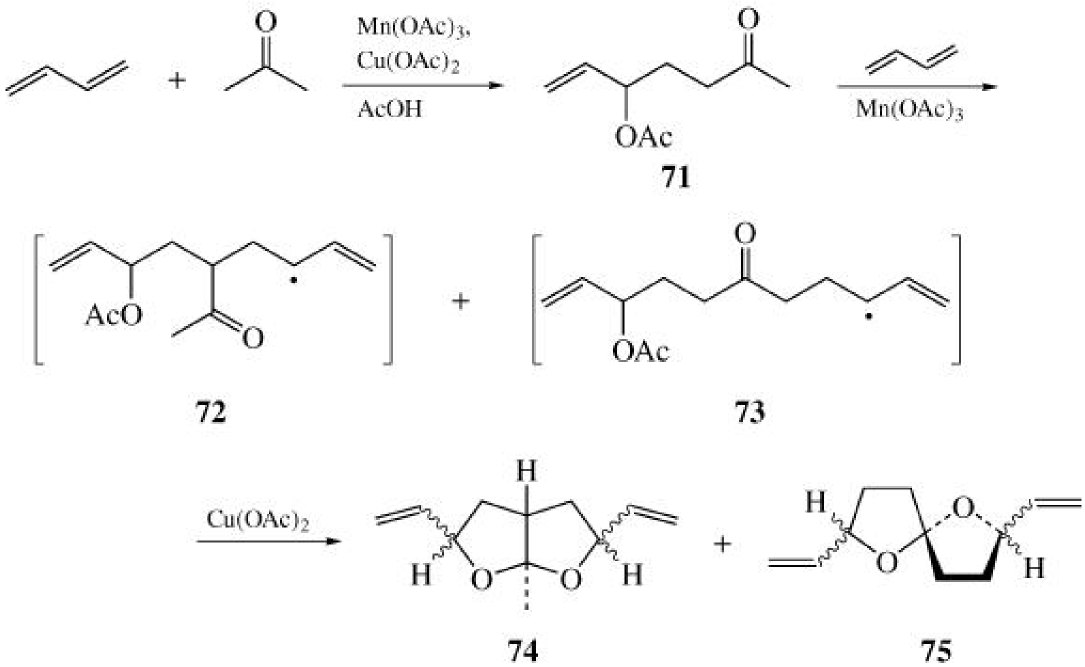
-substituted styrenes, (128, 147, 148) as does the α -oxygen atom in enol ethers. (149) *tert*-Butyl crotonate also reacts regioselectively with cyanoacetic acid with exclusive attack of the educt radicals on the β carbon. (129) Regioselective functionalization of acyclic (109) and cyclic (147) nonconjugated alkadienes has also been described (Table XV).

The stereoselectivity has not been fully established for every reaction (Table X). *cis* Stereoselection has been reported for the lactonization of norbornene with monoethyl malonate, its chloro derivative, and cyanoacetic acid. (147) To the contrary, the formation of isomeric mixtures has been observed in reactions of 1-octene, (129) 1-decene, (129, 147) α , β -unsaturated esters, (129) cyclohexene, (129, 147) cyclooctene, (129) and α- and β -substituted styrenes. (129, 147)

Alkynes remain one of the least investigated substrates (Table XII). Their interactions with mono- and dicarbonyl compounds have been reported, although apparently unoptimized procedures were used. (44, 49, 50, 152) The major theoretical issue here is the reactivity pattern of vinylic radicals (**28**, Eq. 6), which affects both the yield and synthetic outcome of the processes. Based on a limited number of examples, the present level of knowledge does not permit reliable prediction of the reaction outcome.

3.1.2. Conjugated Systems—Chemo-, Regio-, and Stereoselectivity

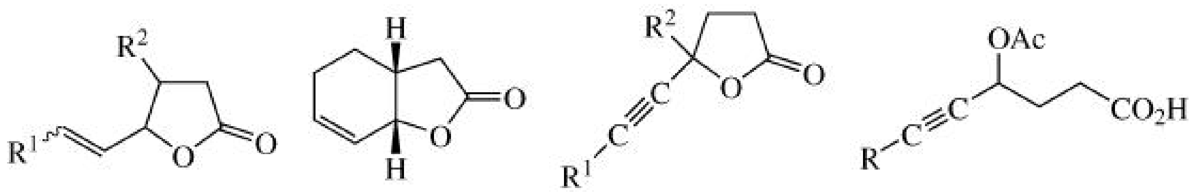
The interaction of 1,3-alkadienes with ketones is represented by a single reaction between 1,3-butadiene and acetone. (61) 1,2-Conjugate addition to the double bond results in 5-acetoxy-6-hepten-2-one (**71**), which undergoes a nonregioselective oxidation of both the methylene and methyl groups. Adduct radicals **72** and **73** undergo a sequential five-membered ring annulation with the formation of isomeric 2,8-dioxa-*cis*-bicyclo[3.3.0]octanes (**74**, 1:1:2) and 1,6-dioxaspiro[4.4]nonanes (**75**,



3:3:1). Cyclization on the acyl group is an unexpected mode of behavior for secondary adduct radicals (Table II), although it is conceivable that the second annulation makes the overall process irreversible. Phenomenologically this is one of the most intriguing reactions in Mn(III) chemistry, producing complex structures from two parent compounds in a single step. The configuration of the products needs to be fully established, and more conjugated dienes and ketones need to be studied to define the scope and synthetic utility of the method.

γ -Lactones **76** are uniformly produced if 1,3-alkadienes are treated with acetic acid in the presence of potassium acetate (Table XIV). The regioselectivity issue arises with unsymmetrical substrates such as isoprene, (128) (1,3-*Z*)-dodecadiene, (153) 1,1-dichloro-4,4-dimethyl-1,3-butadiene, (154) and methyl sorbate. (108) More stable adduct radicals are preferentially formed if both termini of the substrate are equally accessible, (128) otherwise the less-substituted double bond is the exclusive reaction site. (153) The electrophilic character of the carboxymethyl radical results in selective addition at the more electron-rich double bond, (154) producing a key intermediate in pyrethroid synthesis. (155) For the same reason, the γ , δ -double bond in methyl sorbate is the principal point of attack by the educt radical, with less attack at the α , β -moiety (68 vs. 29%); both regioisomeric γ -lactones are formed with low stereoselectivity. (108) Partial stereomutation of the *cis* allylic adduct radical has been observed in the lactonization reaction that produces the sex pheromone of the Japanese beetle (Eq. 26). (153) Formal *cis*-stereoselective lactonization of 1,3-cyclohexadiene into bicycle **77** has been accomplished in three steps, although in low overall yield. (11, 156) Nonconjugated dienes can be functionalized selectively at one of the double bonds, (128) with the more electron-rich olefin reacting preferentially. (82)

1,3-Alkenynes afford γ -alkynyl- γ -lactones **78** in moderate yields if lactonization is carried out in the presence of potassium acetate (Table XVII). The synthetic usefulness of this method has been demonstrated by the syntheses of natural sex pheromones. (153, 157-159) Acetic anhydride as a cosolvent makes ligand transfer a major reaction pathway for propargylic radicals (**29**, Eq. 6), producing γ -acetoxy acids **79**. (62) The phenomenon of “critical carbon chain length” has been observed in the selective formation of LTR products **79** vs.γ -lactones **78** if R > C_7H_{15}. This result implies a relationship between the reactivity of the adduct radical and carbon chain length in substituent R, although this has not been established. (62)



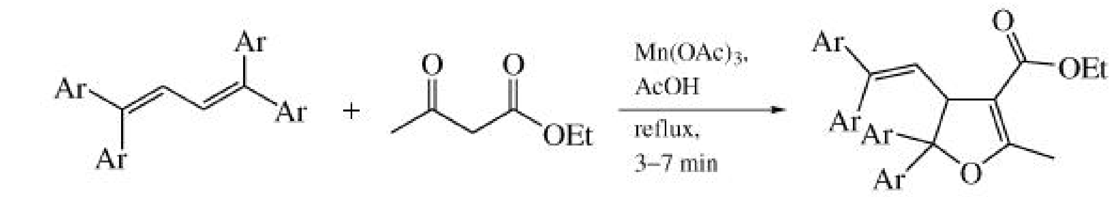
76 R^1, R^2 = H, Cl, Alk, CO_2Me

77

78 $R^1 = C_3–C_8$, R^2 = H, Me

79 $R = C_2–C_{10}$

Dihydrofurans with vinyl or alkenyl side chains are formed in radical cycloaddition reactions of β -dicarbonyl compounds to 1,3-alkadienes (Table XVI). The mechanism is analogous to that of simple alkenes (Eq. 10), and includes the formation of allylic radicals and their subsequent oxidation by metal oxidants. In most cases, $Cu(OAc)_2$ is used to ensure effective oxidation, although phenyl groups α to the radical center greatly facilitate oxidation, enabling Mn(III) ions alone to provide moderate to high yields of cyclization products. (109) Regioselectivity at C_1 vs. C_2 is usually high because educt radicals selectively add to either C_1 or C_4 carbon atoms of the 1,3-butadiene moiety to produce isomeric allylic radicals (Table XVI). Inverse regioselectivity has been observed for diene **80**, heavily substituted with aryl groups. (109) Selective attack at the C_2 carbon affords dihydrofuran **81**, and indicates a higher stability of α , α -diarylalkyl radicals (**23**, Eq. 6)

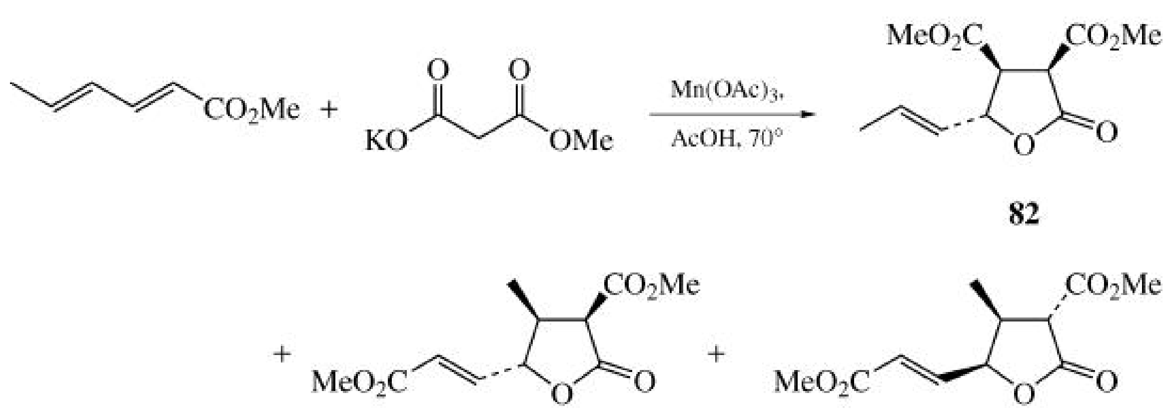


80 **81** (11-46%)

Ar = Ph, p-ClC$_6$H$_4$, p-MeC$_6$H$_4$

in comparison with allylic radicals (C-1 attack). Regioselectivity at C_1 vs. C_4 in 2-substituted 1,3-alkadienes is directed by the relative stabilities of isomeric allylic radicals; rations are 70:10 and 43:8 for isoprene and myrcene, respectively. (72) With 4-substituted dienes, reactions proceed selectively at C_1 directed by steric effects. (73) Low regio-(C_1 vs. C_4) and stereoselectivity has been reported for 1,4-substituted dienes such as methyl sorbate (72, 108) and conjugated dienones. (72) A partial stereomutation of *cis* allylic intermediates was observed, whereas *trans* analogues were configurationally stable. (73)

Lactonization of 1,3-alkadienes and their cyclic analogues with malonic acid derivatives is a practical way to produce highly functionalized and polysubstituted γ -lactones containing unsaturation in a γ side chain (Table XVI). (107, 108, 128, 147) Some noteworthy features are: (1) high C_1 vs. C_2 regioselectivity; (2) preferential participation of the electron-rich double bond in 2-substituted substrates—a ratio of 39:5 was obtained with isoprene and cyanoacetic acid; (128) (3) low C_1 vs. C_4 regioselectivity in the reaction of methyl sorbate and potassium methyl malonate [**82**:(**83** + **84**) = 21:59]; (108) (4) high stereoselectivity in the lactonization of an α , β double bond, producing lactone **82** as a single stereoisomer, and to the contrary, low stereoselectivity if the γ , δ reactive site participates (**83**:**84** = 44:15). (108)

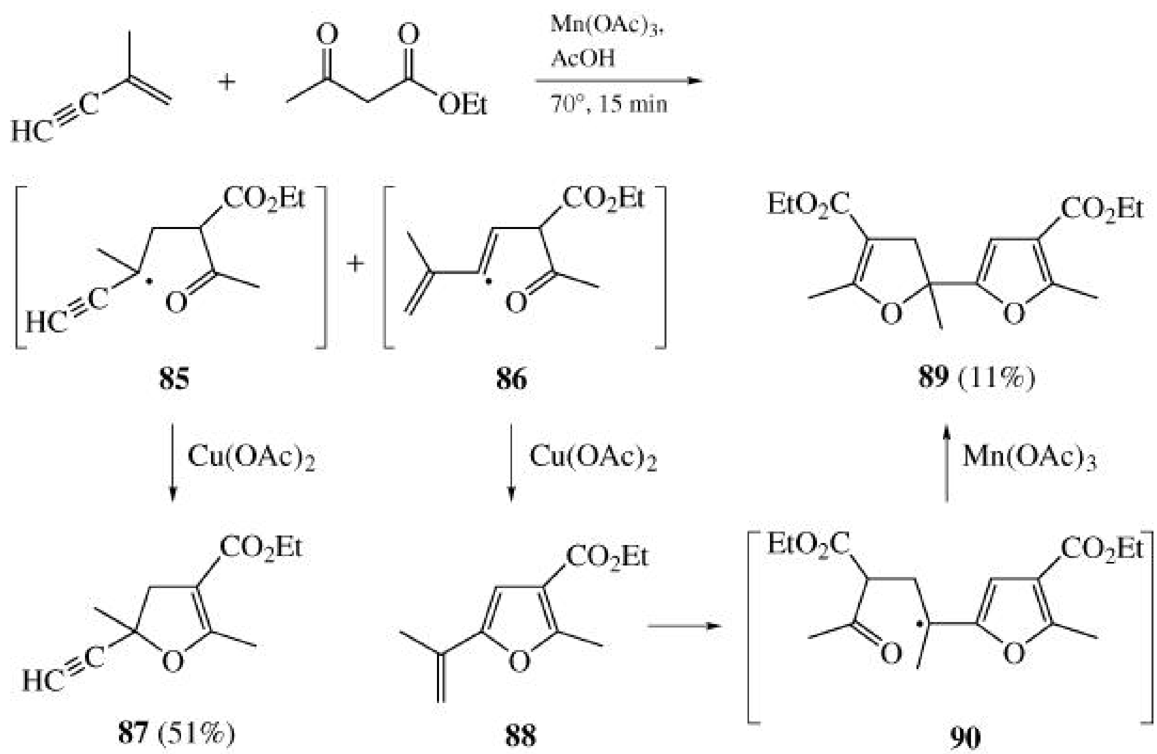


82

83 **84**

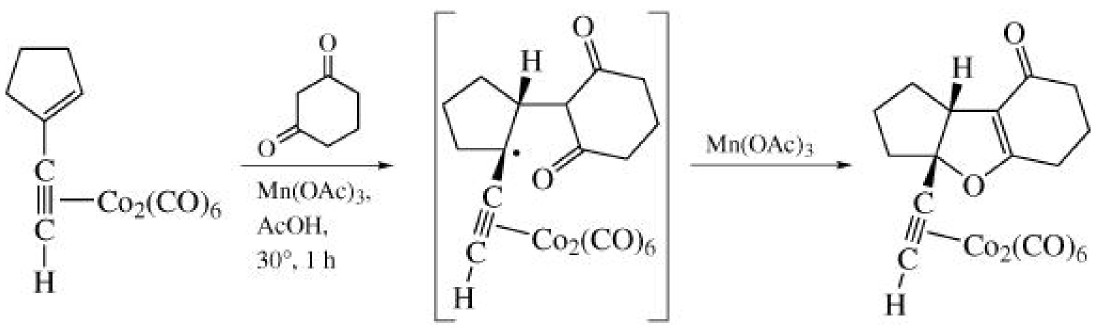
82 + **83** + **84** = (63%)

Chemoselectivity is the most critical aspect in Mn(III)-mediated reactions of 1,3-alkenynes, and it depends upon the type and degree of substitution in the substrate (Table XVIII). (74-77, 160, 161) When grouped according to selectivity, 1,3-butenyne and its derivatives form three pairs that react nonchemoselectively (0-2-substituted) and chemoselectively at the triple (1-substituted, 1,2-disubstituted) or double bond (4-substituted, 2,4-disubstituted). Thus, interaction of isopropenyl-acetylene with ethyl acetoacetate gives rise to propargylic **85** and vinylic **86** adduct radicals. Both are resistant to Mn(III)-induced oxidation (Eq. 6), thus requiring the use of the stronger oxidant $Cu(OAc)_2$. The corresponding cations undergo intramolecular cyclization to the acetyl group to produce dihydrofuran **87** and furan **88**. The latter undergoes a secondary transformation to afford furan **89** via the easily oxidized α -(2-furyl)alkyl radical **90**, an analogue of benzylic radical **22** (Eq. 6). (76)



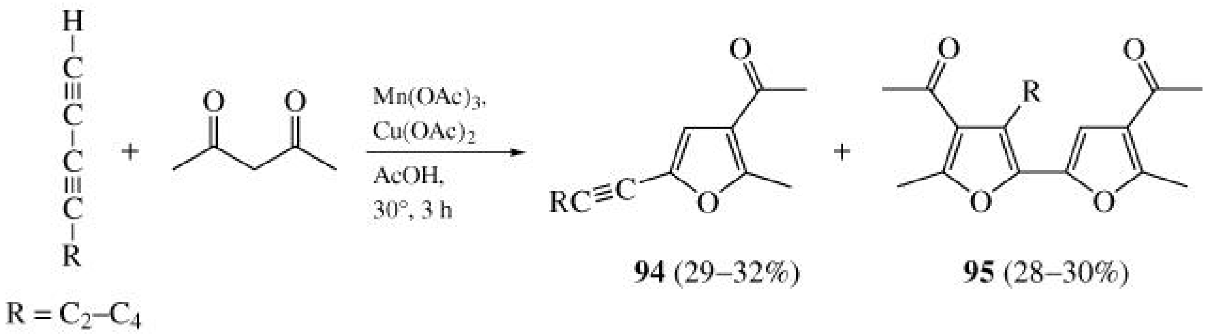
A novel strategy has recently been developed to effect a chemoselective reaction between 1,3-alkenynes and β -dicarbonyl compounds. (57, 162) A three-step sequence includes protection of the triple bond with the $Co_2(CO)_6$

group, Mn(III)-mediated radical reaction with selective participation of the double bond, and oxidative demetalation. This sequence leads to reversal of the chemoselectivity for 1,2-substituted derivatives like cyclohexenylacetylene, which otherwise reacts chemoselectively at the triple bond. (77) The efficiency of the method has been demonstrated for both acyclic and cyclic enynes and carbonyl compounds (Table XIX). Thus, $Co_2(CO)_6$-protected cyclopentenylacetylene **91** reacts with 1,3-cyclohexanedione to produce propargyl adduct radical **92**, which can be oxidized by a Mn(III) salt to the corresponding $Co_2(CO)_6$-stabilized carbocation, (57) in contrast to its uncomplexed counterpart (**26** vs. **29**, Eq. 6). Tricyclic product **93** is formed with high *cis* stereoselectivity, and can be oxidatively decomplexed to give a pure organic product. Metal-protected cyclohexenylacetylene also produces *cis*-fused systems in moderate yields. (57)



91 **92** **93** (28%)

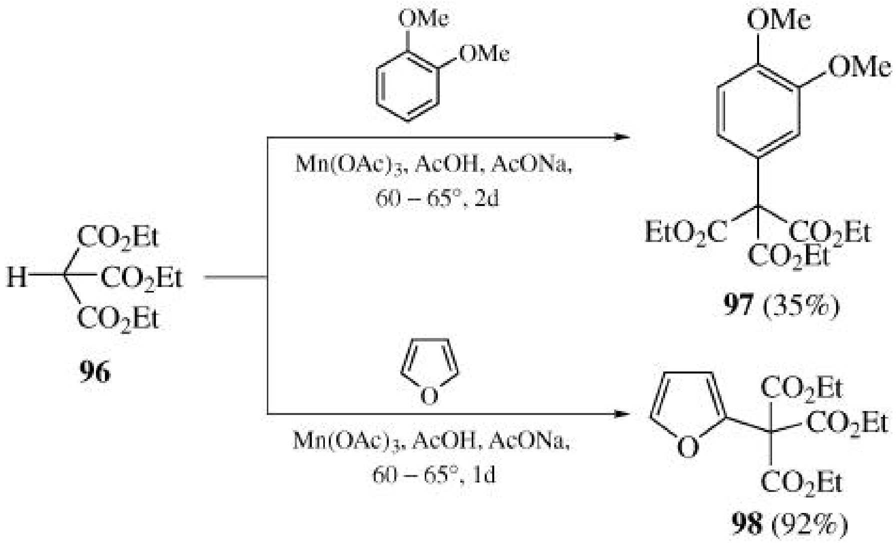
1,3-Alkadiynes comprise a relatively uninvestigated class of conjugated systems (Table XX). In monosubstituted compounds, both triple bonds are attacked by electrophilic educt radicals (C_1–C_4 addition) to produce isomeric vinylic radicals of type **30** (Eq. 6). The latter undergo polymerization even in the presence of catalytic amounts of $Cu(OAc)_2$. Cyclization products **94** and **95** can be isolated in moderate yields only when a four-fold excess of cooxidant is used. (78, 163) With a straight-chain substituent R, the process is nonregioselective because furan **94** is inactive under the reaction conditions. To the contrary, high regioselectivity is achieved with a *tert*-butyl-like substituent R, effectively protecting one of the triple bonds. (78)



3.1.3. Aromatics

Arenes were among the first substrates investigated in Mn(III)-mediated reactions (Table XXIA). (27, 33, 164) The interaction of benzene and its monosubstituted derivatives with acetic acid suffers from low selectivity because initial carboxymethylation is followed by stepwise overoxidation. Regioselectivity is also lacking, although there is preponderant formation of *ortho* isomers (30–78%)—typical for aromatic radical substitutions. (32) With acetone, substituted methyl-benzyl ketones are formed (30–80%) containing 52–85% of *ortho* isomers. (34, 35) With β -dicarbonyl compounds and diethyl malonates, the regioselectivity depends upon the type of substitution: 1,2- and 1,4-dimethoxybenzene and 1-methoxy-2,3-dimethoxynaphthalene produce single regioisomers, whereas anisole and naphthalene and its 2-methoxy derivative can react nonregioselectively depending on the nature of the carbonyl component. (38, 165) Use of malonic acid provides a new synthetic method for one-step regioselective formylation and carboxylation of naphthalene derivatives. (39)

A novel type of educt radical, tris(ethoxycarbonyl)methyl, has been successfully generated by oxidation of *ortho* ester **96**. (37) It has proven to be a viable supplement to α -oxoalkyl radicals in reactions with arenes and heterocycles (Tables XXIA and B). Thus, 2,3-dimethoxybenzene and furan are selectively functionalized to produce **97** and **98**, respectively. More “conventional” carbonyl components, like acetone and dicarbonyl compounds, also react with heterocycles (furan, thiophene, pyrrole) selectively at the α position. (166, 167)

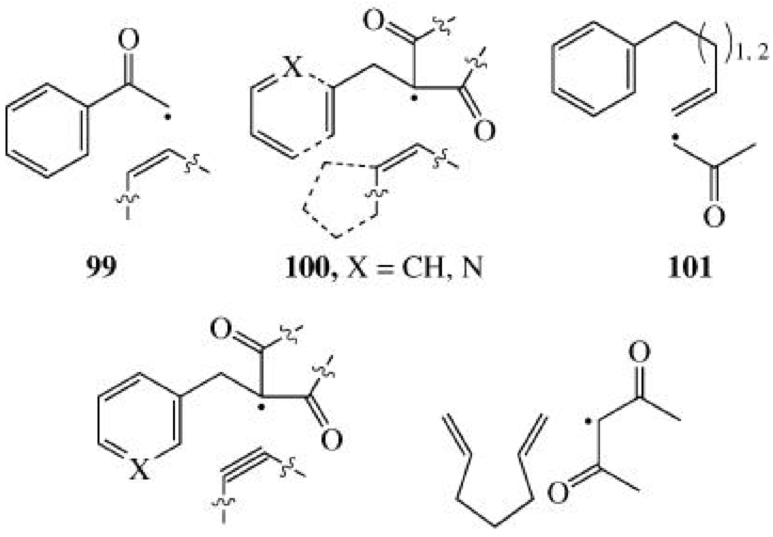


A related species is the nitromethyl radical, which can be generated by oxidation of nitromethane with $Mn(OAc)_3$ (Table XXII). Its reactions with arenes (36, 168, 169) and alkenes (79) have the same characteristics as those of α -oxoalkyl radicals.

3.2. Addition–Cyclization Reactions

Addition–cyclization reactions require that three functional groups, such as a carbonyl moiety and unsaturated fragments (double or triple bond, aromatic ring, nitrile group) be present in the two components. Topologically numerous combinations are possible, differing in connectivities between major constituent parts. By function, a carbonyl moiety gives rise to an educt radical, and unsaturated sites undergo sequential radical–radical (or radical–electrophilic) attack. Literature data are summarized in Table XXIII, arranged according to the class of substrate (A, alkene; B, alkyne; and C, alkadiene). Structural analysis reveals their common features and major topological differences (Eq. 14). Combinations **99**, **100**, and **102** have a carbonyl and one of the unsaturated moieties in the same molecule, whereas unsaturated groups are disposed of together in combinations **101** and **103**. The specific feature of **99** is the location of a carbon-centered radical on one side of both functions; in contrast, the oxidation site is located between **100** and **102**.

Addition–cyclization remains a relatively unexplored dimension in Mn(III) chemistry, although the first examples of type **99** and **102** were reported quite early (Table XXIIIA). (170) The synthetic potential of this reaction is truly outstanding, and includes novel approaches to the synthesis of monocyclic, bicyclic,



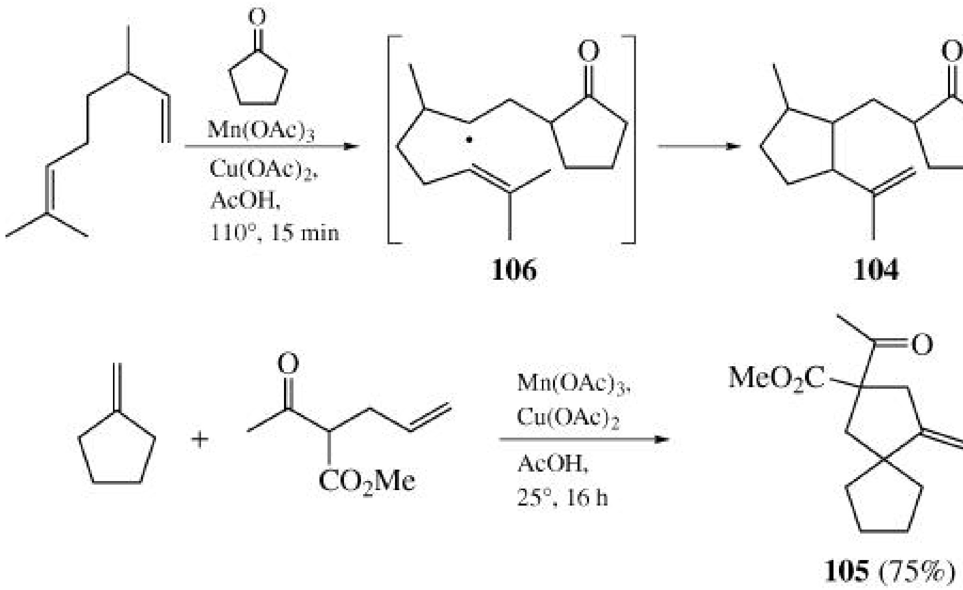
99 **100,** X = CH, N **101**

(14)

102, X = CH, N **103**

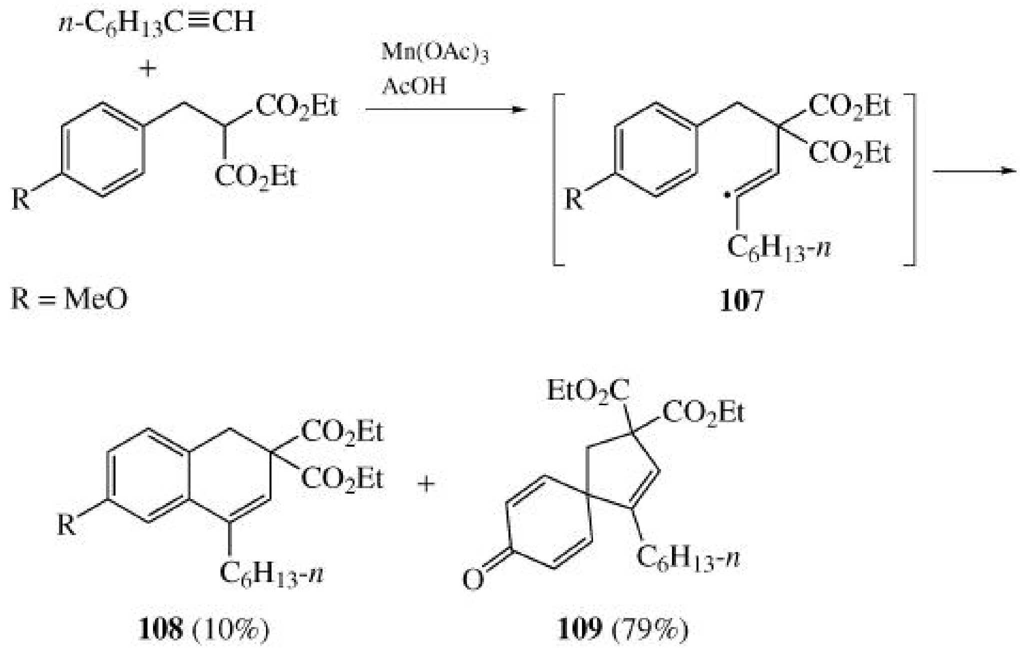
fused, and spiro compounds, (80-82, 117, 171) as well as derivatives of tetralone, tetralin, indane, (170) quinoline, isoquinoline, (172) and naphthalene. (173, 174)

Regioselectivity of the addition to unsymmetrical alkenes and alkynes is normally high and the addition occurs according to the Markovnikov rule (Table XXIIIA–C). Selectivity in the second, intramolecular step is most crucial for the synthetic outcome of the overall process. With a double bond as the second reaction site, 5-exo and 6-endo cyclizations are the alternatives. (175, 176) In most cases (with one exception (81)) the corresponding cyclopentane derivatives have been isolated, indicating that intramolecular cyclizations occur under kinetic control. Selected examples demonstrate the formation of cyclopentanes **104** and **105** by regioselective 5-exo cyclization of intermediate radicals such as **106** (Eq. 15). (80, 82) A second annulation of the alkyl adduct radicals on benzene or



(15)

pyridine rings proceeds selectively at the ortho position. (170, 172, 173, 177) In contrast, alkyne-derived vinylic adduct radicals suffer from low regioselectivity (Table XXIIIB). Thus, vinylic intermediate **107** undergoes both 6-endo and 5-exo cyclization to afford dihydronaphthalene **108** and spiro compound **109**, with loss of aromaticity in the latter (Eq. 16). (174) In unsymmetrical aromatics the regioselectivity of the second annulation has a double sense, involving both 6-endo vs. 5-exo cyclization modes and competitive participation of unequivalent *ortho* positions. Thus, 3-substituted pyridines cyclize nonselectively at positions 2 and 4 with both alkyl and vinylic adduct radicals. (172)

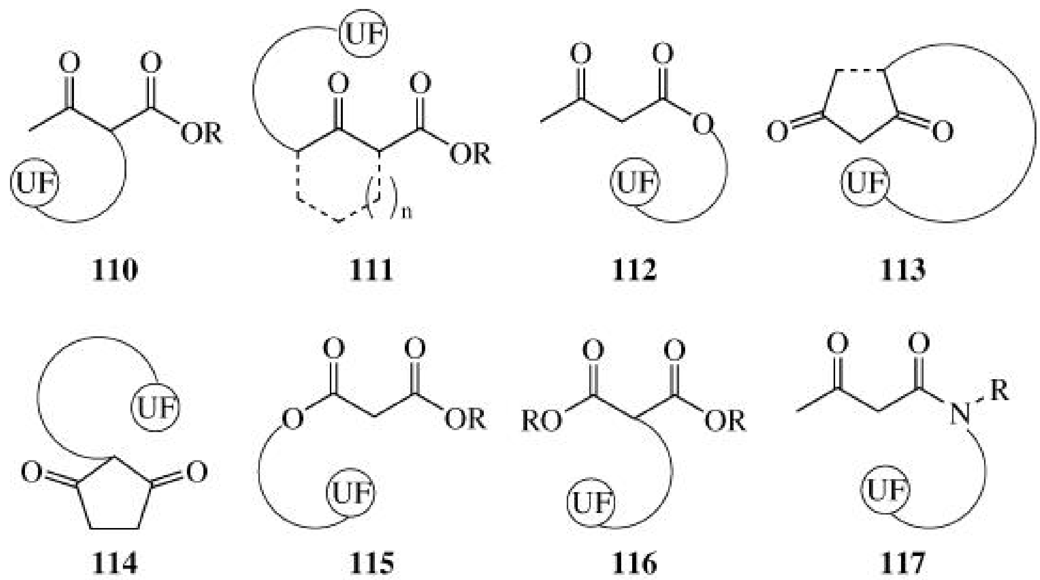


(16)

3.3. Intramolecular Reactions

Manganese(III)-mediated intramolecular reactions constitute an important area in the field of radical chemistry. They have led to better understanding of the driving forces in radical cyclization processes and of the reactivity patterns of different types of adduct radicals. They have also yielded a bewildering array of organic compounds not otherwise easily accessible. The accumulated collective experience provides a solid basis for the optimal design of new substrates for intramolecular reactions to effect a given type of cyclization, or for constructing a certain type of complex target.

Starting materials for intramolecular cyclization can be designed by incorporating both carbonyl and unsaturated moieties in the same molecule. Not only can the nature of active fragments be varied, but also their disposition, in particular the location of a side chain bearing the unsaturated fragment (UF). Known types of substrates (Eq. 17) include 2- and 4-substituted 3-ketoesters **110**, **111**, *O*-substituted 3-ketoesters **112**, 4- and 2-substituted 1,3-diketones **113**, **114**, *O*- and *C*-substituted malonic ester derivatives **115**, **116**, and *N*-substituted 3-ketoamides **117** (Tables XXIV–XXXI). Monocyclization products are often accompanied by products of tandem cyclizations (Tables XXXII–XXXVII). To avoid duplication in the Tabular Survey, the major product is given a higher priority in determining the location of certain reactions.



(17)

3.3.1. Regioselectivity

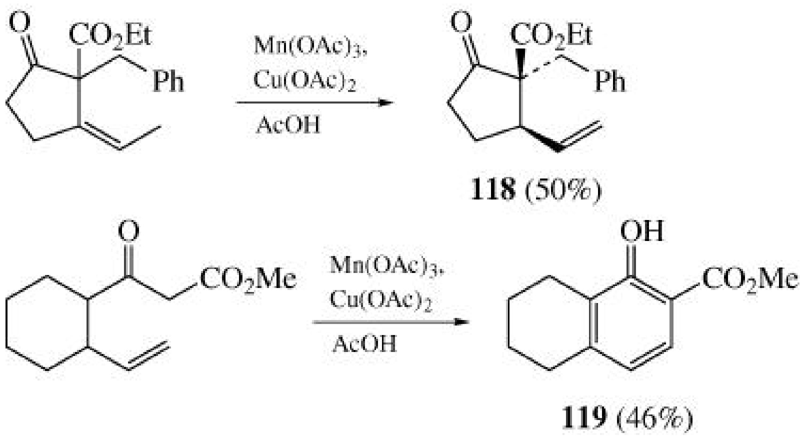
Regioselectivity is one of the most critical aspects of intramolecular cyclizations. The competing formation of different ring sizes occurs under kinetic or thermodynamic control, and is best understood for the classical 5-hexenyl radical cyclizations. (175, 176) Since both steric and electronic effects contribute to the reversibility or irreversibility of the addition step, the nature of carbonyl-containing groups, unsaturated moieties, and substituents, as well as the location of the latter at vital positions of the substrates, are of primary importance. In particular, terminal double or triple bonds are preferentially attacked at their termini (*endo* mode), whereas introduction of alkyl substituents activates the *exo* mode.

3.3.1.1. Cyclopentane Vs. Cyclohexane (5-exo Vs. 6-endo Mode)

The largest number of experimental data deal with the formation of five- and/or six-membered rings by cyclizations of polysubstituted 5-hexenyl adduct radicals. All types of substrates (except **114**) have been subjected to this reaction, although to varying degrees. The regioselective 5-*exo* mode leading to cyclopentanes clearly dominates, producing a variety of structures from substrates **110**, (83) **111**, (85, 89-91, 99) **112**, (92) **115**, (83, 92, 94-96) **116**, (97, 99, 178) and **117**. (179) Cyclohexanes have been obtained as single regioisomers from substrates **111** (56, 180) and **113**. (83) A synthetically useful method is the novel and general approach to salicylic acid derivatives employing a large number of substrates **111** (80, 86, 90) and **113**. (84, 89) Nonregioselective reactions are rather uncommon, although lack of regiocontrol has been observed for substrate **111** in cyclizations upon double (83) and triple bonds. (99) The benzene ring directs radical attack selectively at *ortho* positions, producing fused bi- and tricyclic systems. (29, 181, 182) Examples are shown in Eq. 18, including regioselective formation of cyclopentane **118** (90) and salicylic acid derivative **119**. (84)

3.3.1.2. Cyclobutane Vs. Cyclopentane (4-exo Vs. 5-endo Mode)

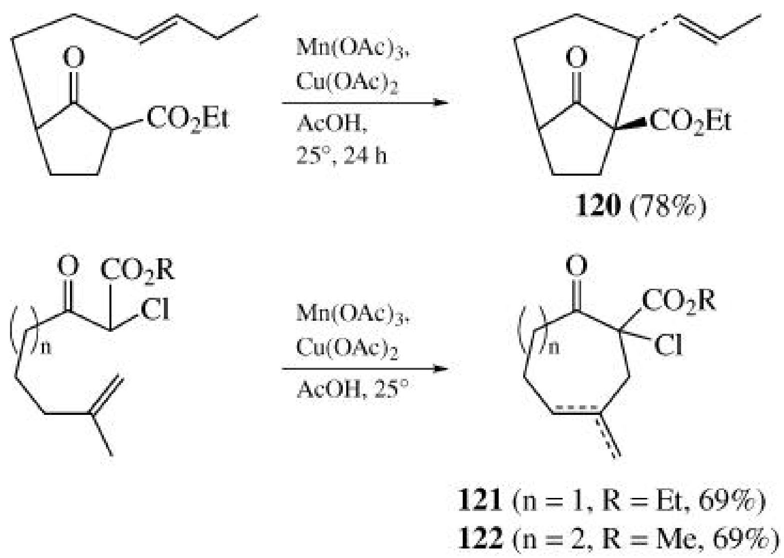
This type of cyclization is represented by a single reaction that produces a *spiro* system by regioselective 5-*endo* annulation (Table XXVIII). (93)



(18)

3.3.1.3. Cyclohexane Vs. Cycloheptane (6-exo Vs. 7-endo Mode)

Competing formation of six- and seven-membered rings has been studied for a limited number of 4-substituted 3-ketoesters **111** (Table XXV). Regioselective formation of cyclohexanes (83, 85, 87) and cycloheptanes, (87, 88) as well as their mixtures, has been observed. (87, 88, 180) Thus, the effective construction of bridged compound **120** has been achieved by the 6-*exo* regioselective addition of cyclopentyl radical to the pendant double bond (Eq. 19). (83) In contrast, the formation of cycloheptane **121** as a single regioisomer has been reported in the cyclization of an α -chloroacetoacetic ester on an isopropenyl group (Eq. 19). (87)



(19)

3.3.1.4. Cycloheptane Vs. Cyclooctane (7-exo Vs. 8-endo Mode)

Several examples of regioselective intramolecular cyclizations producing eight-membered rings have also been described. (87, 88) Thus, cyclooctene **122** is formed as a mixture of two regioisomers by the selective 8-*endo* addition of a highly electrophilic educt radical to the terminus of the double bond. (87)

3.3.2. Stereoselectivity

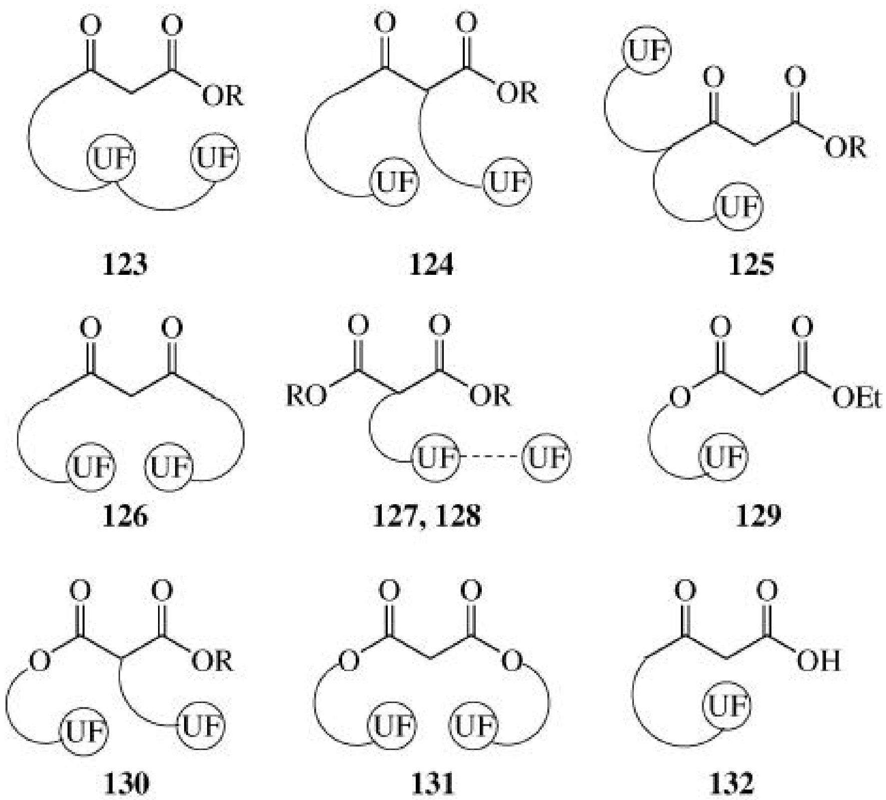
Stereocontrol is another critical aspect of monocyclization reactions from the viewpoint of synthetic utility. Although a large number of annulations have been reported, the stereochemistry of the products remains unelucidated in many reactions (Tables XXIV–XXXI). Especially deficient are data on the configuration of seven- and eight-membered rings. For cyclopentane and cyclohexane derivatives, the relative configurations have been elucidated fully. There are several aspects to the stereochemical outcome; the most important is the spatial relationship of the substituents at a newly formed C — C bond. Of secondary importance is the stereochemistry of double bonds in the side chains, which are usually formed in the *exo* cyclization mode.

Two examples are given above for the stereoselective formation of a five-membered ring (Eq. 18) and a bridged system (Eq. 19). Tables XXVA, XXIX, and XXXA contain more examples of stereoselective annulations that produce five-membered carbocycles or lactones, (83, 90, 94, 178) as well as six-membered rings (85) and bridged systems. (83, 180) A nonstereoselective pathway has been reported for the cyclizations of *O*-substituted malonic esters (Table XXIX) to yield γ -lactones (92, 95, 96) and 4-substituted 3-ketoesters (Table XXVA) resulting in cyclopentanes (83, 85, 90, 91) or cyclohexanes. (83)

Some additional highly stereoselective cyclizations used as key steps in directed syntheses can be found in the section Applications to Natural Product Synthesis.

3.4. Tandem and Polycyclization Reactions

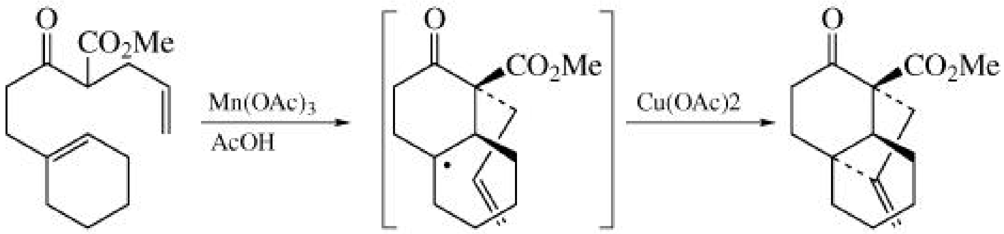
Tandem cyclizations include as key steps two consecutive intramolecular additions to unsaturated fragments. The nature of the dicarbonyl and unsaturated moieties can be varied, along with their relative disposition, thus creating an array of starting materials with different topology. According to the type of radical (carbocation) recipients, six modes of tandem cyclizations are designated DD-mode (double bond–double bond, Table XXXII), DB-mode (double bond–benzene ring, Table XXXIII), TD-mode (triple bond–double bond, Table XXXIV), TB-mode (triple bond–benzene ring, Table XXXV), DC-mode (double bond–carbalkoxy/carboxy/carboxylate group, Table XXXVI), and DN-mode (double bond–nitrile group, Table XXXVII), as well as DDDD-mode (Table XXXVIII) for multiple cyclizations. The types of substrates involved are given in Eq. 20, each bearing two UFs and representing 4-, 2,4-, and 4,4-substituted 3-ketoesters (**123**, **124**, **125**); β -diketones **126**; *C*-substituted malonates with one or two unsaturated fragments (**127**, **128**); *O*-substituted malonate **129**; *C,O*- and *O,O*-disubstituted malonates (**130**, **131**) and their analogues; and 4-substituted 3-ketoacid **132**. The first step of a tandem cyclization is analogous to that of a monocyclization, involving regioselective generation of α , α -dioxoalkyl radicals and their addition across multiple bonds. The thus-generated alkyl and vinyl intermediates can attack intramolecularly an unsaturated fragment, that is, double bond, benzene ring, carbalkoxy/carboxy, or nitrile group. Copper(II) acetate can be used to promote the second cyclization step when the oxidizing power of $Mn(OAc)_3$ appears to be insufficient. Copper(II) acetate is especially useful for cyclizations on carbalkoxy groups, although it can affect the product pattern in many other reactions as well.



(20)

3.4.1. Regioselectivity

The synthetic result of a tandem reaction depends upon the regioselectivity of the first and second annulations, either of which can occur by an *exo* or *endo* mode. The disposition of unsaturated fragments and the positions of substituents are major structural factors that determine the direction of initial attack, the conformation of the intermediate radical, and the ease and selectivity of the second cyclization. A large variety of highly substituted and functionalized bridged and fused systems become available from cleverly designed starting materials (Tables XXXII–XXXVII). Among different modes of tandem cyclizations, those with participation of two double bonds are the most common (DD-mode, Table XXXII). Thus, regioselective 6-*endo* and 5-*exo* cyclizations in substrate **133** afford bridged compound **134** via intermediate cyclohexyl adduct radical **135** (Eq. 21). (100) It is noteworthy that the same cyclization mode can produce

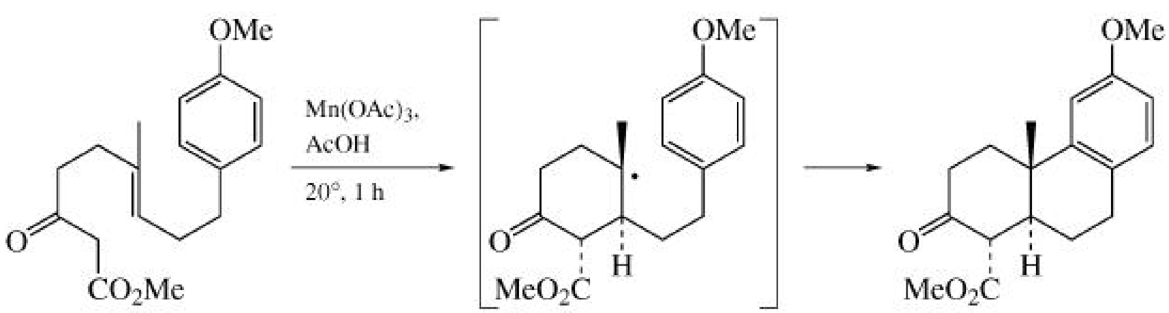


(21)

133 **135** **134** (73%)

different structures depending on the starting material, and in contrast, different modes can afford the same structure by utilizing isomeric substrates. Additional examples of the mode of cyclization vs. type of structure are the following: (a) 6-*endo*, 5-*exo*: bicyclo[4.3.0]nonanes (97, 98, 101) or bicyclo[3.2.1]octanes; (86, 99-102) [3.2.1]octanes; (86, 99-102) (b) 5-*exo*, 6-*endo*: bicyclo[4.3.0]nonane; (103) (c) 6-*endo*, 6-*endo*: bicyclo[4.4.0]decane; (56, 91) (d) 6-*exo*, 5-*exo*: bicyclo[4.3.0]nonane; (100, 103) (e) 7-*endo*, 5-*exo*: bicyclo[4.2.1]nonane (87, 88) and (f) 8-*endo*, 5-*exo*: bicyclo[5.2.1]decane. (87, 88)

Tandem cyclizations by the DB-mode include an initial addition across a double bond and subsequent cyclization upon a benzene ring (Table XXXIII). In most cases, the first step proceeds regioselectively, that is, either 5-*exo* (90, 94, 103) or 6-*endo* (85, 86, 103) annulations have been observed for 5-hexenyl radicals, and exclusively the 6-*exo* (90, 103) mode for 6-heptenyl radicals. There is a single report of a nonregioselective reaction of a 5-hexenyl radical to produce 5-*exo* and 6-*endo* products in a ratio of 1:3. (90) The cyclization on a benzene ring is selectively directed to the *ortho* position, formally representing the 6-*endo* mode (Table XXXIII). A doubly regioselective 6-*endo*, 6-*endo* mode is exemplified by the transformation of 3-ketoester **136** to phenanthrene derivative **137** via tertiary adduct radical **138**.

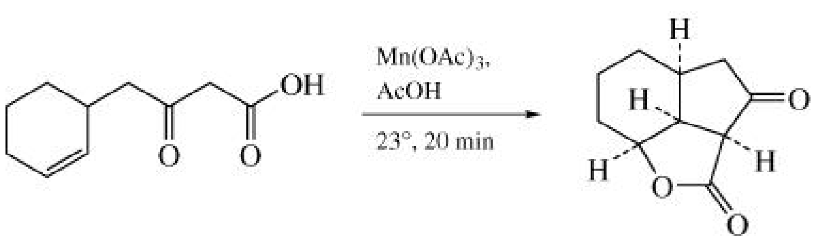


(22)

136 **138** **137** (70%)

Few examples of TD- and TB-mode tandem cyclizations have been reported (Tables XXXIV and XXXV). For the former, 2,4-substituted 3-ketoesters (Type **124**, Eq. 20) with tethered triple and double bonds undergo regioselective cyclization on a disubstituted triple bond (5-*exo*), whereas in terminal alkynes both acetylenic carbons undergo radical attack (5-*exo*:6-*endo* ca. 2:1). Subsequent cyclization of vinylic radicals on a double bond proceeds selectively in the 5-*exo* mode to produce bicyclo[3.3.0]octanes. (99) β -Diketones of type **126** (Eq. 20) were the first substrates for TB-type tandem cyclizations (Table XXXV). The first cyclization is 6-*exo* selective, the second one involves attack of vinylic radicals on the benzene ring (6-*endo* mode). (103)

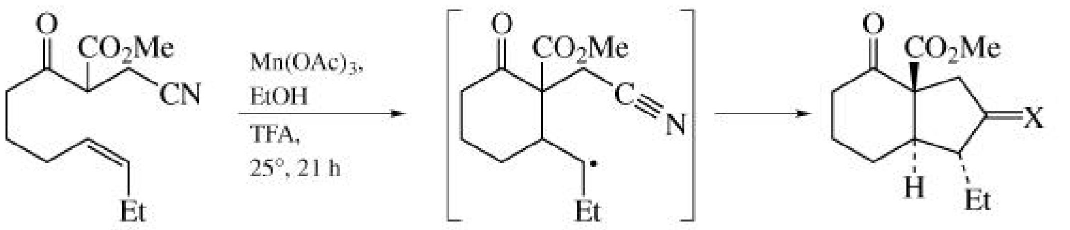
DC-mode tandem cyclizations represent the second widely investigated group of reactions (Table XXXVI). The principal types of substrates employed are *C*-substituted malonate **127**, *O*-substituted malonate **129**, *C,O*-disubstituted malonate **130**, and 4-substituted 3-ketoacid **132** (Eq. 20). Each substrate contains a tethered double bond that reacts in the first step, and a carbalkoxy/carboxy/carboxylate group that undergoes intramolecular attack by the adduct radical. In most cases the initiation step generates 5-hexenyl educt radicals, which undergo 5-*exo* selective cyclization to afford cyclopentane or γ -lactone rings. (94, 96, 99, 178, 183) The formation of a cyclohexane ring from both 5-hexenyl (91) and 6-heptenyl (178) radicals has been also reported. The second step involves cyclization of alkyl adduct radicals upon carbalkoxy, carboxy, or carboxylate groups. The nature of these closely related moieties is nevertheless different, as is the mechanism of cyclization. Thus, addition on a carbalkoxy group requires the use of $Cu(OAc)_2$, as a cooxidant, (91, 94, 96, 99) whereas both carboxy (91, 183) and carboxylate (178) fragments produce γ -lactones with $Mn(OAc)_3$ alone. It is noteworthy that the species that cyclize on carbalkoxy groups are mostly primary radicals, (94, 96, 99) although secondary radicals also afford γ -lactones even in the absence of $Cu(OAc)_2$, although in lower yield. (91) One of the pioneering DC-mode tandem reactions is the Mn(III)-mediated cyclization of the appropriately designed ketoacid **139**. (183) Angularly *cis*-fused ketolactones **140**, as well as related dilactones, are key intermediates for the construction of naturally occurring polycyclic compounds.



139 **140** (63%)

(23)

The nitrile group is a novel type of radical trap recently utilized in intramolecular reactions. Its combination with a double bond creates a new dimension in tandem cyclizations, a DN-mode (Table XXXVII). Thus, secondary adduct radical **141** adds regioselectively across the C ≡ N bond to produce intermediate imine **142** and subsequently bicyclic ketone **143** (Eq. 24). (171)



141

142 X = NH
143 X = O, (57%)

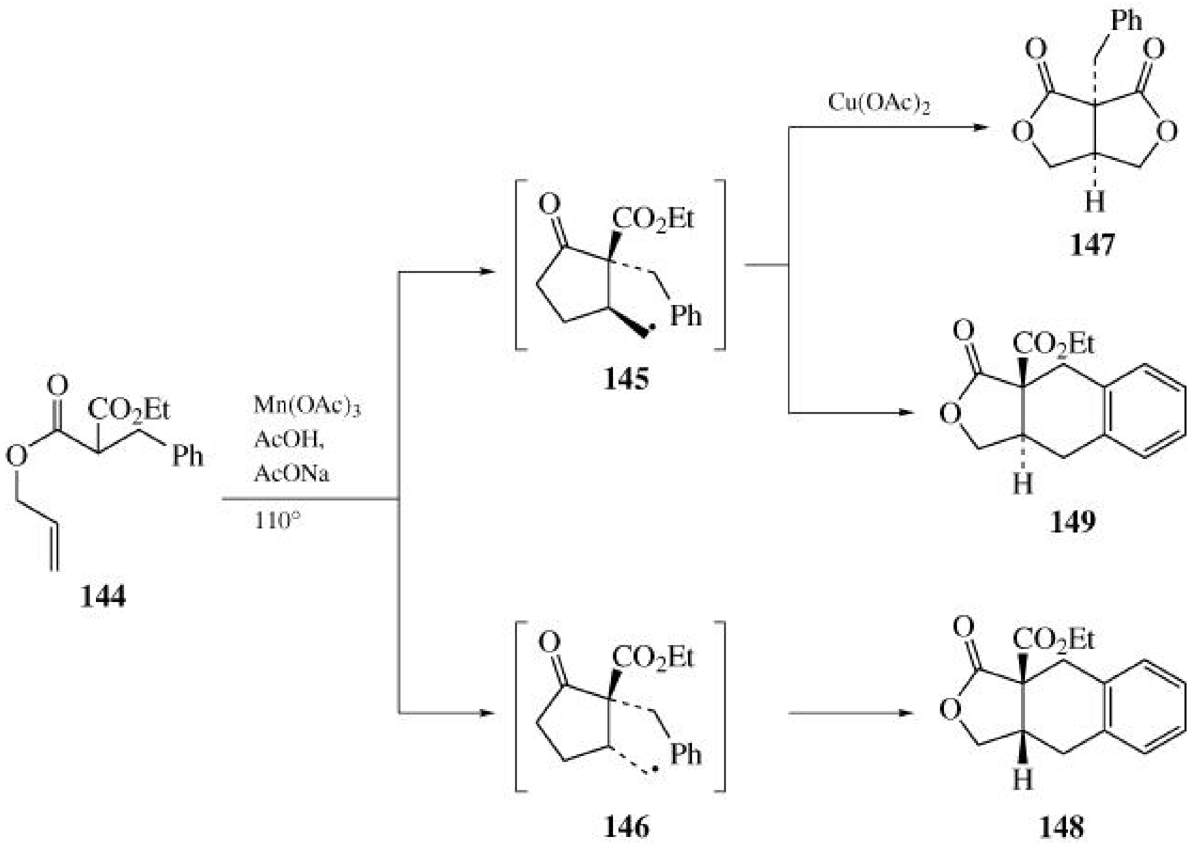
(24)

The polycyclization reaction upon multiple double bonds (DDDD-mode) is represented by a single example, (104) producing a tetracyclic skeleton by regioselective all-6-*endo* cyclizations (Table XXXVIII).

3.4.2. Stereoselectivity

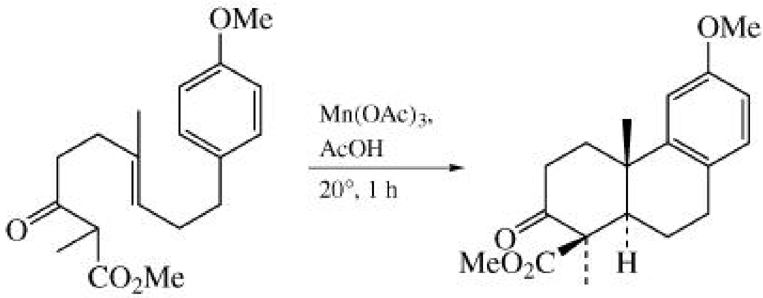
The stereochemistry of tandem cyclizations is one of the most important aspects of the reaction, which determines its significance for organic synthesis, and also its place among other stereoselective methods for the construction of cyclic assemblies. As substantiated by examples given in Tables XXXII–XXXIX, Mn(III) chemistry provides a powerful and highly versatile tool for stereoselective generation of complex organic molecules. There is no complete understanding of the observed selectivity for every reported reaction; even more, in many cases the reasons for the selectivity remain beyond the scope of discussion. Nevertheless the development of such knowledge is critical to predicting the stereochemical outcome of tandem cyclizations. We largely limit our coverage of this topic to two selected reactions where the observed stereoselectivity has become a subject of special consideration. Other examples of highly stereoselective tandem reactions of DD-, DB-, DC-, and DN-modes are shown in Eqs. 21–24, and can also be found in the tables.

Detailed investigation of the tandem cyclization of *O*-allyl malonate **144** has been undertaken recently. (94) The first cyclization converts the starting compound into diastereomeric primary alkyl radicals **145** and **146**. The reaction is regioselective (5-*exo* mode), although stereoselectivity is lacking. In the presence of $Cu(OAc)_2$, the cyclization of adduct radicals **145** and **146** proceeds stereoselectively upon molecular fragments that occupy positions *cis* to the radical center, that is carbethoxy and phenyl groups. *Cis*-fused products **147** and **148** are formed in a ratio of 2:1. In the absence of cooxidant, primary alkyl radical **145** attacks the phenyl group, even though it is in a *trans* position on the five-membered ring. Isomeric lactones **148** and **149** are isolated almost in equal amounts, clearly indicating that cyclization on the benzene ring is purely radical and thus not affected by $Cu(OAc)_2$.



(25)

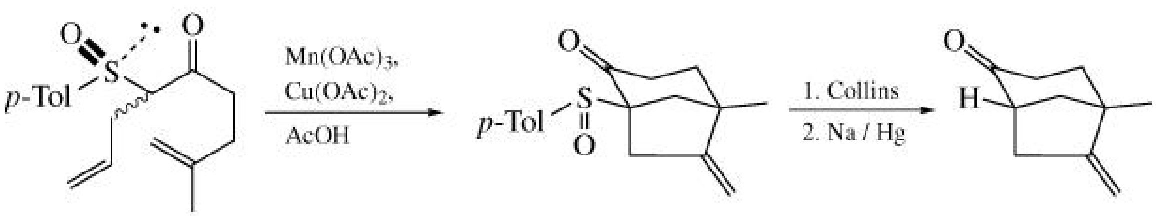
A tandem cyclization of the DB-mode produces *trans*-fused phenanthrene derivative **137** with a *cis* relationship between the methoxycarbonyl group and the bridgehead proton (Eq. 22). (85) The observed stereochemistry might not be genuine if the initially formed stereoisomer undergoes inversion at one of the stereocenters. In particular, enolization could intervene to cause stereomutation at the α carbon. To check this hypothesis, the methyl-substituted analogue **150** has been used in the reaction under identical conditions. Product **151** also has a *trans* junction between cyclohexyl rings, although the methoxycarbonyl group and bridgehead proton are *trans* to each other. This represents the initial stereochemical relationship between these groups, which remains fixed with the methyl substituent, but might also isomerize to the thermodynamically more stable isomer by subsequent enolization. (91)



150 **151** (50%)

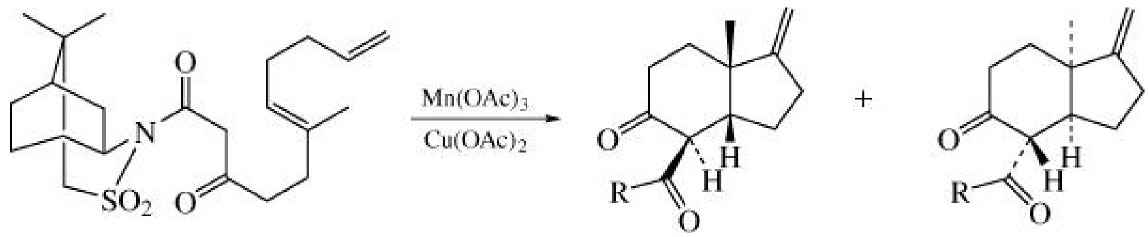
3.4.3. Enantioselectivity

Complete stereocontrol in radical C — C bond-forming reactions remains a major challenge for synthetic chemists. The first success in this area was reported in 1991; the utilization of an enantiomerically pure sulfoxide moiety provides effective asymmetric induction in DD-mode tandem cyclizations. (184) Thus, β -keto sulfoxide **152** undergoes 6-*endo*, 5-*exo* double annulation to afford bicyclo[3.2.1]octanone **153** as a single enantiomer. The chiral auxiliary is removed in two steps to produce the enantiomerically pure target **154**. This strategy of using chiral auxiliaries in the β -dicarbonyl site of the substrate has been further developed by utilizing optically active alcohols (phenylmenthol, *trans*-2-phenylcyclohexanol, naphthylborneol) or amines (i.e., 2,5-dimethylpyrrolidine). (185, 186) The level of asymmetric induction is 23–92%, with the best result obtained with phenylmenthol (90% yield, 92% de).



152 **153** (44%) **154**

Oppolzer's D-camphorsultam has been used to effect asymmetric induction in β -ketoamide **155**. (187) Manganese(III)-promoted tandem cyclization (DD-mode) produces diastereomers **156** and **157** in the ratio 3:1 (50% de). The opposite stereochemical result has been obtained with the L form of the chiral auxiliary. Reductive liberation of separable diastereomers **156** and **157** has also been described.



155

156 (49%)
R = D-Camphor sultam

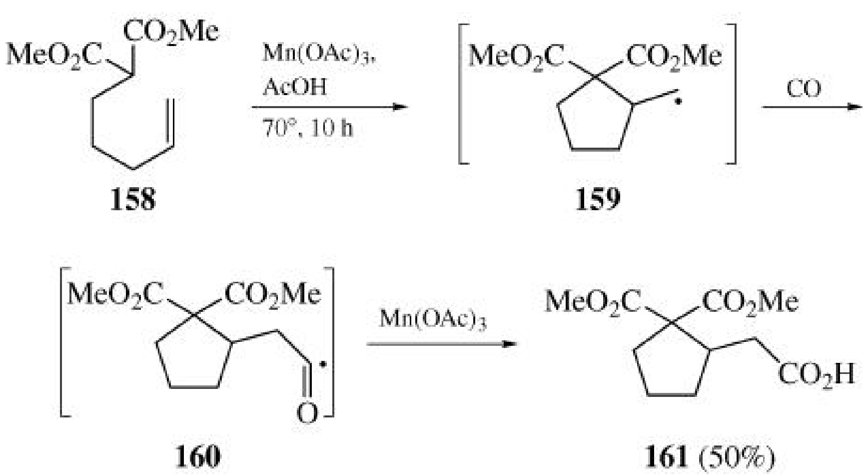
157 (17%)

4. New Directions in Manganese(III) Chemistry

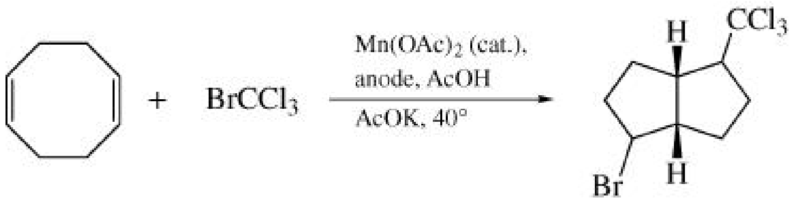
There have been many recent advances in the field of Mn(III)-mediated reactions. Among them are the use of carbon monoxide as a trapping agent for adduct radicals (Table XXXIX), electrochemical generation of trivalent manganese (Table XL), the use of ultrasound as a promoter (Table XLI), and novel methods for alkyl radical generation by oxidation of cycloalkanols (Table XLII) or Cr(0) complexes (Table XLIII) by Mn(III) salts.

4.1.1.1. Carbon Monoxide Trapping Reactions

Mn(III)-mediated inter- and intramolecular reactions, as well as addition–cyclizations, are altered in the presence of carbon monoxide owing to its effective interaction with intermediate adduct radicals. (188) Thus, 5-*exo* cyclization of alkenyl malonate **158** initially produces primary radical **159** and subsequently acyl radical **160**, which oxidatively converts to carboxylic acid **161**. This novel modification is highly useful for synthetic chemistry, and also valuable from a mechanistic point of view as another proof for the formation of free-adduct radicals.



Electrochemical generation of Mn(*OAc*)*3* is an environmentally benign procedure because it allows use of catalytic amounts of $Mn(OAc)_2$. The results of intermolecular reactions (Table XLA), addition–cyclizations (Table XLB), as well as intramolecular processes (189) are virtually the same as those of the nonelectrochemical variants, although some new types of proradicals, such as $BrCCl_3$, CBr_4, CF_2Br_2, and alkyl iodides and dibromoacetates, have been successfully employed. (190) The stereoselectivity is remarkably high in the addition–cyclization reaction of 1,5-cyclooctadiene, affording *cis*-bicyclo[3.3.0]octane **162** in high yield. (190)

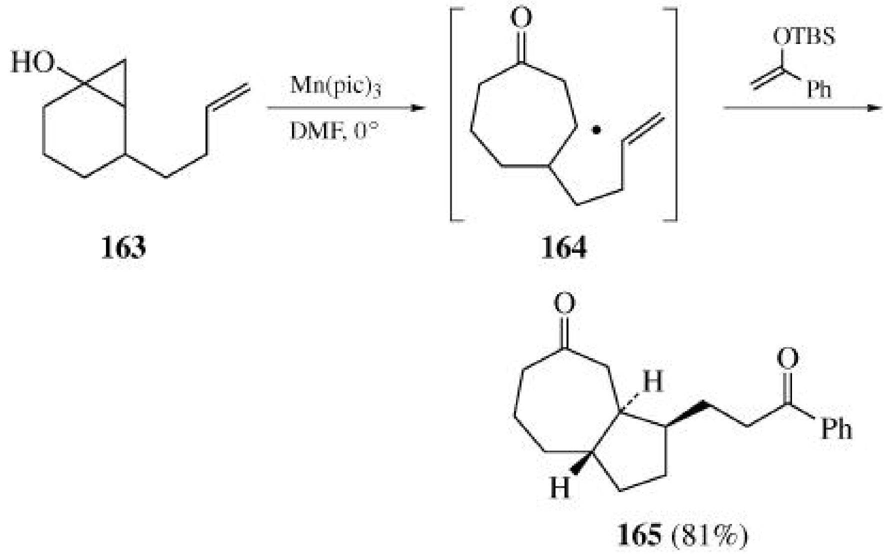


162 (83%)

Sonochemical reactions between alkenes and cyanoacetic acid and potassium methyl malonate produce γ -lactones (Table XLI). (191) Noteworthy features are lower reaction temperature (0°) and high stereoselectivity in the annulation of cycloalkenes and enol ethers. Thus, cyclohexene is lactonized with both carbonyl compounds producing *cis*-fused bicyclics with high stereoselectivity. (191)

4.1.1.2. Cycloalkanols and Cr(0)-Complex-Derived Alkyl Radicals

Oxidation of cyclopropanols, cyclobutanols, and Cr(0) complexes with Mn(III) salts constitute new methods of alkyl radical generation (Eq. 2). (22, 23, 25) Trapping the alkyl radicals with a large number of enol ethers and silyl enol ethers, as well as with electrondeficient alkenes, results mostly in the formation of H-atom transfer products (Tables XLIIA and XLIII). Intramolecular additions of the cyclobutanol-derived alkyl radicals produce polycyclic compounds with *cis* stereoselectivity (Table XLIIC). (24) In contrast, analogous cyclizations of cyclopropanol-derived alkyl radicals afford *trans*-fused bicyclic systems (Table XLIIB). (23) Thus, substrate **163** undergoes oxidative ring enlargement with the formation of cycloheptenyl radical **164**; the latter attacks the double bond in 5-*exo* mode to produce *trans*-fused bicycle **165**. Trapping of adduct radicals has also been accomplished with silyl enol ethers, tributyltin hydride, and diphenyl diselenide. (192)



165 (81%)

5. Applications to Natural Product Synthesis

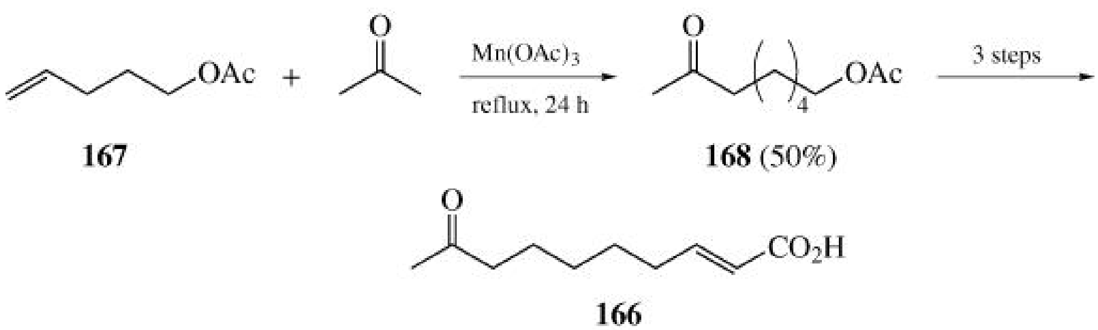
The maturity and significance of any field of organic chemistry can be assessed by its applications to the synthesis of natural and biologically active compounds. Manganese(III) chemistry is at the initial stage of its "practical" utilization, which at this point looks very promising. The common approach is the use of the original intra- and intermolecular model reactions between certain types of substrates and reagents as key steps in the construction of naturally occurring molecules or their analogues and precursors. As the examples of this section demonstrate, manganese(III) mediation is highly efficient in the construction of the diverse structural types ranging from straight-chain acyclic compounds to architecturally complex polycyclic multifunctional derivatives.

5.1. Pheromones

Pheromones constitute a group of naturally occurring compounds that effect chemical communication among insects and animals. In particular, sex pheromones are highly efficient in field trials for monitoring purposes as well as for plant protection. In the past two decades, major efforts have been directed toward the elaboration of novel synthetic methods for supplying sufficient amounts of these compounds for their practical use. Manganese(III)-mediated reactions have made a solid contribution to this field, which is substantiated by examples described in this section.

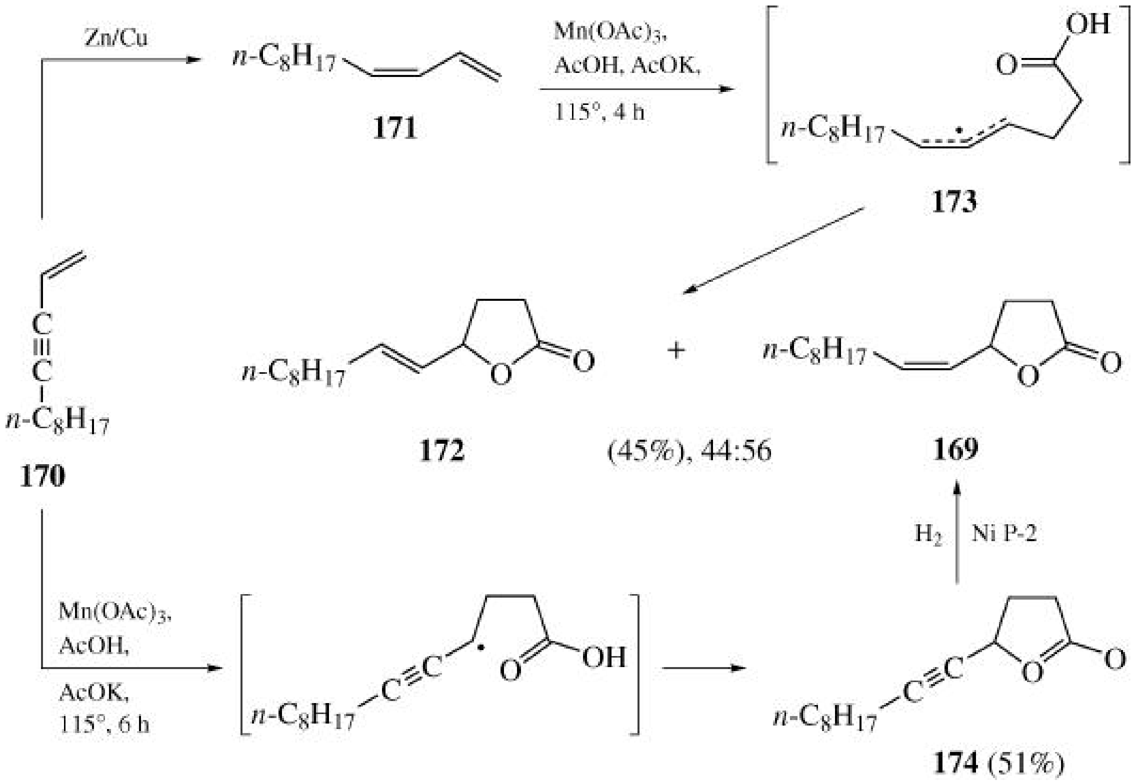
5.1.1. Queen Substance (193)

Queen bee pheromone **166** plays an important role in the metabolism of bees. An alkene–ketone reaction (Table II) has been used for three-carbon homologation of the starting material **167**. The useful yield of **168**, as well as its easy conversion to the final product, make this approach one of the most effective among those reported in literature. (193)



5.1.2. Popillia Japonica (153)

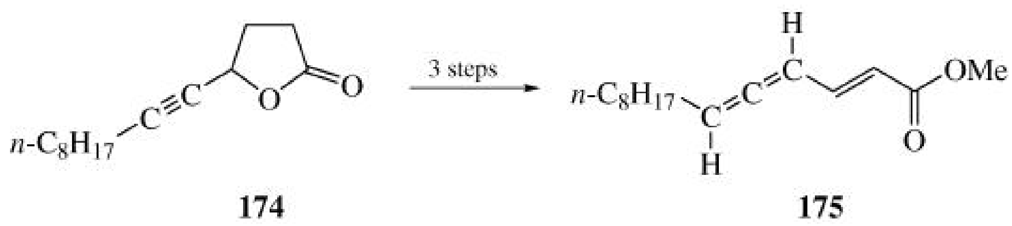
Manganese(III)-mediated lactonization of conjugated enynes (Table XVII) has been used as a key step in the synthesis of (5*Z*)-tetradecen-4-olide (**169**), the sex pheromone of the Japanese beetle *Popillia japonica*. Stereoselective hydrogenation of the triple bond and subsequent lactonization with acetic acid have been used in both direct and reversed order, providing different stereochemical results. In the former sequence, enyne **170** is reduced stereoselectively to (1,3*Z*)-dodecadiene (**171**), which reacts with acetic acid to afford an isomeric mixture of the natural compound (**169**:**172** = 56:44). The observed partial inversion of the *Z* double bond occurs in *Z*-allylic adduct radical **173**, analogous to that in dihydrofuran synthesis. (73) In contrast, lactonization—hydrogenation sequence **170** ® **174** ® **169** produces the sex pheromone **169** with high stereoselectivity (Eq. 26). (153)



(26)

5.1.3. Acanthoscelides Obtectus (157)

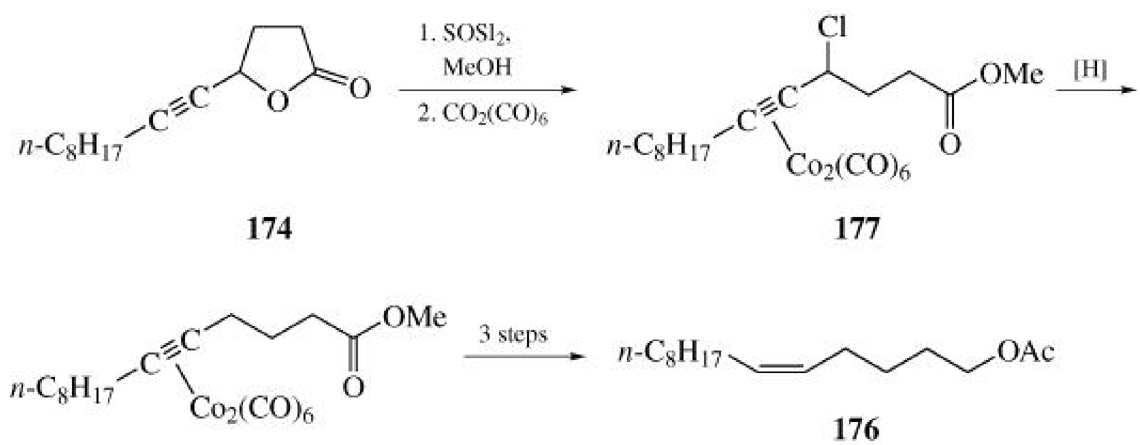
Acetylenic lactone **174** has also been used as an intermediate in the synthesis of methyl (2*E*,4,5)-tetradecatrienoate (**175**), the sex pheromone of the bean weevil moth *Acanthoscelides obtectus*. The method effectively produces multigram quantities of racemic **175**, although its potential for enantioselective synthesis remains to be explored (Eq. 27). (157)



174 175 (27)

5.1.4. Scotia Exclamationis (159)

The “magic” lactone **174** has become the source of (5*Z*)-tetradecenyl acetate (**176**), the sex pheromone of the butterfly *Scotia exclamationis*. Along with $Mn(OAc)_3$-promoted lactonization, another crucial step in this approach is the novel regioselective reduction of the secondary propargyl chloride **177** effected by the $Co_2(CO)_6$ group (Eq. 28). (159)

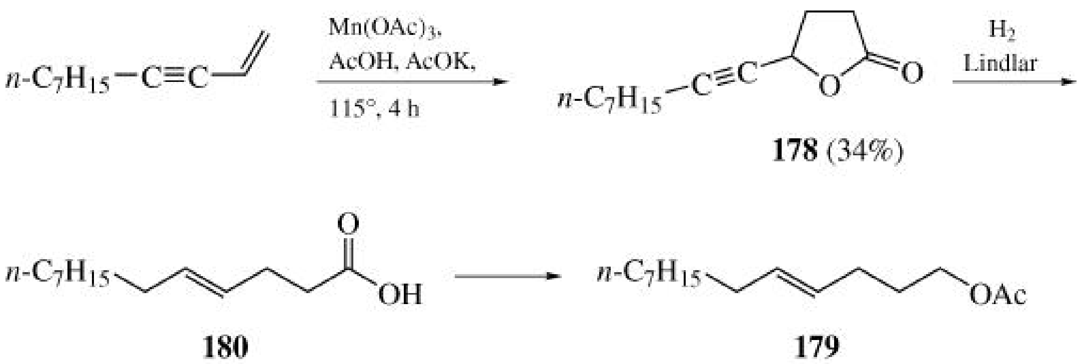


174 177 (28)

176

5.1.5. Keiferia Lycopersicella (158)

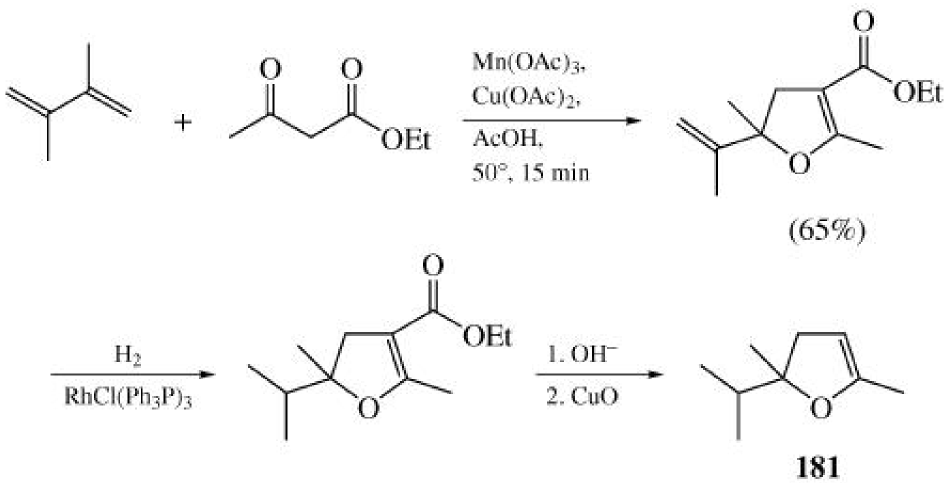
Lactonization of 1,3-undecenyne with acetic acid (Table XVII) provides lactone **178**, a key intermediate in the synthesis of (4*E*)-tridecenyl acetate (**179**), the sex pheromone of the tomato pinworm *Keiferia lycopersicella*. This scheme features the highly regio- and *E*-stereoselective one-step conversion of lactone **178** into carboxylic acid **180** (hydrogenolysis–migration reaction, Eq. 29). (158)



(29)

5.1.6. Hylecoetus Dermestoides (156)

The manganese(III)-mediated reaction of 1,3-alkadienes and β -dicarbonyl compounds (Table XVI) has been used as an initial step in the synthesis of 2-isopropyl-2,5-dimethyl-2,3-dihydrofuran (**181**), the sex pheromone of the beetle *Hylecoetus dermestoides* (Eq. 30). (156)

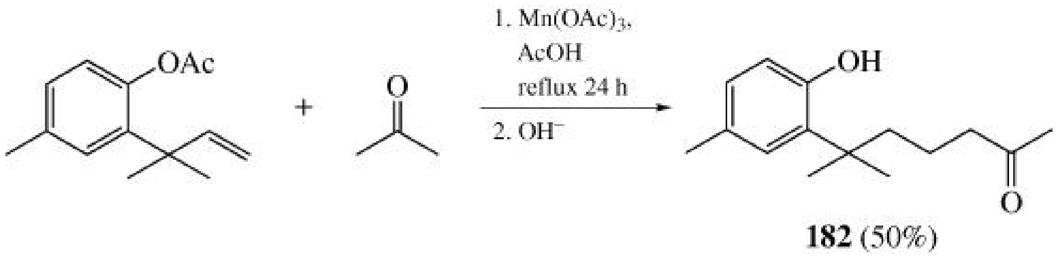


(30)

5.2. Terpenes and Terpenoids

5.2.1. Himasecolone (194)

An alkene–ketone reaction (Table II) has been utilized in the short synthesis of *Himasecolone* **182**, a phenolic sesquiterpenoid isolated from plant sources (Eq. 31). (194) Secondary adduct radicals formed in the addition step abstract a proton from acetone or acetic acid, since $Mn(OAc)_3$ does not oxidatively interact with these transient species (**32**, Eq. 6). Subsequent hydrolysis of the HAA product releases target molecule **182**.



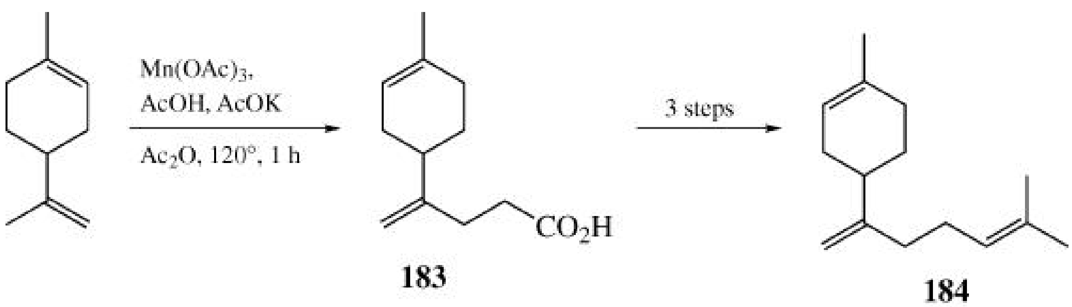
(31)

5.2.2. β -Bisabolene (195)

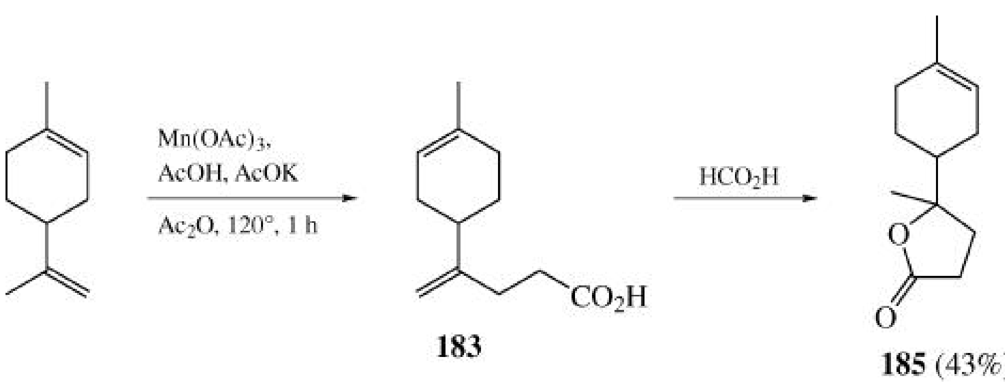
Carboxymethylation of limonene with acetic acid and acetic anhydride (Tables III and XV) has produced 4-alkenoic acid **183** in low yield. Other products formed remain undescribed, although based on related studies their nature could be anticipated. Compound **183** was converted to the natural sesquiterpene β -bisabolene **184** in three conventional steps (Eq. 32). (195)

5.2.3. Norbisabolide (195, 196)

The C_{12} terpene lactone **185**, isolated from plants, was first synthesized from limonene in one step and in low yield. (195) In an optimized protocol, the same composition $Mn(OAc)_3$–AcOH–Ac_2O produces 4-alkenoic acid **183**, which undergoes acid-catalyzed cyclization to the target molecule **185** in 43% overall yield (Eq. 33). (196)



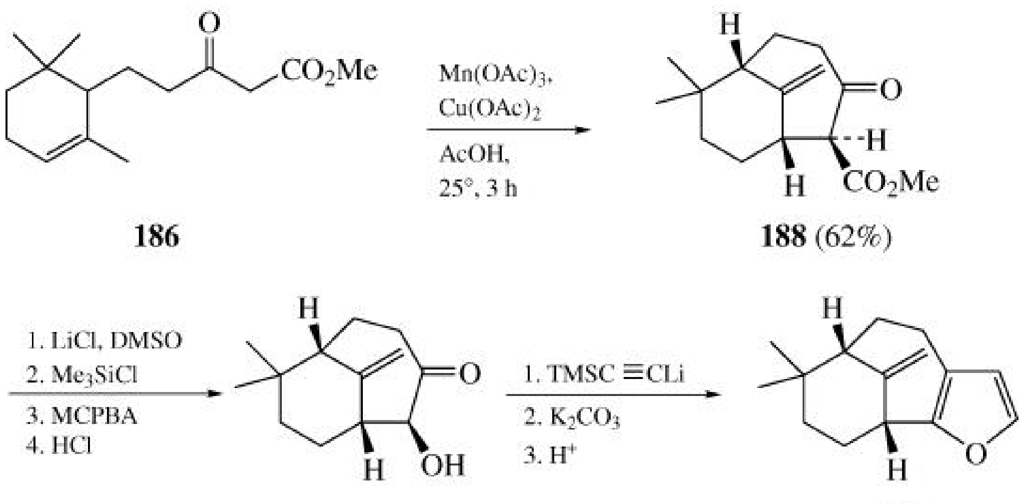
(32)



(33)

5.2.4. Dihydropallescensin D (197)

Intramolecular cyclization of olefinic β -ketoester **186** (Table XXVA) has been used as a key step in the synthesis of dihydropallescensin D, the natural furanosesquiterpene **187**. (197) The cyclization proceeds with high regio- and stereoselectivity and affords bicyclo[4.3.1]decane **188** as a single stereoisomer with a *cis* relationship between bridgehead hydrogens and the carbomethoxy group. Copper(II) acetate is used as a cooxidant to promote an oxidative deprotonation of the intermediate tertiary radical adduct. The regioselectivity of the elimination step is determined by the higher thermodynamic stability of regioisomer **188** with the exocyclic double bond (Eq. 34). (197)

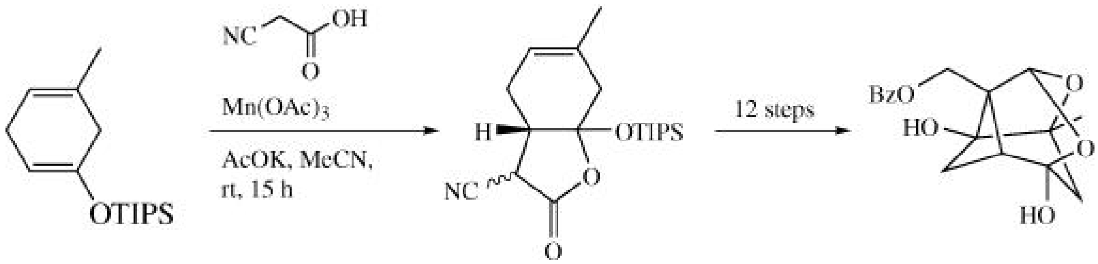


(34)

5.3. Bioactive Compounds

5.3.1. (±)-Paeoniflorigenin (198)

Paeoniflorigenin (**189**) is the nonglucoside part of Paeoniflorin, an active ingredient of the essential oils from *Paeonia lactiflora* that have diverse biological activity. (198) Their syntheses remained an unsolved problem until recently, when both target molecules were successfully constructed. The first step is of immediate relevance, and consists of the lactonization of unsymmetrically substituted 1,4-cyclohexadiene **190** with cyanoacetic acid (Tables X and XV). Lactone **191** is formed chemo-, regio-, and stereoselectively, that is, the electron-rich double bond is exclusively attacked by an electrophilic educt radical, and the bicyclic[4.3.0] system with *trans* configuration is formed. It is noteworthy that lactonization of the unsubstituted cyclohexene with cyanoacetic acid at elevated temperatures produces a mixture of four stereoisomers. (129) The observed *trans* stereoselectivity may be produced by the bulky substituent at the double bond (Eq. 35). (198)

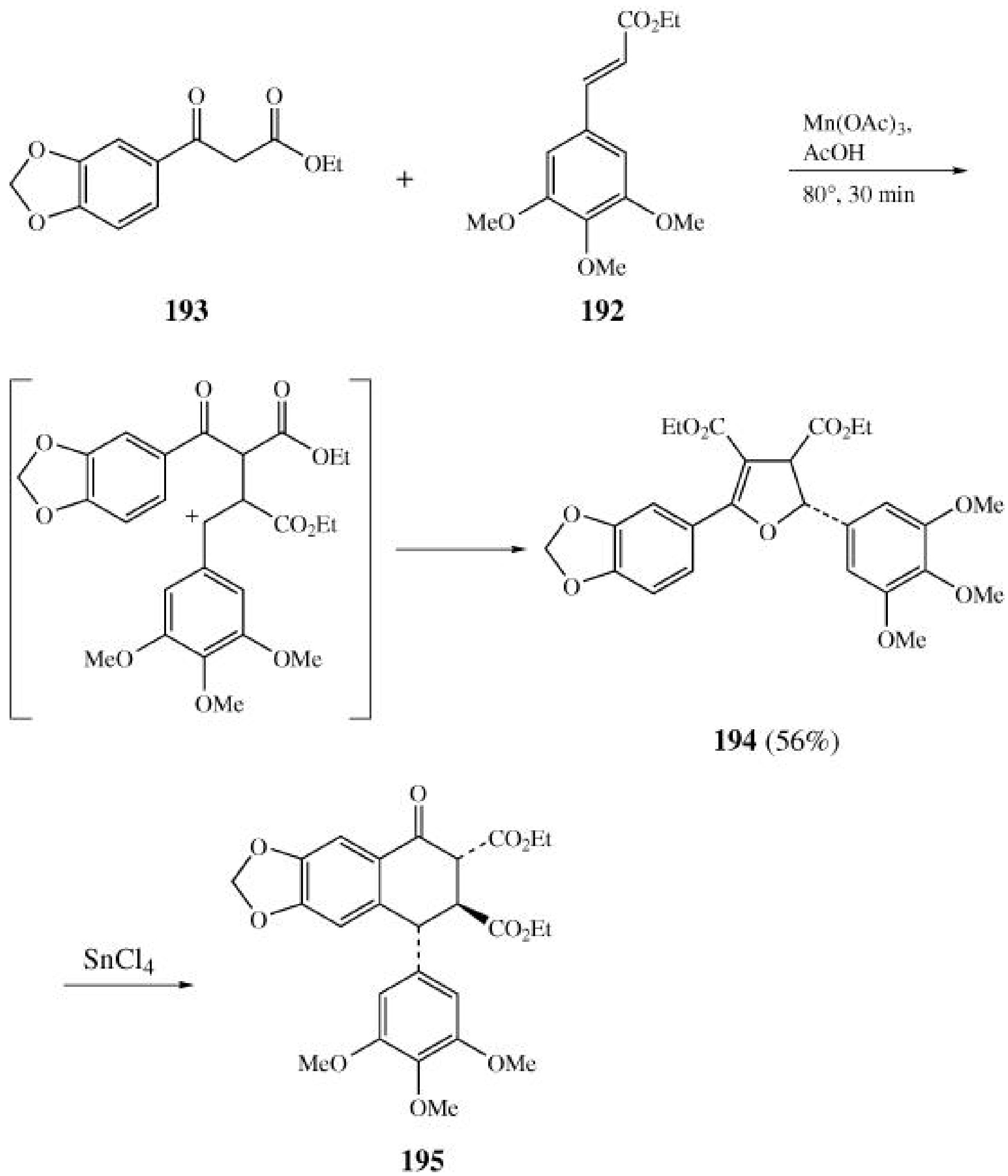


(35)

190 **191** (48%) **189**

5.3.2. Podophyllotoxin Analogue (136)

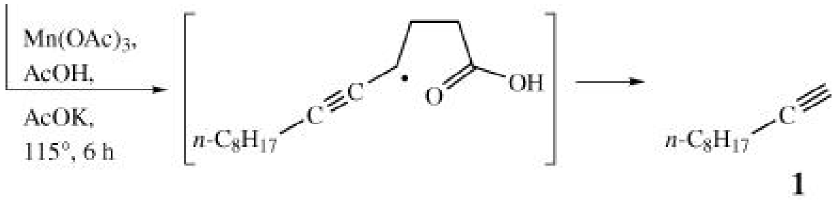
Reactions between styrenes and β -ketoesters have long been known to produce 4,5-dihydrofurans. (33) Styrenes with activated double bonds and aromatic 3-ketoesters react analogously (Eq. 11). (136) In particular, styrene **192** and carbonyl compound **193** produce dihydrofuran **194** by intramolecular cyclization of the intermediate benzylic cation on the benzoyl group. This reaction proceeds with high regioselectivity in the addition step and high stereoselectivity in the intramolecular cyclization. Under acidic conditions, *trans* isomer **194** is rearranged into 4-aryltetralone **195**, a structural analogue of the naturally occurring lignane podophyllotoxin (Eq. 36). (136)



(36)

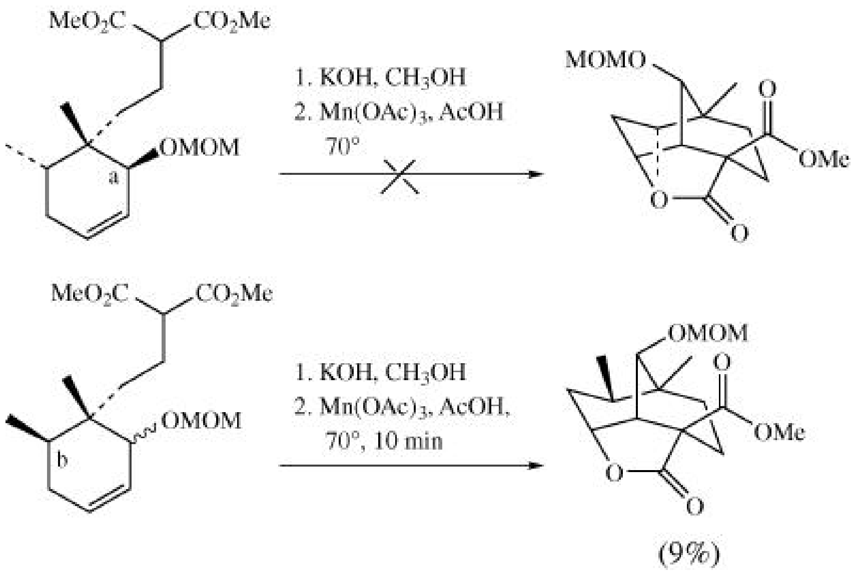
5.3.3. (±)-14-Epiupial (199)

Racemic 14-epiupial (**196**) represents one of the most sophisticated natural molecules that has been synthesized using Mn(III) methodology. Cyclohexene derivative **197**, containing a malonic ester moiety, undergoes partial hydrolysis and subsequent tandem intramolecular cyclization with the sequential formation of six-membered and γ -lactone rings (Eq. 37). The lactone-bridged bicyclo[3.3.1]nonane **198** has been converted by a sequence of steps into target molecule **196**, which appeared to be isomeric with the natural compound.



(37)

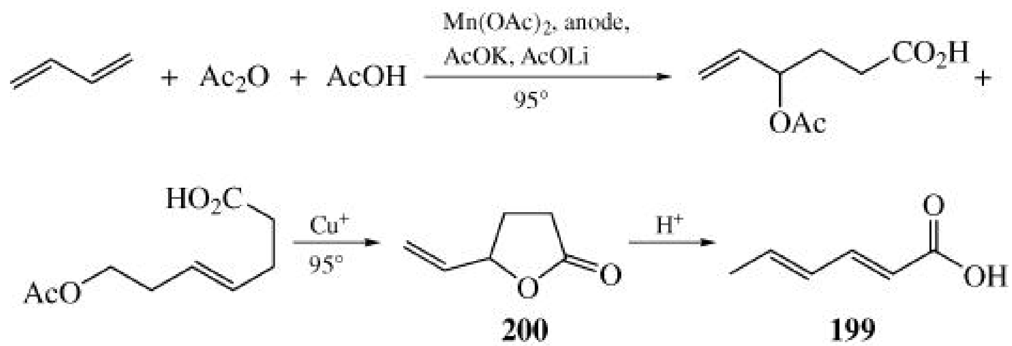
Further attempts to construct the “right” isomer clearly revealed the high sensitivity of Mn(III)-mediated cyclizations toward the configuration of stereogenic centers. Thus, the reaction fails completely after epimerization of the MOMO-bearing carbon atom (a) and proceeds with low yield (9%) if the stereochemistry of carbon (b) is inverted (Eq. 38). (199)



(38)

5.3.4. Sorbic Acid (200)

Sorbic acid (**199**) is a food preservative that is produced on a large commercial scale. An efficient practical method for its synthesis has been developed, including (a) 1,2 and 1,4 conjugate addition to butadiene mediated by electrochemically generated $Mn(OAc)_3$; (b) Cu(I)-promoted conversion of the isomeric acetoxy acids into γ -vinyl- γ-butyrolactone (**200**); and (c) acid-catalyzed rearrangement of the latter into sorbic acid (**199**, Eq. 39). (200)

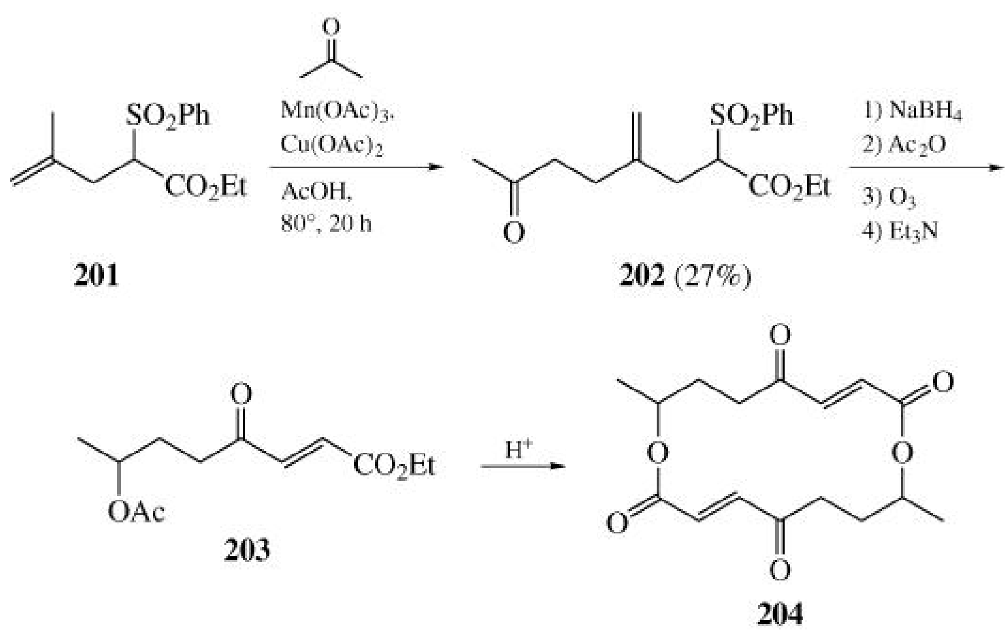


(39)

5.4. Formal Syntheses

5.4.1. Pyrenophorin (201)

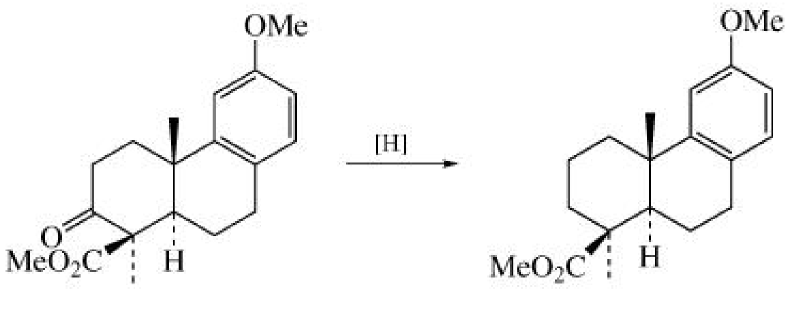
The model reaction between alkenes and ketones mediated by $Mn(OAc)_3$ and producing saturated ketones (Table II) has been modified, first by using $Cu(OAc)_2$ to effect oxidative deprotonation of adduct radicals, and second by introducing a sulfonyl group into substrate **201**. The latter allegedly directs regioselective deprotonation in adduct radicals, producing *exo*-methylene derivative **202**. The scope of the reaction was later expanded (59) by involving both acyclic and cyclic ketones. γ , δ -Enone **202**, isolated in moderate yield (27%), was converted into the known precursor **203** in four steps. This method constitutes a facile access to functionalized γ -keto acrylates, and a formal synthesis of the natural fungicide pyrenophorin (**204**) (Eq. 40). (201)



(40)

5.4.2. Podocarpic Acid (85)

Intramolecular tandem cyclization in the DB-mode (Table XXXIII) has been used to construct stereoselectively the tricyclic core of the phenanthrene derivative **151**. The latter has been reduced to **205**, a racemic precursor in the synthesis of podocarpic acid (Eq. 41). (85, 91)



151 (50%) **205**

(41)

6. Experimental Conditions

6.1. Manganese(III) Salts

6.1.1. Mn(OAc)$_3$

Manganese(III) acetate has two modifications, a dihydrate form $Mn(OAc)_3 \cdot 2\ H_2O$ and an anhydrous form $Mn(OAc)_3$. The dihydrate is commercially available (Fluka). It can be synthesized in the laboratory by oxidation of $Mn(OAc)_2$ with $KMnO_4$, (164, 202) or in situ by anodic oxidation. (169, 190, 203-205) Anhydrous $Mn(OAc)_3$ can be prepared by oxidation of $Mn(OAc)_2$ with $KMnO_4$ in glacial AcOH in the presence of Ac_2O, (9, 27) or by treating $Mn(NO_3)_2 \cdot 6H_2O$ with Ac_2O. (164) The structure of the anhydrous form has been elucidated by X-ray diffraction, (206) and is polymeric with repeating units consisting of three molecules of $Mn(OAc)_3$. Manganese atoms form an equilateral oxo-centered triangle surrounded by six bridging acetate ligands and another two acetate moieties that link repeating units to each other. The trimer of $Mn(OAc)_3$ might be capable of oxidizing up to three radical precursors, although the fact that an excess is often required to bring reactions to completion indicates that its oxidizing power and mode of performance depends on the nature of the process. The hydrated form has been used in the vast majority of Mn(III)-mediated reactions because of its availability and because the anhydrous form has no apparent advantages. In one comparative study on lactonization of alkenes, (117) the hydrated form provided higher yields of γ -lactones.

The thermal decomposition of $Mn(OAc)_3$ has been investigated by TG, DTG, and DTA methods, (207) as well as in AcOH (27) and Ac_2O. (208) Thermogravimetric analysis reveals its stability up to 110° in air and, surprisingly, only up to 40° under anaerobic conditions. (207) At 110° it undergoes chemical degradation by releasing carboxymethyl radical, which produces acetoxyacetic (20%) and succinic (2%) acids along with carbon dioxide (15%) and methane (2%). (27) The reduction reaction is first order in trivalent manganese with an energy of activation of ~ 28 kcal mol^{-1}. (27) Succinic anhydride and acetoxyacetic acid are the major products when it is treated at 120° in Ac_2O containing 10% AcOH. (208) This reaction is zero order in Mn(III) salt and is accounted in terms of enolization of Ac_2O as the rate-determining step. Trifluoroacetic acid is suggested to accelerate the enolization step, and thus the reduction overall. (208)

6.1.2. Mn(acac)$_3$

Tris(acetylacetonato)manganese(III) has been used in some reactions to produce acetylacetonyl radicals. (38, 45, 55, 109, 135) The chemistry of the process is virtually the same as that of acetylacetone oxidation by $Mn(OAc)_3$, although the former appears to be a milder oxidant. (13)

6.1.3. Mn(pic)$_3$

$(PyCO_2)_3Mn$, or Mn(III) tris(2-pyridinecarboxylate), has a short history as a mediator of radical reactions between unsaturated systems and carbonyl compounds. Japanese authors have recently described its use under mild conditions in DMF. (22, 23, 25, 118, 209) Analogous to $Mn(OAc)_3$, it is able to oxidize carbonyl compounds, (118, 209) as well as cyclopropanols, (22, 23) cyclobutanols, (24) and Cr(0) complexes. (25)

6.2. Stoichiometry

The initial step of the reaction is a one-electron oxidation of a carbonyl compound with a Mn(III) salt, requiring 1 equivalent of the latter. If manganese(III) ions participate in the oxidation of the intermediate radical-adducts to cations, overall 2 equivalents of metal oxidant will be required, unless regeneration of Mn(III) ions occurs during the reaction. It does occur in the presence of oxygen, which enables the use of catalytic amounts of $Mn(OAc)_3$ or $Mn(OAc)_2$, (52) although this protocol has serious limitations because of the sensitivity of many unsaturated organic compounds to oxygen. One of the latest developments is the electrochemical generation of $Mn(OAc)_3$ by anodic oxidation of equimolar or even catalytic amounts of $Mn(OAc)_2$. (169, 189, 190, 203-205) The use of $Cu(OAc)_2$ as a cooxidant requires doubling the amount of Mn(III) salt, since the latter regenerates Cu(II) from Cu(I) ions. A separate issue is the molar ratio of substrate to carbonyl compound. Although equimolar amounts are normally required by the stoichiometry of the reaction, the carbonyl components have often been used in excess or even as solvent. The optimization of any reaction remains empirical, and not every reported reaction has been optimized. Even if a closely related type of process has been described, one has to realize that structural changes, even subtle ones either in substrate or carbonyl component, might require some additional optimization.

6.3. Solvents

The most common solvent in Mn(III)-mediated reactions is glacial acetic acid. It was first described in the pioneering papers, (28, 125) and since then has been heavily used. Although $Mn(OAc)_3$ is not soluble in acetic acid at room temperature, reactions can be effectively executed with the suspension. At elevated temperatures (50–140°), the system becomes homogeneous. The intermediate case consists of initial homogenization of the solution by short heating, and subsequent cooling to room temperature prior to addition of the reagents. This procedure allows operation with an almost homogeneous system at lower temperatures. Although glacial acetic acid is efficient in a large number of reactions, it is not free of limitations. First, the acidic character makes it incompatible with acid-sensitive substrates. Second, acetic acid can participate in solvolysis or LTR reactions to produce acetoxy derivatives which are not always desired. Alternative solvents used in recent years are aliphatic alcohols (methanol, (57) ethanol (24, 87, 95, 97, 99, 171, 179)), dimethylformamide, (22, 23, 25, 118, 209) hexane, (49) dioxane, (82) acetonitrile, (172) and chloroform. (93)

6.4. Temperature

The temperature of the process is largely determined by the first step—generation of the α -oxo- and α , α -dioxoalkyl radicals by oxidation of the carbonyl compounds. The rate of the reaction is dependent on the structure of the carbonyl component, in particular, the number of carbonyl groups, enolizability, and C — H acidity. Usually, compounds with more carbonyl groups (more easily enolizable and more acidic) react with the oxidant at lower temperatures. The overview for different types of carbonyl compounds provides an idea of the temperature ranges used for different classes of carbonyl compounds:

Aldehydes	50–70°
Ketones	40–120°
Monocarboxylic acids	100–140°
Anhydrides	120–140°
β -Dicarbonyl compounds	20–100°
β -Ketocarboxylic acids	20°
Dicarboxylic acids	70–120°
Dicarboxylic acid derivatives	23–120°
Ortho esters	60–65°
Nitroalkanes	83–120°

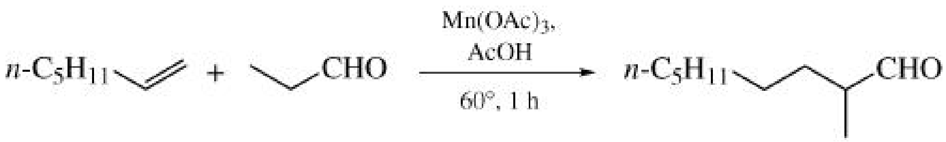
The temperature limit for Mn(III)-promoted reactions has recently been brought down to 0° by using ultrasound (191) or Cr(0) complexes as a source of alkyl radicals. (25)

6.5. Concentration

The role of metal oxidant entails the generation of radicals and the oxidative interaction with adduct-radicals formed along the reaction coordinate. The relative rates of the intermediate steps determine the pattern of products and depend upon the concentration of metal oxidant. Thus, concentration becomes an important parameter of the reaction, and the selectivity of the process is dependent on it. This parameter, which has often been chosen by analogy with previous work or selected empirically, remains mostly arbitrary. It has resulted in the use of different concentrations of $Mn(OAc)_3$ even in the same type of reaction. The most striking example is the interaction of alkenes with acetic acid–acetic anhydride, where the concentration of $Mn(OAc)_3$ has varied widely

(0.01, 0.067, 0.14, 0.35, 0.50, 0.56, 0.69, 0.81, and 1.69 mol L^{-1}). It is not surprising that this results in a diversity of product distributions, including the formation of saturated carbon acids or alkan-4-olides as single products, simultaneous formation of 4-acetoxy-acids, alkan-4-olides, 3- and 4-alkenoic acids, as well as alkan-4-olides together with saturated carboxylic acids or allylic acetates. The importance of this parameter is not adequately recognized; in most publications it is not considered. The Mn(III) concentration should be kept uniform for given types of reactions so that procedures will become standardized and the results predictable for analogous processes. The arguments above are also germane to $Cu(OAc)_2$, which is the commonly used cooxidant.

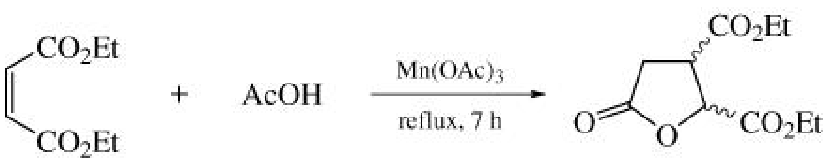
7. Experimental Procedures



206 (28%)

7.1.1. 2-Methylnonanal (206) (41)

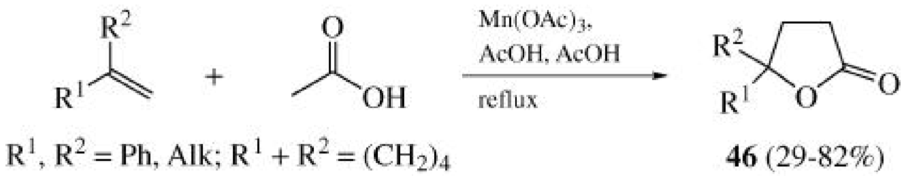
$Mn(OAc)_3$·2 H_2O (23.5 g) was dissolved in 105 mL of AcOH, and propionaldehyde (101.5 g) and 1-heptene (34.2 g) were added to the solution. The mixture was then heated in an atmosphere of nitrogen at 60°. After the brown color of the trivalent manganese salt had disappeared (1 hour), the excess of the original reagents and most of the acetic acid were distilled under vacuum. The residue was treated with water, the mixture was extracted with ether, and the extract was dried and submitted to fractional distillation in a stream of nitrogen. 2-Methylnonanal (**206**, 3.8 g, 28%) was obtained, bp 68–70° (7 mm Hg). DNPH-derivative: mp 87–88°; IR 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.4–9.5(J = 1.6–2.7 Hz). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.62; H, 12.92.



207 (56%)

7.1.2. 4,5-Diethoxycarbonyl-(2H)-tetrahydrofuran-2-one (207) (131)

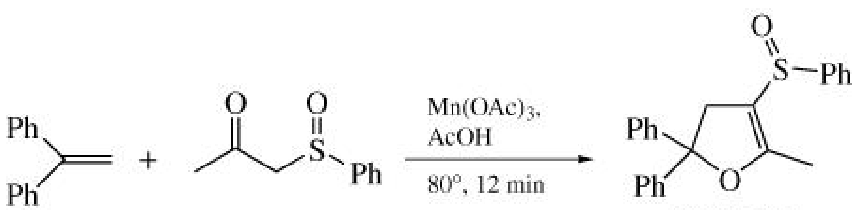
In a round-bottomed flask equipped with a condenser were added diethyl maleate (2.0 mmol), glacial AcOH (40 mL), and $Mn(OAc)_3$·2 H_2O (1.08 g, 4.0 mmol). The mixture was heated under reflux in a nitrogen atmosphere until the dark-brown color of the manganese(III) salt disappeared (7 hours), after which most of the AcOH was removed under reduced pressure, and the mixture was allowed to cool to room temperature. The resulting precipitate of $Mn(OAc)_2$ was separated by filtration and washed carefully with a small amount of EtOAc. The washing and filtrate were combined and evaporated under reduced pressure to afford a residue which was chromatographed on a silica gel column using 50% ethyl acetate–hexane as eluent. Lactone **207** was obtained in a 56% yield as a mixture of *cis*:*trans* isomers (1:5.7), bp 138–143° (0.25 mm Hg). ^{1}H NMR ($CDCl_3$) *cis* isomer: δ 3.7–3.8 (m), 5.10 (d, *J* = 8.4 Hz); *trans* isomer: 3.4–3.5 (m), 5.15 (d, *J* = 4.4 Hz). Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 51.99; H, 6.19.



46 (29-82%)

7.1.3. Lactone Annulation (General Procedure) (117)

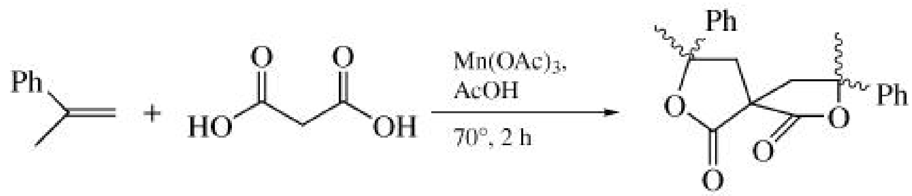
A 100-mL round-bottomed flask equipped with a reflux condenser, nitrogen inlet, and magnetic stirrer was charged with the alkene (5 mmol), $Mn(OAc)_3{\cdot}2\,H_2O$ (4.17 mmol), AcOK (25 mmol), and glacial AcOH (50 mL). The mixture was refluxed until the dark brown color disappeared, cooled, and diluted with water (200 mL). The organic products were extracted with ether (5 × 40 mL). The combined ethereal extracts were washed with H_2O (2 × 40 mL), saturated $NaHCO_3$ solution (2 × 40 mL), dried ($MgSO_4$), evaporated, and chromatographed. Lactones **46** were isolated in 29–82% yield.



208 (76%)

7.1.4. 2-Methyl-3-(phenylsulphenyl)-5,5-diphenyl-4,5-dihydrofuran(208) (53)

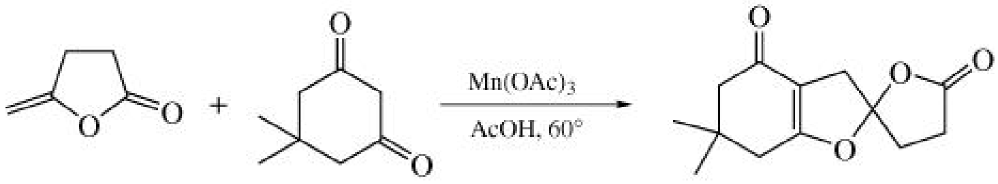
To a heated solution of phenylsulfenylacetone (1 mmol) and 1,1-diphenylethene (1 mmol) in AcOH (25 mL), $Mn(OAc)_3{\cdot}2\,H_2O$ (4 mmol) was added. The mixture was stirred at 80° for 12 minutes. The reaction was quenched by adding H_2O (60 mL), and the mixture was then extracted with benzene. After removing the benzene, the product **208** was separated as a pale yellow oil, either on TLC (Wacogel B10) eluting with $CHCl_3$ or on a silica-gel column eluting with benzene. IR ($CHCl_3$) 1642, 1018 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.38 (t, *J* = 1.6 Hz, 3 H), 2.86 (dq, *J* = 1.6, 14.4 Hz, 1 H), 3.72 (dq, *J* = 1.6, 14.4 Hz, 1 H), 7.07–7.73 (m, 15 H); high-resolution MS *m/e* Calcd for $C_{23}H_{20}O_2S$ 360.1184. Found 360.1273.



61 (81%)

7.1.5. (±)-(3 α ,5 β ,8R)-, (±)-(3 α ,5 α ,8S*)- and (±)-(3 α ,5 α ,8R*)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (61) (spirodilactonization Reaction) (145)*

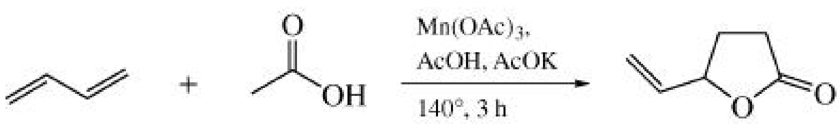
$Mn(OAc)_3 \cdot 2\ H_2O$ (2.7 g, 3.35 mmol) was weighed into a 50-mL flask equipped with a magnetic stirrer. Glacial AcOH (25 mL) was added and the flask was placed in a 70° oil bath and stirred. Malonic acid (0.26 g, 2.5 mmol) was added, immediately followed by addition of α -methylstyrene (0.59 g, 5 mmol). The flask was fitted with a reflux condenser and gas-inlet tube (N_2) and the reaction was allowed to proceed until the mixture turned colorless (2 hours). After being cooled, the reaction mixture was quenched with 250 mL of H_2O and extracted with 50–75 mL of CH_2Cl_2 or Et_2O. The organic extract was washed with saturated $NaHCO_3$ until the washings were no longer acidic, subsequently washed twice with H_2O, dried ($MgSO_4$), and concentrated to give spirodilactones **61**. MPLC separation of the diastereomers employed 20–40% AcOEt–hexane. Diastereomeric ratio ss:u:sa 20:49:31. Total yield 81%. **61-ss** : mp 216.5–217°; IR (KBr) 1775, 1753, 1600, 1495 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.78 (s, 6 H), 2.77 (d, *J* = 13.3 Hz, 2 H), 3.25 (d, *J* = 13.3 Hz, 2 H), 7.5–7.2 (m, 10 H); **61-u** : mp 96.5–97°; IR (KBr) 1775, 1753, 1595, 1495 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.65 (s, 3 H), 1.90 (s, 3 H), 2.10 (d, *J* = 13.6 Hz, 1 H), 2.80 (d, *J* = 13.2 Hz, 1 H), 2.80 (d, *J* = 13.6 Hz, 1 H), 3.15 (d, *J* = 13.2 Hz, 1 H), 7.5–7.1 (m, 10 H); **61-sa** : mp 141–143°; IR (KBr) 1778, 1754, 1600, 1495 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.75 (d, 6 H), 2.17 (d, *J* = 13.3 Hz, 2 H), 2.67 (d, *J* = 13.3 Hz, 2 H), 7.5–7.2 (m, 10 H).



209 (64%)

7.1.6. 6,6-Dimethyl-4,5,6,7,4',5'-hexahydrospiro[benzofuran-2(3H),2'(3'h)-furan-4,5'-dione] (209) (141)

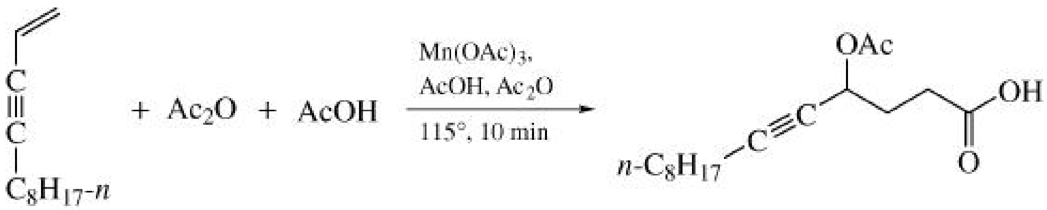
$Mn(OAc)_3 \cdot 2\ H_2O$ (1.0 g, 3.7 mmol) was heated in acetic acid (8 mL) under nitrogen at 60–70° until a black homogeneous solution was obtained. Dimedone (0.38 g, 2.7 mmol) and γ -methylene- γ -butyrolactone (0.24 g, 2.5 mmol) were added and the reaction mixture was kept at 60° until the color had disappeared. To the cold mixture, H_2O was added and the solution was extracted with CH_2Cl_2. The combined organic extracts were washed with saturated $NaHCO_3$ solution and evaporated under reduced pressure to give an oil. Recrystallization (EtOAc) afforded as white flakes compound **209** (0.38 g, 64%), mp 116–117°. IR ($CHCl_3$) 1815 and 1650 cm^{-1}; ^{1}H NMR δ 1.11 (s, 3 H, CH_3), 2.25 (m, 2 H, CH_2), 2.36 (m, 2 H, CH_2), 2.40–2.90 (m, 4 H, $2CH_2$), 2.98 (d, J = 15 Hz, 1 H) and 3.20 (d, J = 15 Hz, 2 H, CH_2). MS *m/z*: M^+ 236 (37%). Anal. Calcd for $C_{13}H_{16}O_4$: C, 65.7; H, 6.76. Found: C, 66.0; H, 6.74.



200 (39%)

7.1.7. γ -Vinyl- γ -butyrolactone (200) (200)

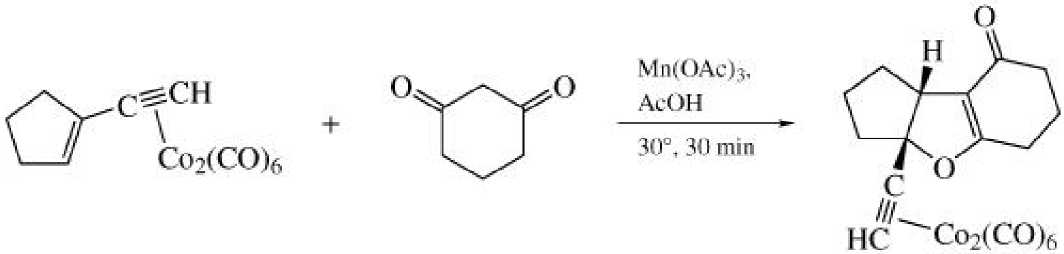
Under nitrogen, 115 g (0.43 mol) of $Mn(OAc)_3 \cdot 2\ H_2O$, 24.5 g (0.35 mol) of AcOK, and 385 mL of glacial AcOH were charged into a 760-mL top-stirred stainless steel Parr reactor. The reactor was chilled and 43 g (0.89 mol) of 1,3-butadiene was condensed into the reactor. Stirring was begun and the reactor was heated to 140° over 20 minutes. The reactor was maintained at 140° with stirring for 3 hours, then cooled and vented. The product mixture, consisting of a white solid plus yellow liquid, was taken up in 210 mL of H_2O and 100 mL of ether. The water layer was separated and extracted with three 75-mL portions of ether. The combined ether solutions were dried over $MgSO_4$ and stripped on a rotary evaporator to remove ether. The residue was distilled through a short-path microware still at 25–160° (0.8 mm Hg) to give 25.3 g of distillate (trapped in dry ice). The distillate was fractionated through a 6-in. Vigreux column to give 9.3 g (39%) of product **200**, bp 97–100° (15 mm Hg), 99% purity by GC analysis. ^{1}H NMR (60 MHz, CD_3CN) δ 1.6–2.7 (m, 4 H), 4.7–6.3 (m, 4 H). MS *m/z*: 112 (100%).



210 (57%)

7.1.8. 4-Acetoxy-5-tetradecynoic Acid (210) (62)

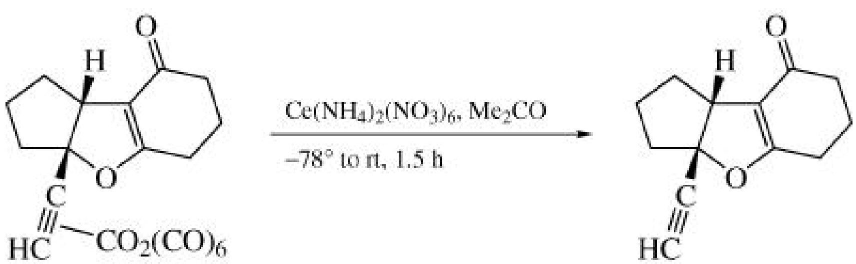
In a dried, argon-filled round-bottomed flask fitted with stirrer and thermometer was placed $Mn(OAc)_3 \cdot 2\ H_2O$ (5.36 g, 20 mmol) and 1-tetradecen-3-yne (1.64 g, 10 mmol); glacial AcOH (120 mL) and Ac_2O (40 mL) were consequently added at room temperature. The suspension was heated to reflux until the brown color disappeared (115°, 10 minutes). The mixture was cooled to room temperature, diluted with H_2O (300 mL), and extracted with Et_2O (2 × 150 mL). The combined ethereal layers were washed with H_2O (2 × 100 mL), and then saturated Na_2CO_3 was poured in slowly until the solution was basic. The aqueous layer was separated, acidified with 5% HCl to pH 1, and extracted with Et_2O (3 × 100 mL). The combined ethereal layers were washed with water (2 × 100 mL) and dried ($MgSO_4$). The ether was evaporated, the residue was chromatographed over silica gel (15 g, hexane–Et_2O, 4:1) to give 1.61 g (57%) of **210**. R_f = 0.42 in hexane–ether 1:2. IR (neat) 3400–2500, 2254, 1745, 1720 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.7 Hz, 3 H), 1.17–1.40 (br.s, 10 H), 1.50 (quintet, *J* = 7.3 Hz, 2 H), 2.06 (s, 3 H), 2.07 (td, *J* = 7.4, 6.1 Hz, 2 H), 2.19 (td, *J* = 1.9 Hz, 2 H), 2.54 (t, 2 H), 5.44 (tt, 1 H), 10.6 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.11, 18.67, 20.98, 22.66, 28.41, 28.85, 29.03, 29.16, 29.70, 29.86, 31.83, 63.35, 76.38, 87.23, 169.74, 178.73.



93 (28%)

7.1.9. (cis-1,8-Dehydro-3-ethynyl-2-oxatricyclo[6.4.0.0^3,7]dodecan-9-one) Dicobalt Hexacarbonyl (93) (57)

A reaction flask was charged with $Mn(OAc)_3 \cdot 2\ H_2O$ (4.34 g, 16.2 mmol) under nitrogen. After five pump-and-fill cycles, a solution of (cyclopentenylacetylene)$Co_2(CO)_6$ complex(1.0 g, 2.7 mmol) and 1,3-cyclohexanedione (3.63 g, 32.4 mmol) in a glacial AcOH (54 mL) was added in one portion [molar ratio substrate: Mn(III): β -dicarbonyl compound 1:6:12]. The mixture was heated for 1 hour at 30° with stirring (TLC monitoring). Aqueous work up and subsequent column chromatography (SiO_2, 200 g, PE/E 1:2) gave **93** (370 mg, 28%) as dark-red crystals together with **211** (56 mg, 10%). $T_{decomp.}$ 130–135°. R_f = 0.48 (PE:E, 1:3). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56–1.73 (m, 1 H), 1.75–2.10 (m, 7 H), 2.26–2.38 (m, 2 H), 2.40–2.54 (m, 2 H), 3.25 (d, *J* = 7.3 Hz, 1 H), 6.05 (s, 1 H). MS *m/z* 488 (1%), 320 (26%). Anal. Calcd for $C_{19}H_{14}O_8Co_2$: C, 46.72; H, 2.87. Found: C, 46.60; H, 2.72.

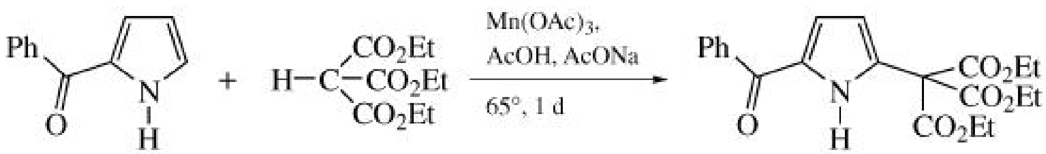


93 **211** (86%)

7.1.10. cis-1,8-Dehydro-3-ethynyl-2-oxatricyclo[6.4.0.0^3,7]dodecan-9-one (211) (57)

Decomplexation of 0.64 mmol of **93** with $Ce(NH_4)_2(NO_3)_6$ at – 78° afforded **211** (111 mg, 86%), R_f = 0.39 (PE:E, 1:3). ^{1}H NMR (300 MHz, ac-d_6) δ 1.45–1.57

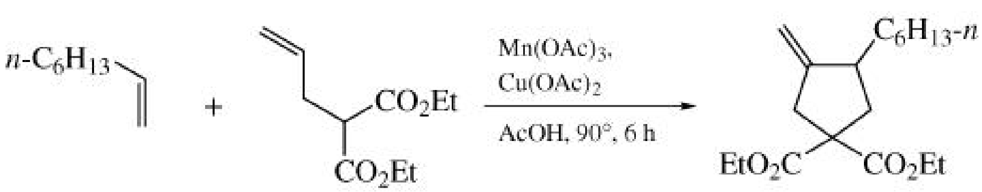
(m, 1 H), 1.71–1.90 (m, 3 H), 1.93–2.09 (m, 4 H), 2.21–2.29 (m, 2 H), 2.39–2.50 (m, 2 H), 3.38 (s, 1 H), 3.55 (d, *J* = 7.9 Hz, 1 H). ^{13}C NMR (ac-d_6): 22.5, 24.2, 24.7, 32.9, 37.3, 43.1, 53.8, 77.1, 84.3, 92.6, 115.7, 176.2, 194.4. MS *m/z* M + 202. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93. Found: C, 77.02; H, 6.89.



212 (86%)

7.1.11. Triethyl (5-Benzoylpyrrol-2-yl)methanetricarboxylate (212) (37)

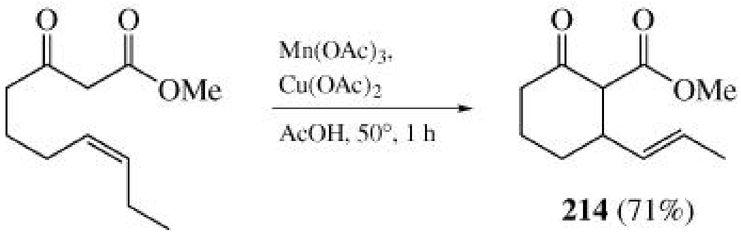
$KMnO_4$ (1.0 g, 6.3 mmol) was added to a hot stirred solution of $Mn(OAc)_2 \cdot 4\ H_2O$ (6.13 g, 25 mmol) in AcOH (50 mL). After 0.5 hour, Ac_2O (9.68 g, 75 mmol) was added cautiously and then the mixture was cooled to room temperature. Triethyl methanetricarboxylate (2.55 g, 11 mmol), 2-benzoylpyrrole (1.88 g, 11 mmol) and AcONa (1.64 g, 20 mmol) were added and the resulting mixture was stirred at 60–65° in a N_2 atmosphere for 1 day. Water (20 mL) was added and the product was extracted into toluene (3 × 100 mL). The extract was washed with H_2O and evaporated in vacuo. The oily residue was purified by flash-column chromatography on silica gel using hexane/EtOAc to produce **212** (86%), mp 72.5–74° (MeOH). ^1H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 9 H), 4.35 (q, *J* = 7.1 Hz, 6 H), 6.36 (dd, J = 2.7, 3.9 Hz, 1 H), 6.82 (dd, J = 2.7 Hz, 1 H), 7.57 (m, 3 H), 7.88 (m, 2 H), 10.48 (br, 1 H). MS *m/z*: 401.



213 (80%)

7.1.12. 1,1-Diethoxycarbonyl-3-hexyl-4-methylenecyclopentane(213) (81)

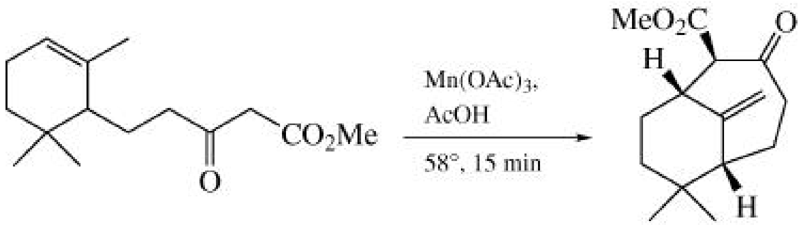
A mixture of 115 mg (0.58 mmol) diethyl allylmalonate, 1.3 g (11.6 mmol) of 1-octene, 462 mg (1.72 mmol) of $Mn(OAc)_3 \cdot 2\ H_2O$, and 178 mg (0.89 mmol) of $Cu(OAc)_2 \cdot H_2O$ in 10 mL of glacial AcOH was heated in a 90° oil bath for 6 hours. The reaction mixture was diluted with 50 mL of EtOAc, washed with three 25-mL portions of saturated $NaHCO_3$, dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed over 10 g of silica gel (EtOAc:hexane, 1:15) to give 1.43 mg (80%) of **213** as colorless oil. IR ($CHCl_3$) 1796 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 5.1 Hz, 3 H), 1.24 (t, *J* = 7.1 Hz, 6 H), 1.05–2.8 (m, 13 H), 2.9–3.1 (m, 2 H), 4.18 (q, *J* = 7.1 Hz, 4 H), 4.7–5.1 (m, 2 H).



214 (71%)

7.1.13. 2-Carbomethoxy-3-(1-propenyl)cyclohexanone(214) (83)

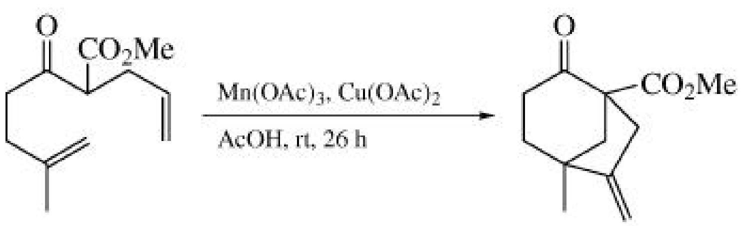
To a solution of $Mn(OAc)_3 \cdot 2\ H_2O$ (1.376 g, 5.1 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.51 g, 2.55 mmol) in 18 mL of glacial AcOH was added a solution of methyl 3-keto-7-decenoate (0.505 g, 2.55 mmol) in 7 mL of glacial AcOH to give an opaque brownish green solution. The mixture was stirred for 1 hour at 50° at which time the solution was light blue and contained a white precipitate. Water was added to give a single cloudy phase in which the white precipitate had dissolved. The solution was extracted with five 15-mL portions of CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$ until neutral and then with water. The aqueous layer was back-extracted with two 15-mL portions of CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the solvent was removed in vacuo to provide crude **214**. Flash chromatography on silica gel (hexane—ether 3:1) gave 0.365 g (71%) of **214** as a 1.3:1 mixture of keto and enol tautomers. IR (neat) 1745, 1715 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 66.90; H, 8.33. Keto tautomer ^1H NMR δ 1.54 (d, *J* = 3.7 Hz, 3 H), 1.57–2.29 (m, 5 H), 2.32–2.35 (m, 1 H), 2.75 (dddd, *J* = 12.0, 12.0, 8.0, 4.0 Hz, 1 H), 3.12 (d, *J* = 12.0 Hz, 1 H), 3.63 (s, 3 H), 5.08–5.47 (m, 2 H). Enol tautomer ^1H NMR δ 1.54 (d, *J* = 3.7 Hz, 3 H), 1.57–2.29 (m, 5 H), 2.36–2.41 (m, 1 H), 3.05–3.15 (m, 1 H), 3.63 (s, 3 H), 5.08–5.47 (m, 2 H).



215 **188** (62%)

7.1.14. Methyl 6,6-Dimethyl-10-methylene-2-oxo-5 β ,9 β -[4.3.1]-bicyclodecane-1 β -carboxylate (188) (197)

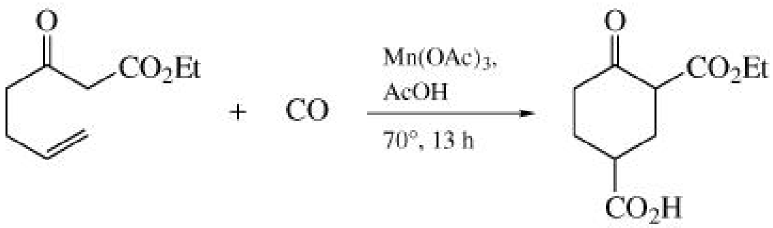
To a stirred solution of $Mn(OAc)_3 \cdot 2\ H_2O$ (213 mg, 0.795 mmol) in glacial AcOH (5 mL) heated at 58° in an oil bath, a solution of keto ester **215** (100 mg, 0.4 mmol) in AcOH (1 mL) was added. After the solution turned colorless (15 minutes) it was poured into H_2O (25 mL) and the mixture was extracted with ether (3 × 25 mL). The combined ether extract was washed successively with H_2O, saturated $NaHCO_3$ and brine, dried over Na_2SO_4, decanted, and evaporated in vacuo. Column chromatography (1% gradient EtOAc in hexane) afforded 61 mg (62%) of **188** as a colorless solid, mp 91–92° (hexane). IR (neat) 1707, 1645 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 3 H), 0.90 (s, 3 H), 1.13 (br d, *J* = 11 Hz, 1 H), 1.38 (br d, *J* = 9.3 Hz, 1 H), 1.7–1.9 (m, 2 H), 1.78–1.9 (m, 1 H), 1.79–1.9 (m, 1 H), 2.05 (t, *J* = 9, 6.1 Hz, 1 H), 2.2 (ddd, *J* = 19, 13.4, 4.3 Hz, 1 H), 2.37 (dt, *J* = 19, 3.5 Hz, 1 H), 3.1 (br d, *J* = 8.65 Hz, 1 H), 3.68 (s, 3 H), 4.03 (d, *J* = 8.65 Hz, 1 H), 4.7 (d, *J* = 1.97 Hz, 1 H), 4.87 (d, *J* = 1.97 Hz, 1 H). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.98; H, 8.89. Found: C, 71.87; H, 9.07.



217 **216** (86%)

7.1.15. Methyl 5-Methyl-6-methylene-2-oxobicyclo[3.2.1]octane-1-carboxylate (216) (101)

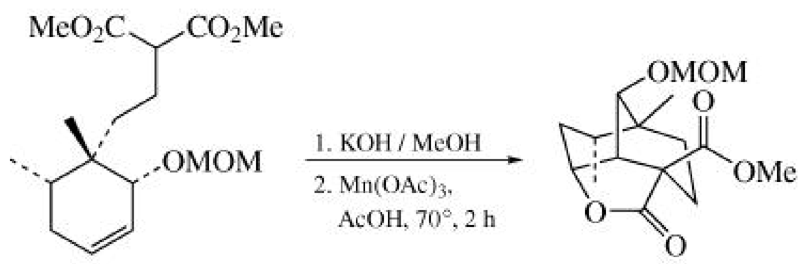
To a stirred solution of $Mn(OAc)_3 \cdot 2\ H_2O$ (0.804 g, 3 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.3 g, 1.5 mmol) in 13.5 mL of glacial AcOH was added ketoester **217** (0.307 g, 1.5 mmol) in 4 mL of glacial AcOH. The reaction mixture was stirred at room temperature for 26 hours, at which time 100 mL of H_2O was added. A solution of 10% $NaHSO_3$ was added dropwise to the mixture to decompose any residual $Mn(OAc)_3$. The resulting solution was extracted with three 30-mL portions of CH_2Cl_2. The combined organic extracts were washed with saturated $NaHCO_3$ solution and dried over Na_2SO_4. Removal of the solvent in vacuo gave 0.301 g (96%) of a yellow solid which was recrystallized from pentane to give pure **216** (86%). A second recrystallization provided an analytical sample, mp 71.8–72.5°. ^{1}H NMR δ 5.08 (dd, *J* = 2.3, 3.1 Hz, 1 H, = CH_2), 5.01 (dd, *J* = 2.3, 3.1 Hz, 1 H, = CH_2), 3.76 (s, 3 H), 2.94 (dddd, *J* = 0.9, 1.9, 2.9, 18.4 Hz, 1 H, H-7 endo), 2.83 (br d, *J* = 18.4 Hz, 1 H, H-7 exo), 2.52 (dddd, *J* = 1.0, 8.9, 12.5, 17.0 Hz, 1 H, H – 3 endo), 2.36 (ddd, *J* = 2.0, 6.9, 17.0 Hz, 1 H, H-3 *exo*), 2.09 (br s, 2 H, 2 H-8), 1.79 (ddd, J = 6.9, 12.0, 12.5 Hz, 1 H, H-4 exo), 1.68 (ddddd, *J* = 2.0, 2.0, 2.0, 8.9, 12.0 Hz, 1 H, H-4 *endo*), 1.25 (s, 3 H). Anal. Calcd for $C_{12}H_{16}O_3$:C, 69.21; H, 7.24. Found: C, 68.89; H, 7.88.



218 (55%)

7.1.16. 2-Ethoxycarbonyl-4-carboxycyclohexanone(218) (188)

Deaerated AcOH (10 mL), $Mn(OAc)_3 \cdot 2\ H_2O$ (0.807 g, 3 mmol) and ethyl 3-keto-6-heptenoate (0.204 g, 1.29 mmol) were placed in a 50-mL stainless steel autoclave containing a glass liner. The autoclave was then pressurized with 600 psi of CO and heated with stirring at 70° for 13 hours. After excess CO was discharged at room temperature, the reaction mixture was filtered through Celite. The filtrate was diluted with ether and washed twice with water, and then the water layer was extracted with ether (3 times). The combined organic extracts were dried over $MgSO_4$. Filtration and solvent removal gave an oil, which was purified by flash chromatography (hexane:EtOAc:EtOH, 8:2:1), affording 152 mg of crystallized **218** (55%).



197 **198** (68%)

7.1.17. Key Intermediate in the Synthesis of 14-Epiupial (198) (199)

A solution of 0.7 g (2.123 mmol) of **219** in 10 mL of anhydrous MeOH was cooled to 0° under argon and 1.12 mL (2.23 mmol) of a 1.99 M solution of KOH in MeOH was added dropwise over a period of 5 minutes. The solution was allowed to warm to room temperature and stirred for 7 days. The solvent was evaporated and 15 mL of glacial AcOH together with 1.1 g (4.46 mmol) of $Mn(OAc)_3 \cdot 2\ H_2O$ were added. The brown solution was heated in an oil bath at 70° for 2 hours, cooled, decolorized by the addition of solid $NaHCO_3$(<25 mg), and poured into 75 mL of H_2O. The aqueous phase was extracted with ether (4 × 25 mL) and the combined organic layers were carefully added to 50 mL of saturated $NaHCO_3$ solution. Solid $NaHCO_3$ was added to this mixture in small portions until bubbling ceased and the solution was basic (pH 9). The phases were separated and the aqueous portion was extracted with ether (2 × 25 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (2 × 25 mL) and brine (25 mL), dried, and evaporated to leave a residue which was purified by MPLC (silica gel, 35% ethyl acetate in petroleum ether). There was isolated 0.45 g (68%) of **198**, mp 91.5–92°. IR ($CHCl_3$) 1770, 1740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 0.96 (d, *J* = 6 Hz, 3 H), 1.44–1.76 (m, 5 H), 2.22 (br. t, *J* = 9 Hz, 1 H), 2.69 (br q, *J* = 9 Hz, 1 H), 3.34 (s and d, 4 H), 3.56 (dd, J = 4, 7 Hz, 1 H), 3.75 (s, 3 H), 4.55 (AB, *J* = 7 Hz, 2 H), 4.80 (br q, *J* = 7 Hz, 1 H). MS *m/z* $M^+C_2H_5O_2$ calcd 251.1286, obsd 251.1268.

8. Tabular Survey

The tabular survey includes all examples found in the literature to April 1995. Computer searches of *Chemical Abstracts and Science Citation Index* were conducted using key papers.

Table entries are in order of increasing **total** carbon and hydrogen numbers of the **substrate**. Departures from this criterion are made to group closely related compounds. Intramolecular reactions are further prioritized by the ring size of the products (cyclopentanes, cyclohexanes, etc.); in tandem cyclizations the first step is taken into account. If several reagents react with the same substrate, they are also arranged in order of increasing **total** carbon and hydrogen numbers. The same criterion is used for manganese(III) salts. Reagents with the same count of carbon and hydrogen atoms are further prioritized based on their structural features (i.e., acyclic—cyclic, straight-chain–branched-chain, terminal–internal alkenes, or hydrocarbons–functionalized derivatives). Chronology is used as a last criterion when all other parameters are identical.

Yields in parenthesis are isolated yields; numbers separated by colons are ratios of products or stereoisomers. A dash indicates that no datum for yield is reported.

$Mn(OAc)_3$ refers to the dihydrated form $Mn(OAc)_3 \cdot 2\ H_2O$ unless it is specifically mentioned that the anhydrous form was used.

The following abbreviations are used in the tables:

Bs	Benzenesulfonyl
$Mn(pic)_3$	Manganese(III) tris(2-pyridinecarboxylate)
TBDMS	*tert*-Butyldimethylsilyl
TMS	Trimethylsilyl
Ts	*p*-Toluenesulfonyl

Table I. Alkenes and Aldehydes

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Table II. Alkenes and Ketones

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Table III. Alkenes and Acetic Acid or its Derivatives

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Table IV. Cycloalkenes and Acetic Acid

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Table V. Alkenes or Cycloalkenes and Monocarboxylic Acids Other than AcOH

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Table VI. Alkenes and Carboxylic Acid Anhydrides

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Table VII. Alkenes or Cycloalkenes and β -Dicarbonyl Compounds

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Table VIII. Alkenes and β -Ketocarboxylic Acids

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Table IX. Alkenes or Cycloalkenes and Dicarboxylic Acids

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Table X. Alkenes or Cycloalkenes and Dicarboxylic Acid Derivatives

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Table XI. Enol Ethers or Enol Lactones and β -Dicarbonyl Compounds

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Table XII. Alkynes and Carbonyl Compounds

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Table XIII. 1,3-Alkadienes and Ketones

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Table XIV. 1,3-Alkadienes and Acetic Acid

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Table XV. Nonconjugated Dienes and Carbonyl Compounds

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Table XVI. 1,3-Alkadienes or 1,3-Cycloalkadienes and Dicarbonyl Compounds

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Table XVII. 1,3-Alkenynes and Acetic Acid

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Table XVIII. 1,3-Alkenynes and β -Dicarbonyl Compounds

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Table XIX. Co-Complexed 1,3-Alkenynes and β -Dicarbonyl Compounds

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Table XX. 1,3-Alkadiynes and β -Dicarbonyl Compounds

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Table XXIA. Arenes and Carbonyl Compounds

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Table XXIB. Heterocycles and Carbonyl Compounds

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Table XXII. Nitroalkylation Reactions

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Table XXIIIA. Addition-Cyclization Reactions - Alkenes

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Table XXIIIB. Addition-Cyclization Reactions - Alkynes

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Table XXIIIC. Addition-Cyclization Reactions - Alkadienes

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Table XXIV. Intramolecular Cyclizations of 2-Substituted 3-Ketoesters

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Table XXVA. Intramolecular Cyclizations of 4-Substituted 3-Ketoesters (D-mode)

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Table XXVB. Intramolecular Cyclizations of 4-Substituted 3-Ketoesters (T-mode)

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Table XXVC. Intramolecular Cyclizations of 4-Substituted 3-Ketoesters (B-mode)

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Table XXVI. Intramolecular Cyclizations of *O*-Substituted 3-Ketoesters

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Table XXVII. Intramolecular Cyclizations of 4-Substituted 1,3-Diketones

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Table XXVIII. Intramolecular Cyclizations of 2-Substituted 1,3-Diketones

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Table XXIX. Intramolecular Cyclizations of *O*-Substituted Malonic Esters

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Table XXXA. Intramolecular Cyclizations of *C*-Substituted Malonic Ester Derivatives (D-mode)

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Table XXXB. Intramolecular Cyclizations of *C*-Substituted Malonic Esters (B-mode)

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Table XXXI. Intramolecular Cyclizations of *N*-Substituted Amides

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Table XXXII. Tandem Cyclizations (DD-mode)

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Table XXXIII. Tandem Cyclizations (DB-mode)

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Table XXXIV. Tandem Cyclizations (TD-mode)

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Table XXXV. Tandem Cyclizations (TB-mode)

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Table XXXVI. Tandem Cyclizations (DC-mode)

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Table XXXVII. Tandem Cyclizations (DN-mode)

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Table XXXVIII. Polycyclization Reactions (DDDD-mode)

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Table XXXIX. Carbon Monoxide Trapping Reactions

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Table XLA. Intermolecular Reactions with Electrochemically Generated $Mn(OAc)_3$

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Table XLB. Addition-Cyclizations with Electrochemically Generated $Mn(OAc)_3$

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Table XLI. Sonochemical Reactions

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Table XLIIA. Cyclopropanol Derived Alkyl Radicals: Intermolecular Additions

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Table XLIIB. Cyclopropanol Derived Alkyl Radicals: Intramolecular Additions

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Table XLIIC. Cyclobutanol Derived Alkyl Radicals: Intramolecular Additions

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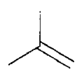
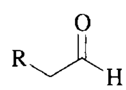
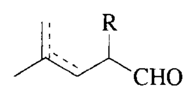
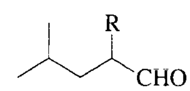
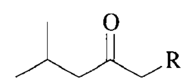
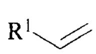
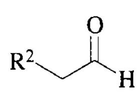
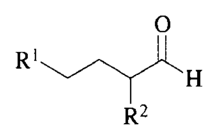
Table XLIII. Cr(0) Complex-Derived Alkyl Radicals

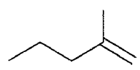
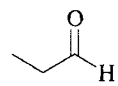
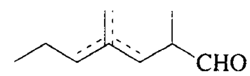
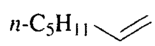
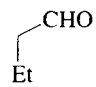
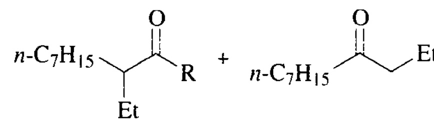
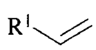
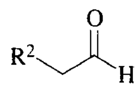
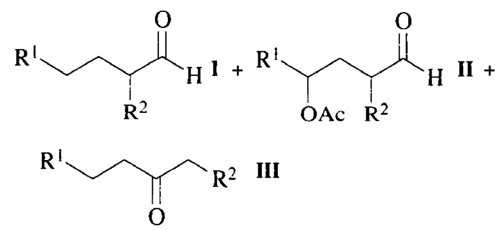
View PDF

TABLE I. ALKENES AND ALDEHYDES

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 			 I +  II +  III	110
	R = Me R = Et R = *i*-Pr	Mn(OAc)$_3$, AcOH, 60°, 1 - 2 h	**I : II : III** 70 : 27 : 3 (15) 50 : 45 : 5 (17) 67 : 17 : 16 (10)	
	R = H R = Me R = Et R = *i*-Pr R = *n*-C_7H_{15}	Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, 50°, 5 - 10 h	**I : II** 93 : 7 (10) 93 : 7 (36) 93 : 7 (45) 90 : 10 (30) 87 : 13 (46)	
C_5-C_{10} 		Mn(OAc)$_3$, AcOH, 60°, 1 h		41

R^1	R^2		R^1	R^2	
n-Pr	Me	(20)	*n*-Bu	Et	(20)
n-Bu	Me	(25)	*n*-C_5H_{11}	Et	(25)
n-C_5H_{11}	Me	(30)	*n*-Bu	*i*-Pr	(20)
n-C_6H_{13}	Me	(25)	*n*-C_5H_{11}	*i*-Pr	(20)
n-C_8H_{17}	Me	(25)			

TABLE I. ALKENES AND ALDEHYDES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		$Mn(OAc)_3$, AcOH, 60°, 1 - 2 h	 (22)	110
C_7 		$Mn(OAc)_2$, O_2, AcOH, 70°, 5 h	 (23) R = H (48), R = OH (14)	121
C_7-C_9 				72

R^1	R^2	Conditions	I : II : III	Yield
n-C_5H_{11}	H	$Mn(OAc)_3$, 50°, 12 h	20 : 0 : 73	(92)
		$Mn(OAc)_3$, AcOH, 23°, 20 h	51 : 39 : 10	(38)
n-C_7H_{15}	Me	$Mn(OAc)_3$, AcOH, 20°, 50 h	74 : 17 : 9	(38)
n-C_5H_{11}	n-Pr	$Mn(OAc)_3$, AcOH, 70°, 1.5 h	27 : 22 : 48	(89)
n-C_7H_{15}	n-Pr	$Mn(OAc)_3$, AcOH, 70°, 12 min	72 : 28 : 0	(44)

TABLE I. ALKENES AND ALDEHYDES (*Continued*)

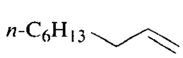
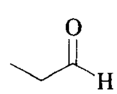
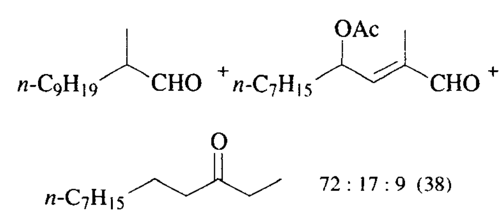
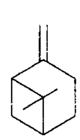
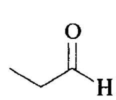
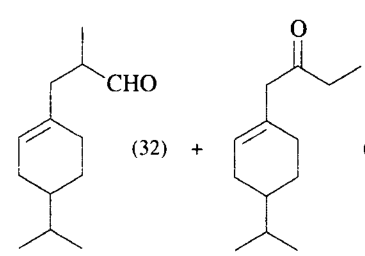
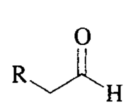
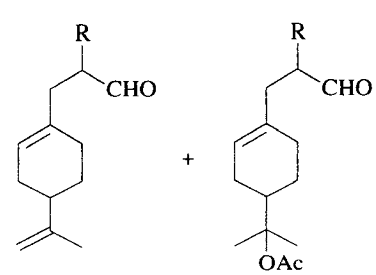
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		$Mn(OAc)_3$, AcOH, 60°, 1 - 2 h	 72 : 17 : 9 (38)	110
C_{10} 		$Mn(OAc)_3$, AcOH, 60°	 (32) + (6)	65
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°		65
	R = H		(5) + (6)	
	R = Me		(34) + (6)	
	R = Et		(12) + (3)	

TABLE II. ALKENES AND KETONES

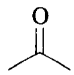
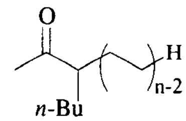
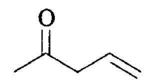
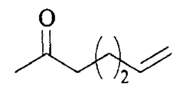
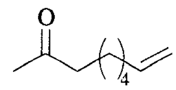
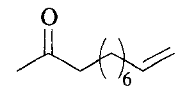
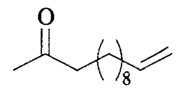
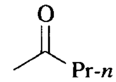
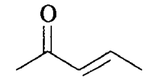
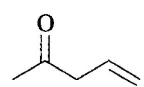
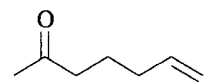
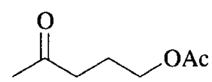
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 $CH_2{=}CH_2$		$Mn(OAc)_3$, AcOH, 85°, 6 h, 50 atm	 (—) n = 3 - 9	123
"		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, EtOAc, 80°, 2 h, 100 atm	 (4) +  (58) +  (24) +  (10) +  (4)	67
"		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 85°, 4 h, 50 atm	 **I** +  **II** +  **III** +  **IV** +  **V** **I:II:III:IV:V** 10:18:30:28:1 4 (28)	66

TABLE II. ALKENES AND KETONES *(Continued)*

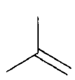
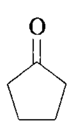
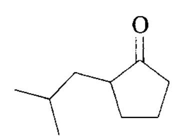
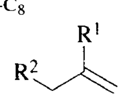
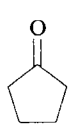
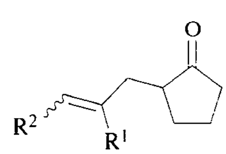
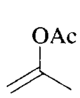
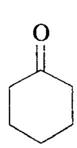
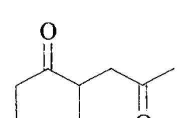
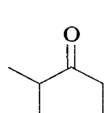
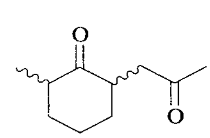
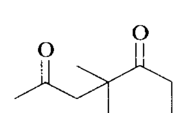
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$Mn(OAc)_3$, C_6H_{14}, 40°, 24 h	 (65)	49
C_4-C_8 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH		49
R^1 Me, R^2 H		40°, 9 h	(44)	
R^1 H, R^2 *n*-Pr		60°, 0.5 h	(43)	
R^1 H, R^2 *n*-Bu		60°, 0.5 h	(52)	
R^1 H, R^2 *n*-C_5H_{11}		80°, 0.5 h	(56)	
C_5 		$Mn(OAc)_3$, AcOH, 70°, 10 min	 (22)	46
		$Mn(OAc)_3$, AcOH	 +  *Z* : *E* 6 : 1 (—) (—)	46

TABLE II. ALKENES AND KETONES (*Continued*)

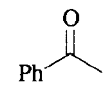
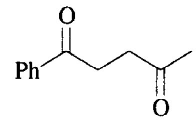
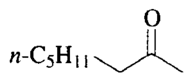
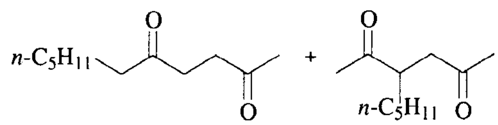
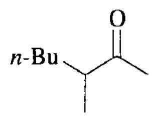
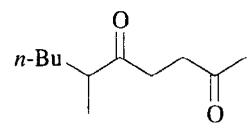
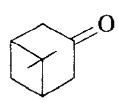
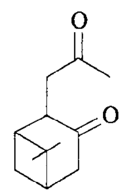
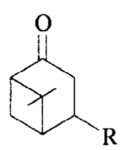
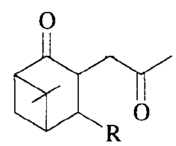
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH	 (—)	46
		"	 1.5 : 1 (—)	46
		"	 (—)[a]	46
		"	 (—)	46a
		"		46a
	R = H		(—)	
	R = Me		(—)	

TABLE II. ALKENES AND KETONES (*Continued*)

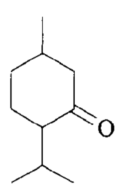
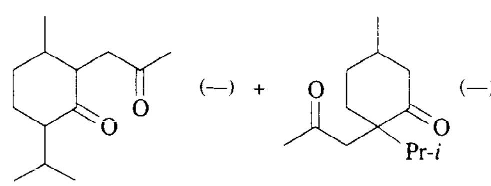
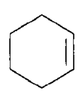
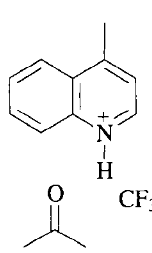
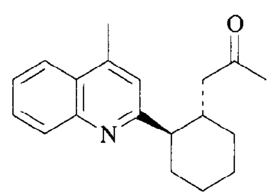
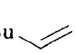
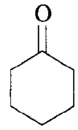
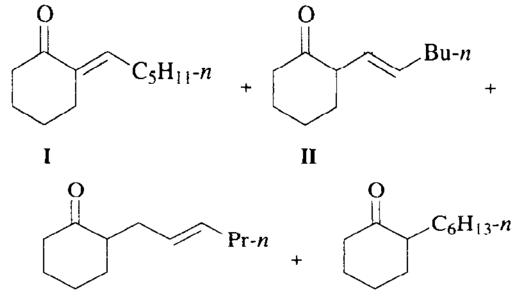
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH	 (—) + (—)	46a
C_6 	 $CF_3CO_2^-$	$Mn(OAc)_3$, AcOH, reflux, 1-3 h	 (15)[b]	124
n-Bu 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 50°, 15 h	 **I** + **II** + **III** + **IV** **I : II : III : IV** 35 : 15 : 35 : 15 (56)	44

TABLE II. ALKENES AND KETONES (*Continued*)

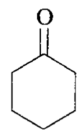
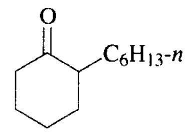
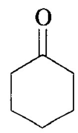
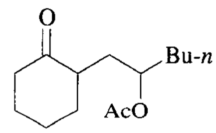
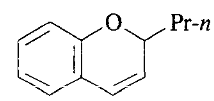
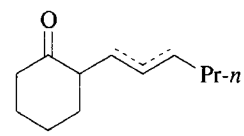
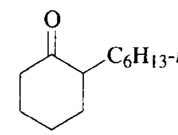
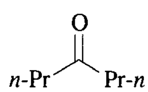
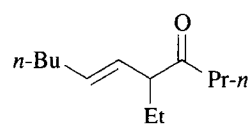
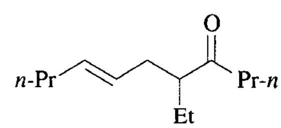
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, 75°, 3 h	 (53)	44
		$Mn(OAc)_3$, AcOH, Ac_2O, 100°	 (16) +  (13) +  (12) +  (6)[c]	48
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 70°, 10 h	 +  (50) 3 : 1	44

TABLE II. ALKENES AND KETONES (*Continued*)

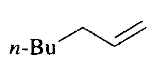
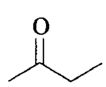
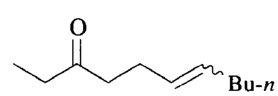
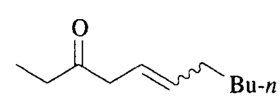
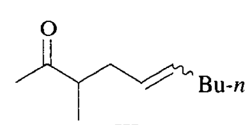
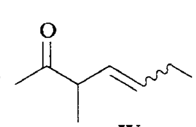
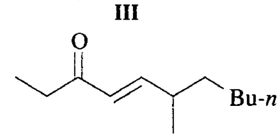
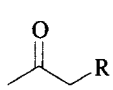
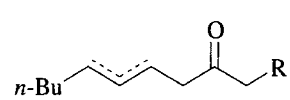
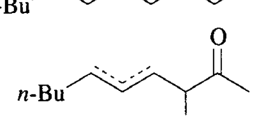
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 70°, 10 h	 **I** +  **II** +  **III** +  **IV** +  (15) **I : II : III : IV** 18 : 7 : 25 : 50 (28)	44
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 2 h	 **I** +  **II**	45
	R = CH_2CH_2OAc		**I : II** 30 : 70 (24)	
	R = CH_2CO_2Me		40 : 60 (35)	
	R = OAc		55 : 45 (32)	
	R = $Me_2C(OAc)$		100 : 0 (30)	

TABLE II. ALKENES AND KETONES (*Continued*)

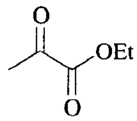
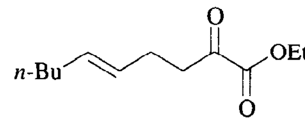
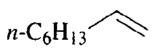
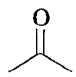
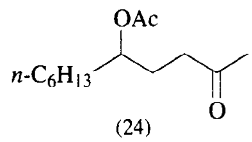
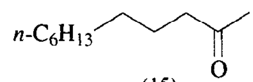
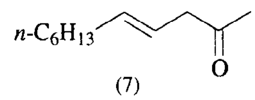
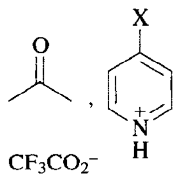
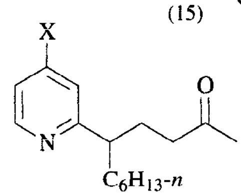
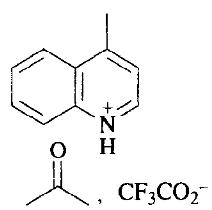
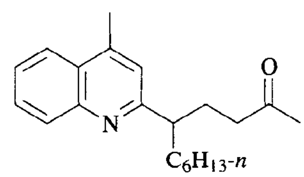
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 2 h	 (24)	45
C_8 		$Mn(OAc)_3$, AcOH, AcOK, 85°	 (24) +  (15) +  (7)	58
	 X = CN X = COMe	$Mn(OAc)_3$, AcOH, reflux, 1 - 3 h	 (40) (36)	124
		$Mn(OAc)_3$, AcOH, reflux, 1 - 3 h	 (60)	124

TABLE II. ALKENES AND KETONES (*Continued*)

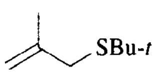
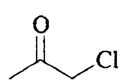
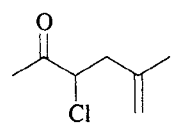
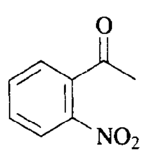
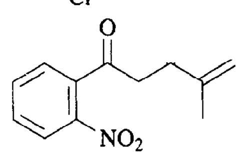
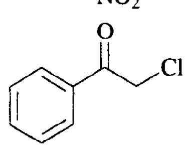
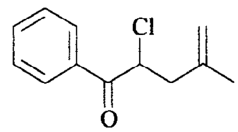
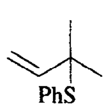
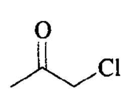
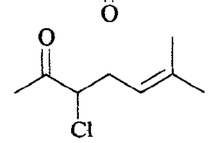
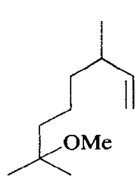
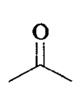
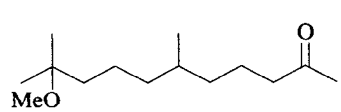
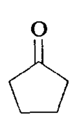
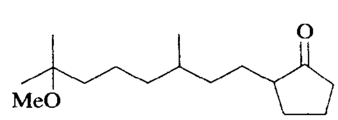
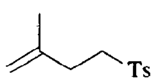
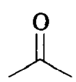
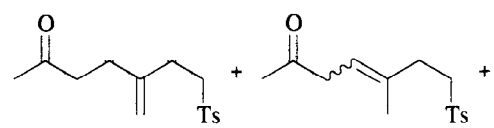
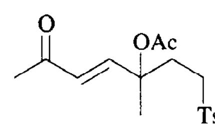
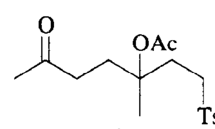
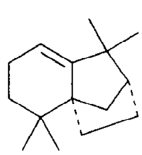
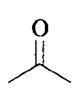
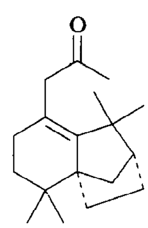
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, PbO_2, AcOH, rt, 2 d	 (43)	71
		"	 (85)	71
		"	 (84)	71
C_{11} 		"	 (—)	71
		$Mn(OAc)_3$, reflux, 24 h	 (—)	82
		$Mn(OAc)_3$, dioxane	 (—)	82

TABLE II. ALKENES AND KETONES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 50°, 1.5 h	 90 : 10 (30)  (25) +  (5)	59
C_{15} 		$Mn(OAc)_3$, AcOH, 110°, 24 h	 (—)[d]	111

[a] This was the major isomer.
[b] The content of the cis isomer was 10%.
[c] 4-Acetoxyoctanoic acid (4%) and 4-octanolide (12%) were also isolated.
[d] Allylic oxidation products were formed.

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES

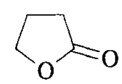
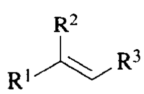
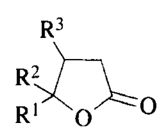
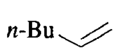
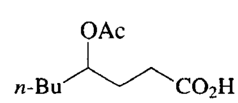
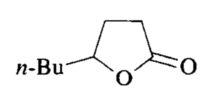
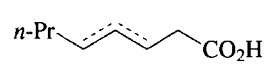
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
$CH_2=CH_2$	AcOH	$Mn(OAc)_3$, AcOH, 120°, 4 h, 15 atm	 (73)	210
C_4-C_{14}				
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux		125, 128
R^1, R^2, R^3				
n-C_6H_{13}, H, H			(74)	
Ph, H, H			(60)	
Ph, Me, H			(74)	
Me, Me, H			(30)	
n-Bu, H, H			(48)	
n-Pr, H, n-Pr			(44)	
Ph, H, Ph			(16)	
Ph, H, Me			(79)	
$CH_2C≡CC_5H_{11}$-n, H, H			(50)	
C_6				
	AcOH	$Mn(OAc)_3$, Ac_2O, AcOH, 100°	 (61) +  (19) +  (13) + n-$C_7H_{15}CO_2H$ (7)	126

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

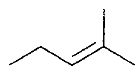
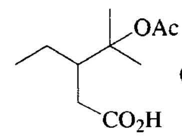
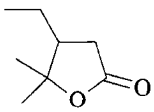
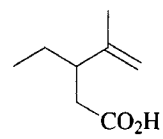
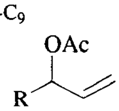
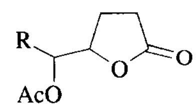
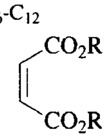
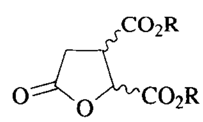
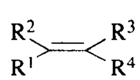
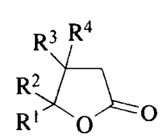
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, Ac_2O, AcOH, 100°	 (14) +  (55) +  (22)	126
C_6-C_9  R = Me, Et, *i*-Pr, *i*-Bu, *s*-Bu	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, reflux, 15 min	 (20 - 40)	211
C_6-C_{12} 	AcOH	$Mn(OAc)_3$, AcOH, reflux, 7 h		131
R			*Z* : *E*	
Me			1 : 6.8 (44)	
Et			1 : 5.7 (56)	
n-Pr			1 : 4.2 (49)	
i-Pr			1 : 4.2 (73)	
n-Bu			1 : 3.9 (43)	
i-Bu			1 : 4.2 (63)	

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6-C_{14} 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, reflux, 0.5-1 h		28

R^1	R^2	R^3	R^4	Yield (%)
Ph	H	H	H	(39)
Ph	Me	H	H	(31)
Ph	H	Me	H	(21)
Bn	H	H	H	(16)
Ph	H	H	Ph	(20)
t-Bu	H	H	H	(12)

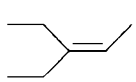
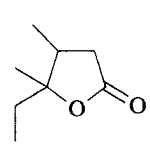
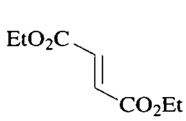
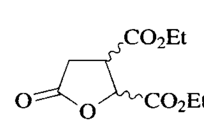
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (43)	117
C_8 	AcOH	$Mn(OAc)_3$, AcOH, reflux, 7 h	 *Z*:*E* 1 : 5.7 (83)	131

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

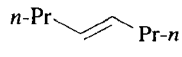
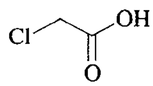
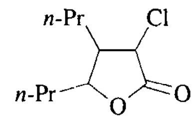
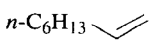
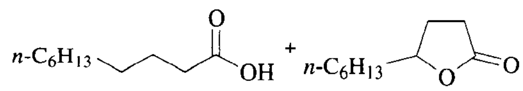
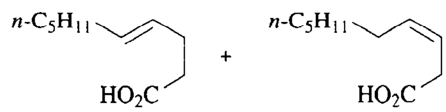
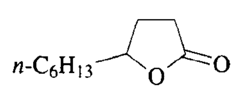
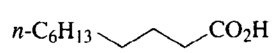
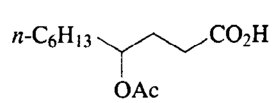
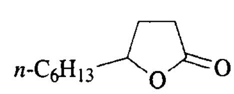
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, 120°, 2-2.5 h	 1.0 : 7.3 : 6.3 : 2.0 (33)	129
	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, reflux, 20 min	 (—) + (38)	212
				
	AcOH	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH : Ac_2O, 1 : 1 115°, 10 min	(56) (20)	68
	AcOH	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH : Ac_2O, 1 : 4 110°, 69 min	(56) (0)	68
	AcOH	$Mn(OAc)_3$, $CuCl_2$, AcOH : Ac_2O, 1 : 9, 120°, 15 min	(42) (9)[a]	68

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH, 100°, 95 h	 (57)	60
	AcOH		 I +  II +  III +  IV	60

Conditions	I	II	III	IV
$Mn(OAc)_3$, AcOH, Ac_2O, 100°, 2 h	(7)	(19)	(54)	(21)
$Mn(OAc)_3$, AcOH, Ac_2O, AcOK 100°, 48 min	(16)	(6)	(64)	(14)

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

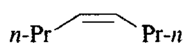
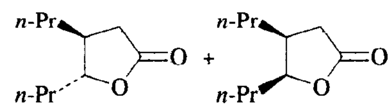
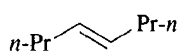
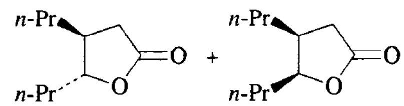
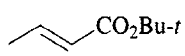
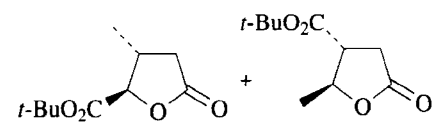
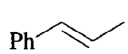
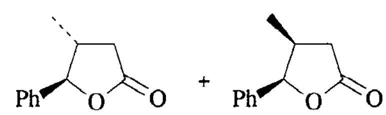
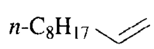
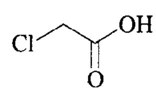
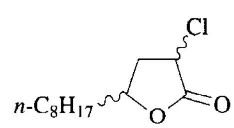
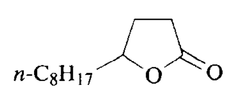
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 3.3:1 (60)	117
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 3.4:1 (69)	117
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 3.8:1 (57)	117
C_9 	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 67:1 (68)	117
C_{10} 		$Mn(OAc)_3$, 120°, 2-2.5 h	 1.25:1 (52)	129
	AcOH	$Mn(OAc)_3$, AcONa, AcOH, Ac_2O, reflux, 2 h	 (85)	213

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

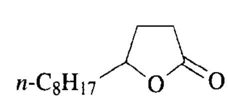
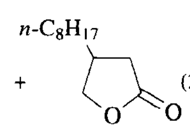
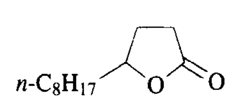
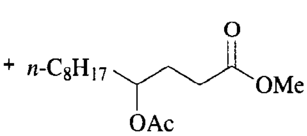
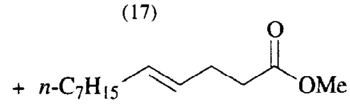
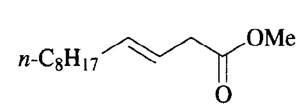
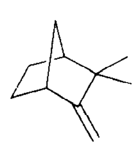
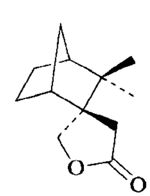
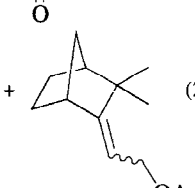
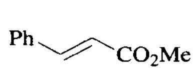
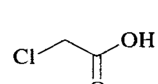
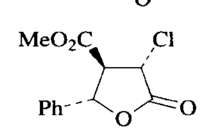
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (79) +  (2)	117
	AcOH	1. $Mn(OAc)_3$, AcOH, Ac_2O, reflux, 1.5 h 2. CH_2N_2	 (17) +  (20) +  (10) +  (3)	117
	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, AcOK, reflux, 1.5 h	 (50) +  (20)	214
		$Mn(OAc)_3$, 120°, 2 - 2.5 h	 (35)	129

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

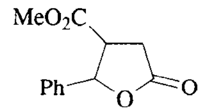
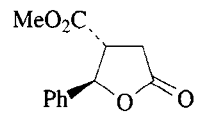
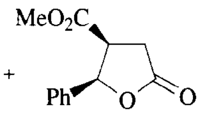
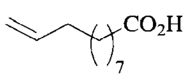
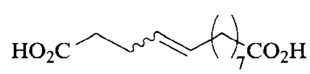
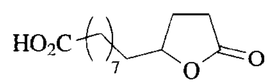
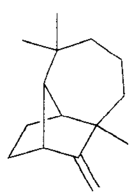
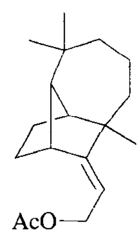
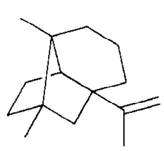
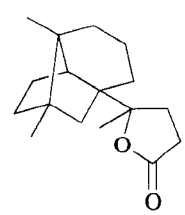
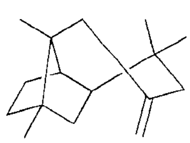
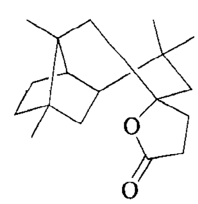
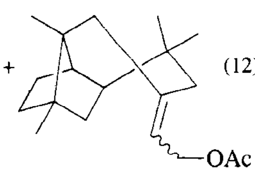
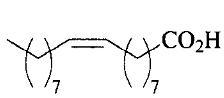
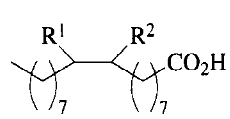
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (45)	128
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 +  26:1 (82)	117
C_{11} 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, AcOK, reflux, 5 h	 (25) +  (65)	127
C_{15} 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, AcOK, reflux, 1.5 h	 (47)	214

TABLE III. ALKENES AND ACETIC ACID OR ITS DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, AcOK, reflux, 2 h	 (32)	215
C_{16} 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, AcOK, reflux, 2 h	 (34) +  (12)	215
C_{18} 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, AcOK, reflux, 8 h	 (20)[b] R^1 / R^2 OAc / CH_2CO_2H[c] CH_2CO_2H / OAc[c]	127

[a] γ-Hexyl-γ-butyrolactone was also formed (7%).
[b] The corresponding allylic acetates were major products (60%).
[c] The structures were not fully established.

TABLE IV. CYCLOALKENES AND ACETIC ACID

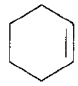
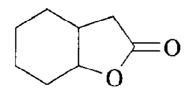
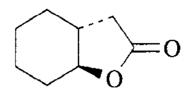
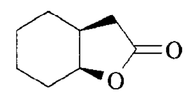
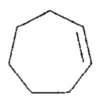
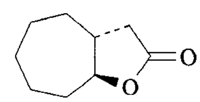
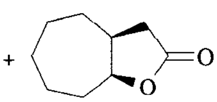
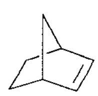
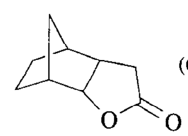
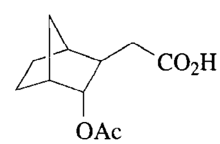
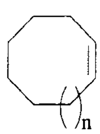
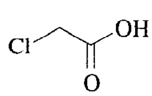
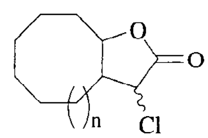
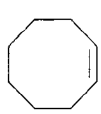
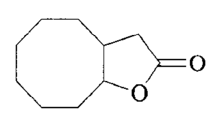
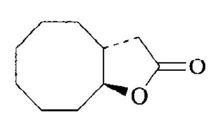
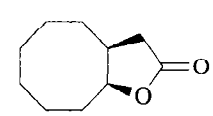
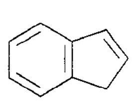
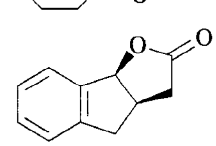
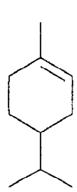
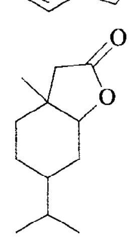
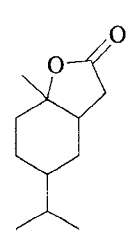
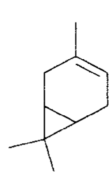
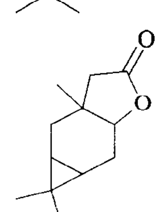
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	AcOH, Ac_2O	$Mn(OAc)_3$, AcOH, Ac_2O, reflux, 30-60 min	 (10)	28
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 +  1:5.4 (29)	117
C_7 	AcOH	$Mn(OAc)_3$, AcOH, A cOK, reflux	 +  1:1.4 (75)	117
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (63) +  (5)	117
		$Mn(OAc)_3$, 120°, 2 - 2.5 h		129
C_7 n = 0			1.2 : 1.1 : 1.0 : 1.5 (41)	
C_8 n = 1			1.0 : 7.3 : 6.3 : 2.0 (53)	

TABLE IV. CYCLOALKENES AND ACETIC ACID (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (62)	125, 128
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 +  2.4:1 (68)	117
C_9 	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (40)	117
C_{10} 	Ac_2O, AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, 110°, 45 min	 (—) +  (—)	216
	Ac_2O, AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, 110-130°, 1.5 h	 (8)	217

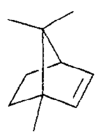
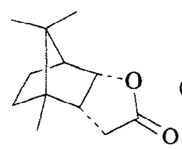
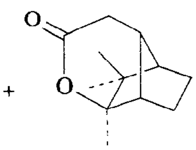
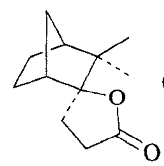
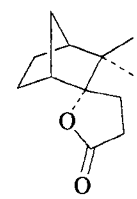
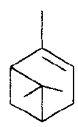
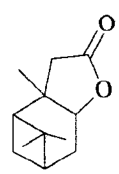
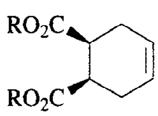
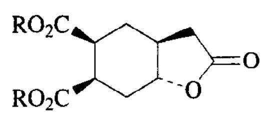
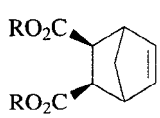
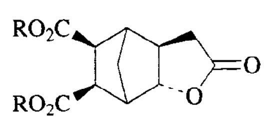
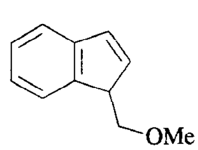
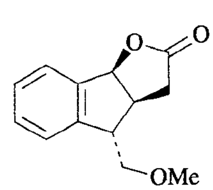
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	Mn(OAc)$_3$, AcOH, Ac$_2$O, AcOK, 118°, 5 h	 (—) +  (—) +  (—) +  (—)	133
	AcOH	Mn(OAc)$_3$, AcOH, Ac$_2$O, 110-130°, 45 min	 (—)[a]	218
C_{10}-C_{16}				
	AcOH	Mn(OAc)$_3$, AcOH, reflux, 8 - 10 h		131
R = Me			(56)	
R = Et			(26)	
R = *n*-Pr			(32)	
R = *i*-Pr			(40)	
R = *n*-Bu			(35)	

TABLE IV. CYCLOALKENES AND ACETIC ACID (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}-C_{15}				
	AcOH	Mn(OAc)$_3$, AcOH, reflux, 9 h		131
R = Me			(42)	
R = Et			(38)	
R = *n*-Pr			(33)	
C_{11}				
	AcOH	Mn(OAc)$_3$, AcOH, Ac$_2$O, reflux, 30 min	 (68)	134

[a] α-Terpineol acetate and four isomeric allylic acetates were also formed.

TABLE V. ALKENES OR CYCLOALKENES AND MONOCARBOXYLIC ACIDS OTHER THAN ACOH

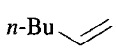
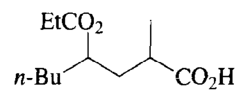
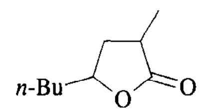
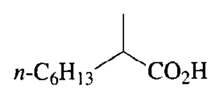
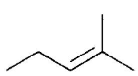
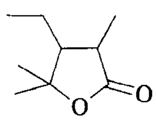
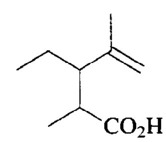
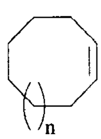
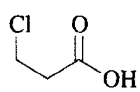
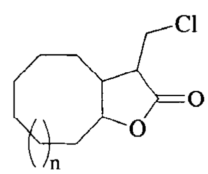
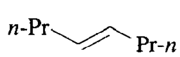
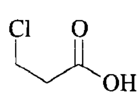
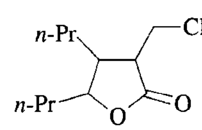
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$(EtCO)_2O$, $EtCO_2H$	$Mn(OAc)_3$, $(EtCO)_2O$, $EtCO_2H$, 100°	 (44) +  (15) +  (41)	126
	$(EtCO)_2O$, $EtCO_2H$	$Mn(OAc)_3$, $(EtCO)_2O$, $EtCO_2H$, 100°	 (35) +  (38)	126
		$Mn(OAc)_3$, 100°, 2 - 3 h	 I	129
C_7 n = 0			I (30)	
C_8 n = 1			I (50) 1.9:1.7:1.0:1.7	
C_8 		$Mn(OAc)_3$, 100°, 2 - 3 h	 (29)	129

TABLE V. ALKENES OR CYCLOALKENES AND MONOCARBOXYLIC ACIDS OTHER THAN ACOH (*Continued*)

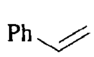
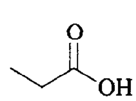
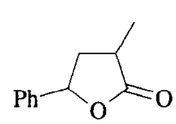
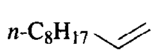
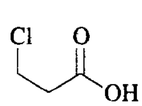
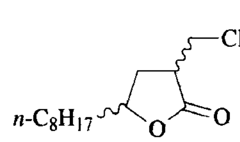
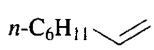
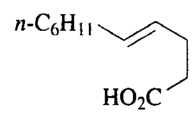
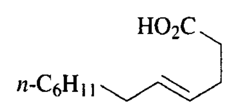
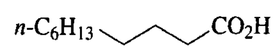
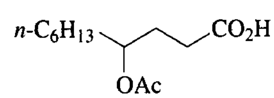
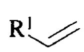
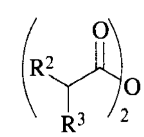
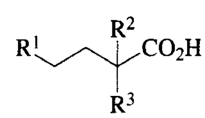
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, AcOK, reflux	 (50)	128
C_{10} 		$Mn(OAc)_3$, 100°, 2 - 3 h	 1.5 : 1.0 (50)	129

TABLE VI. ALKENES AND CARBOXYLIC ACID ANHYDRIDES

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	Ac_2O	$Mn(OAc)_3$, $Cu(OAc)_2$, Ac_2O, 119°, 40 min	 (63) +  (8)	68
	Ac_2O	$Mn(OAc)_3$, Ac_2O, 100°, 2.5 h	 (29) +  (21)	60
C_8-C_{12}				
		1. $Mn(OAc)_3$, 120 - 140°, 3 h 2. AcOH, H_2O, 110°, 1 h	 (70 - 80)	219

R^1	R^2	R^3
n-C_6H_{13}	H	H
n-C_8H_{17}	H	Me
n-C_8H_{17}	Me	Me
n-C_8H_{17}	H	Et
n-$C_{10}H_{21}$	H	H

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS

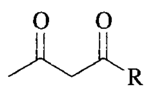
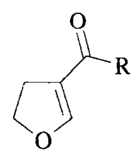
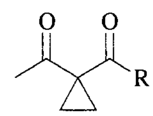
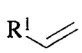
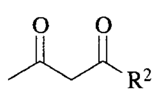
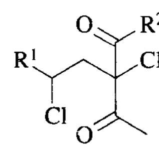
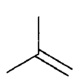
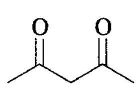
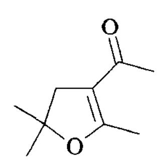
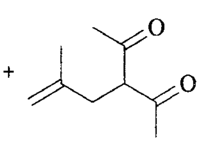
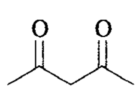
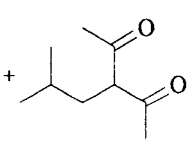
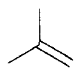
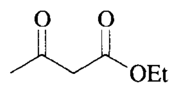
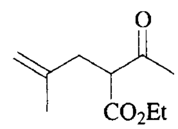
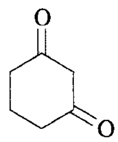
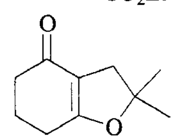
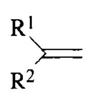
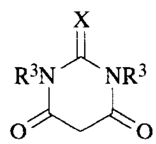
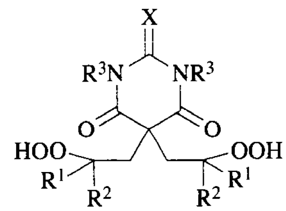
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
$CH_2{=}CH_2$		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 2 h, 50 atm	 + 	69
	R = Me		8 : 1 (20)	
	R = OEt		15 : 1 (20)	
		$Mn(OAc)_3$, LiCl, AcOH		63
R^1	R^2			
C_2 H	Me	55°, 45 min, 45 atm	(30)	
C_6 *n*-Bu	Me	50°, 40 min	(60)	
C_6 *n*-Bu	OEt	70°, 40 min	(67)	
C_4				
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 40°, 5 h	 **I** (35) +  **II** (24)	70
		$Mn(OAc)_3$, AcOH, 40°, 6 h	**I** (35) + **II** (18) +  (3)	70

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 2 h	 (48)	45
		$Mn(OAc)_3$, AcOH, 45°, 10 min	 (40)	106
C_4-C_{18} 		$Mn(OAc)_2$, O_2, AcOH, 20-28°		54

R^1	R^2	R^3	X	(h)	Yield (%)
Ph	Ph	Me	O	5	(94)[a]
Ph	Ph	H	O	6	(86)
Ph	Ph	Et	S	4	(62)
Me	Me	Me	O	5	(81)
Et	Et	Me	O	3	(88)
4-MeC_6H_4	4-MeC_6H_4	Me	O	3	(97)
4-ClC_6H_4	4-ClC_6H_4	Me	O	3	(99)
4-FC_6H_4	4-FC_6H_4	Me	O	3	(92)
Me	Ph	Me	O	2	(73)
Ph	4-ClC_6H_4	Me	O	3	(97)
Ph	4-BrC_6H_4	Me	O	3	(84)
Ph	1-naphthyl	Me	O	3	(93)

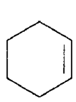
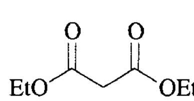
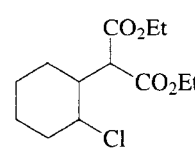
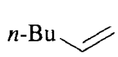
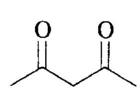
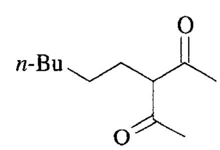
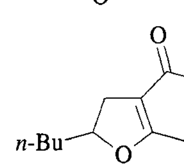
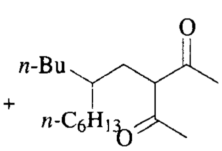
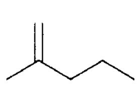
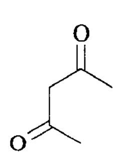
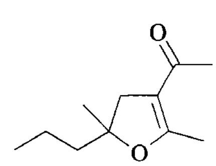
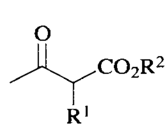
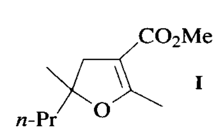
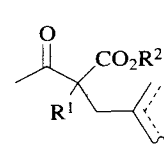
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		$Mn(OAc)_3$, LiCl, AcOH, 80°, 50 min	 (25)[b]	63
		$Mn(OAc)_3$, AcOH, 60°, 1 h	 (15) +  (10) +  (6)	105
		$Mn(OAc)_3$, AcOH, 45°, 10 min	 (40)	106
		$Mn(OAc)_3$, AcOH, 40°, 24 h	 I +  II +	31

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

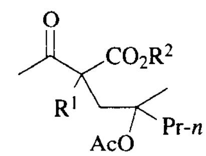
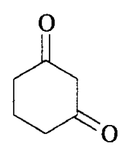
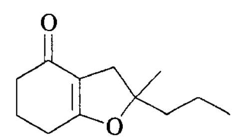
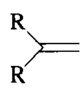
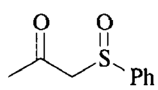
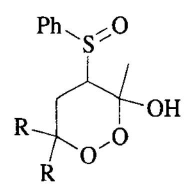
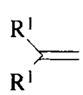
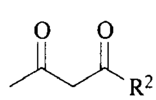
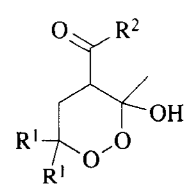
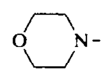
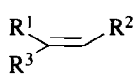
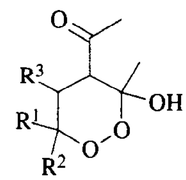
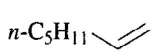
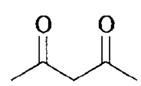
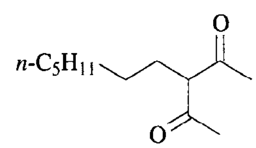
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
			 III	
	R^1 R^2		I II III	
	H Me		(30) (16) (13)	
	Me Et		(0) (35) (5)	
		$Mn(OAc)_3$, AcOH, 45°, 10 min	 (74)	106
C_6-C_{16}				
		$Mn(OAc)_3$, O_2, AcOH, 32°, 10 - 12 h		53
R				
Ph			92 : 8 (63)	
p-ClC_6H_4			65 : 35 (69)	
p-MeC_6H_4			85 : 15 (76)	
p-FC_6H_4			81 : 19 (72)	
p-$MeOC_6H_4$			88 : 12 (58)	
Et			70 : 30 (51)	

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, O_2, AcOH, 23°, 11-14 h	 I	51
R^1	R^2			
4-MeC_6H_4	4-MeC_6H_4NH		(99)	
4-MeC_6H_4	PhNH		(98)	
4-MeC_6H_4	2-MeC_6H_4NH		(100)	
4-MeC_6H_4	4-ClC_6H_4NH		(99)	
4-MeC_6H_4	2-ClC_6H_4NH		(100)	
4-MeC_6H_4	NH_2		(96)	
4-FC_6H_4	PhNH		(94)	
4-FC_6H_4	Me_2N		(59)	
4-ClC_6H_4	2-ClC_6H_4NH		(87)	
4-ClC_6H_4	Me_2N		(89)	
4-$MeOC_6H_4$	2-ClC_6H_4NH		(83)	
4-$MeOC_6H_4$	Me_2N		(78)	
Et	PhNH		(68)	
Et	4-ClC_6H_4NH		(62)	
Ph	4-MeC_6H_4NH		(92)	
Ph	PhNH		(96)	
Ph	4-$MeOC_6H_4NH$		(82)	
Ph	2-$MeOC_6H_4NH$		(84)	
Ph	2-MeC_6H_4NH		(94)	
Ph	4-ClC_6H_4NH		(94)	
Ph	2-ClC_6H_4NH		(93)	
Ph	NH_2		(88)	
Ph	MeNH		(85)	

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
R^1	R^2		I	
Ph	Me_2N		(87)	
Ph	Et_2N		(89)	
Ph			(88)	
	$Mn(acac)_3$, O_2	$Mn(acac)_3$, AcOH, 23°, 11 h		55
R^1 / R^2 / R^3				
Ph / H / Ph			(92)	
$4\text{-}ClC_6H_4$ / H / $4\text{-}ClC_6H_4$			(90)	
$4\text{-}MeOC_6H_4$ / H / $4\text{-}MeOC_6H_4$			(87)	
$4\text{-}MeC_6H_4$ / H / $4\text{-}MeC_6H_4$			(77)	
$4\text{-}FC_6H_4$ / H / $4\text{-}FC_6H_4$			(72)	
Ph / H / H			(34)	
$n\text{-}C_6H_{13}$ / H / H			(8)	
$n\text{-}C_7H_{15}$ / H / H			(35)	
$(CH_2)_4$ / H			(11)	
$(CH_2)_6$ / H			(43)	
C_7				
		$Mn(OAc)_3$ or $Mn(acac)_3$, 100°, 30 h	 (60)	70

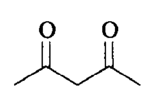
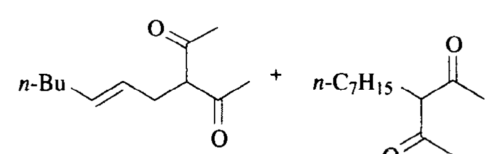
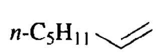
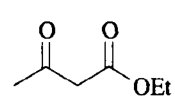
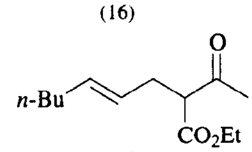
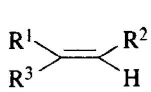
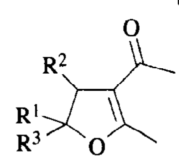
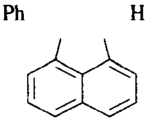
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 3 h	 (16) + (8)	70
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 2 h	 (33)	45
	$Mn(acac)_3$	$Mn(acac)_3$, AcOH, reflux, 1-5 min		135
R^1 / R^2 / R^3				
Ph / H / Ph			(89)	
$4\text{-}MeOC_6H_4$ / H / $4\text{-}MeOC_6H_4$			(88)	
Me / H / Ph			(97)	
Ph / H / H			(75)	
 / H			(70)	
Ph / Ph / Ph			(41)	
$4\text{-}MeOC_6H_4$ / Ph / $4\text{-}MeOC_6H_4$			(29)	
$4\text{-}MeOC_6H_4$ / $4\text{-}MeOC_6H_4$ / $4\text{-}MeOC_6H_4$			(13)	
$n\text{-}C_5H_{11}$ / H / H			(12)	

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

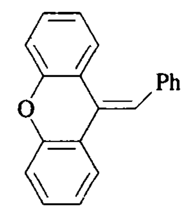
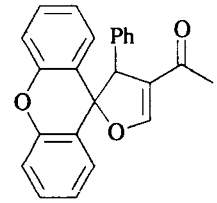
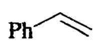
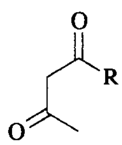
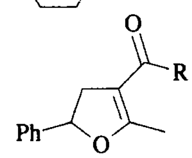
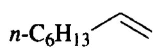
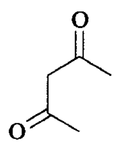
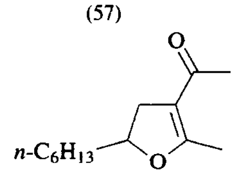
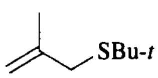
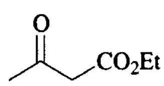
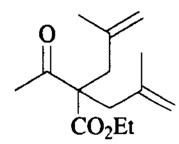
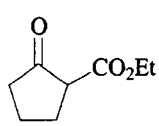
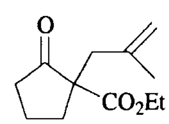
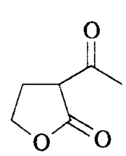
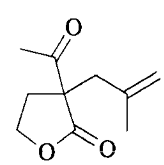
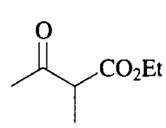
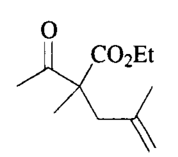
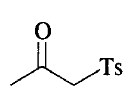
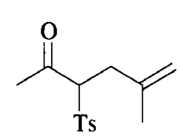
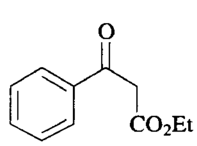
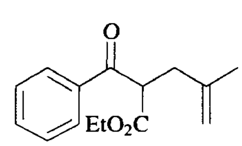
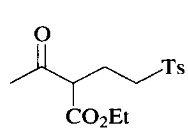
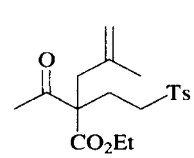
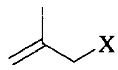
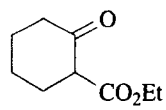
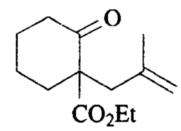
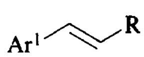
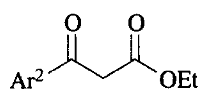
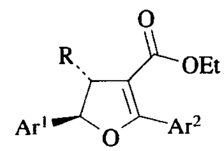
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn(acac)_3$	$Mn(acac)_3$, AcOH, reflux, 1-5 min	 (44)	135
C_8 	 R = Me R =OEt	$Mn(OAc)_3$, AcOH, 45°, 10 min	 (30) (57)	106
		$Mn(OAc)_3$, AcOH, 45°, 10 min	 (10)	106
		$Mn(OAc)_3$, $Cu(OAc)_2$, PbO_2, AcOH, rt, 2 d	 (35)	71
		"	 (86)	71

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, PbO_2, AcOH, rt, 2 d	 (78)	71
		"	 (88)	71
		"	 (69)	71
		"	 (20)	71
		"	 (96)	71

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8-C_{10} 		$Mn(OAc)_3$, $Cu(OAc)_2$, PbO_2, AcOH, rt, 2 d		71
X				
$PhSO_2$			(36)	
t-$BuSO_2$			(41)	
PhS			(65)	
t-BuS			(73)	
PhSO			(—)	
C_8-C_{14} 				136

R	Ar^1	Ar^2	Conditions	Yield (%)
H	Ph	Ph	$Mn(OAc)_3$, AcOH, 75-85°, 10-30 min	(27)
CO_2Me	Ph	Ph		(40)
CH_2OAc	Ph	Ph		(61)
Me	4-$MeOC_6H_4$	$3,4$-$(MeO)_2C_6H_3$		(52)
CO_2Et	$3,4$-$(MeO)_2C_6H_3$	$3,4$-$(MeO)_2C_6H_3$		(57)
CH_2OAc	$3,4$-$(MeO)_2C_6H_3$	$3,4$-$(MeO)_2C_6H_3$		(48)
CO_2Et	$3,4$-$CH_2OCH_2C_6H_3$	$3,4$-$(MeO)_2C_6H_3$		(57)
CO_2Et	$3,4$-$CH_2OCH_2C_6H_3$	$3,4$-$CH_2OCH_2C_6H_3$		(71)
CO_2Et	$3,4,5$-$(MeO)_3C_6H_2$	$3,4$-$CH_2OCH_2C_6H_3$		(56)
CH_2OAc	$3,4$-$CH_2OCH_2C_6H_3$	$3,4$-$(MeO)_2C_6H_3$	$Mn(OAc)_3$, AcOH, rt, 1-4 d	(58)
CO_2Et	$3,4$-$CH_2OCH_2C_6H_3$	$3,4$-$CH_2OCH_2C_6H_3$		(71)
CH_2OAc	$3,4$-$CH_2OCH_2C_6H_3$	$3,4$-$CH_2OCH_2C_6H_3$		(55)
CO_2Et	$3,4,5$-$(MeO)_3C_6H_2$	$3,4$-$CH_2OCH_2C_6H_3$		(54)
CH_2OAc	$3,4$-$CH_2OCH_2C_6H_3$	$3,4,5$-$(MeO)_3C_6H_2$		(65)

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

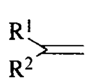
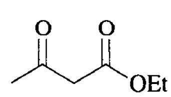
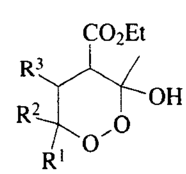
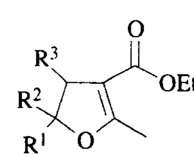
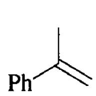
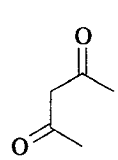
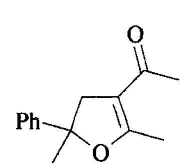
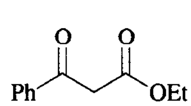
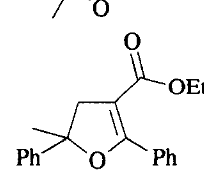
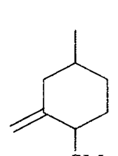
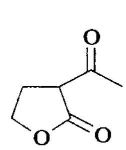
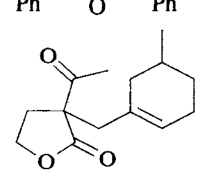
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8-C_{16} 		$Mn(OAc)_3$, AcOH, rt, 11 h	 +		55
R^1 / R^2					
Ph / Ph			(82)	(0)	
4-ClC_6H_4 / 4-ClC_6H_4			(27)	(34)	
4-$MeOC_6H_4$ / 4-$MeOC_6H_4$			(54)	(46)	
4-MeC_6H_4 / 4-MeC_6H_4			(55)	(46)	
4-FC_6H_4 / 4-FC_6H_4			(50)	(17)	
Ph / H			(50)	(13)	
C_9 		$Mn(OAc)_3$, AcOH, 45°, 10 min		(100)	106
		$Mn(OAc)_3$, AcOH, 75-85°, 10-30 min		(56)	136
		$Mn(OAc)_3$, $Cu(OAc)_2$, PbO_2, AcOH, rt, 2 d		(73)	71

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

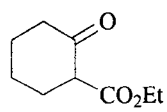
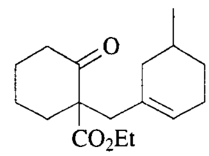
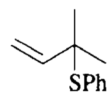
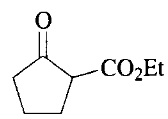
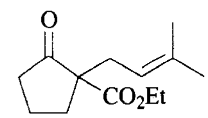
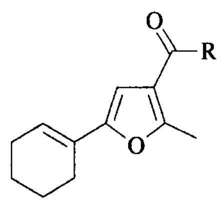
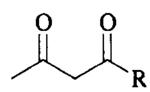
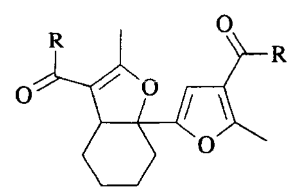
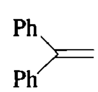
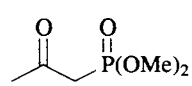
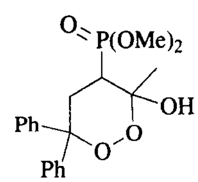
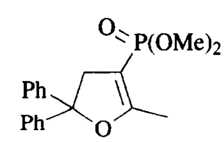
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, PbO_2, AcOH, rt, 2 d	 (63)	71
C_{11} 		"	 (—)	71
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 30°, 3 h		77
C_{13}	R = Me		(70)	
C_{14}	R = OEt		(77)	
C_{14} 		$Mn(OAc)_3$, AcOH, 80°, 0.5-3 h	 (46) +  (21)	53

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS (*Continued*)

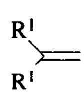
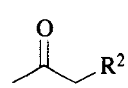
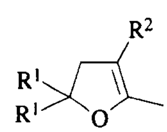
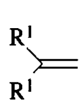
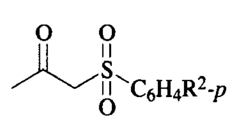
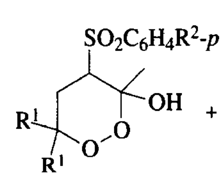
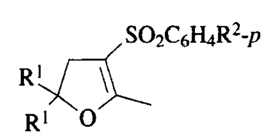
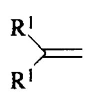
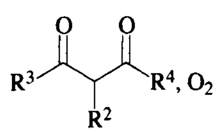
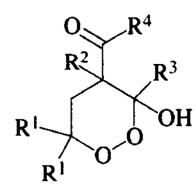
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}-C_{16} 		$Mn(OAc)_3$, O_2 AcOH, 40°, 12 h		53
R^1	R^2			
Ph	SOPh		(62)	
Ph	SOPh		(76)	
Ph	SOPh		(83)	
p-ClC_6H_4	SOPh		(78)	
Ph	SO_2Ph		(88)	
p-ClC_6H_4	SO_2Ph		(80)	
p-MeC_6H_4	SO_2Ph		(82)	
Ph	$SO_2C_6H_4Me$-p		(77)	
Ph	$P(O)(OMe)_2$		(68)	
		$Mn(OAc)_3$, O_2, AcOH, 48°, 10-16 h	 + 	53
R^1 / R^2				
Ph / Me			86 : 14 (58) / (15)	
Ph / H			85 : 15 (52) / (17)	
p-ClC_6H_4 / H			87 : 13 (47) / (11)	
p-MeC_6H_4 / H			89 : 11 (63) / (9)	

TABLE VII. ALKENES OR CYCLOALKENES AND β-DICARBONYL COMPOUNDS *(Continued)*

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_2$, O_2, AcOH, 23°, 11-39 h		52

R^1	R^2	R^3	R^4	Yield (%)
Ph	Me	$(CH_2)_3$		(75)
Ph	Me	$(CH_2)_2$		(93)
Ph	$(CH_2)_4$		Me	(67)
Ph	H	Me	OEt	(48)
Ph	Me	Me	Me	(66)
Ph	H	$(CH_2)_3$		(79)
p-ClC_6H_4	Me	$(CH_2)_3$		(60)
p-$MeOC_6H_4$	Me	$(CH_2)_3$		(54)
Ph	H	Me	Me	(7)
p-ClC_6H_4	H	Me	Me	(6)
p-MeC_6H_4	H	Me	Me	(11)

[a] The same yield was obtained with $Mn(OAc)_3$.
[b] Cyclohexenyl acetate (10%) was also formed.

TABLE VIII. ALKENES AND β - KETOCARBOXYLIC ACIDS

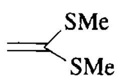
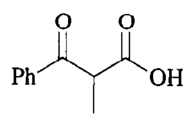
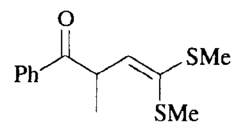
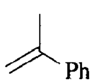
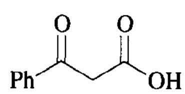
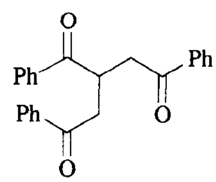
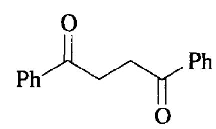
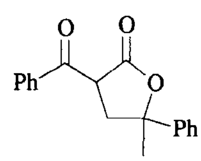
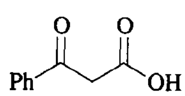
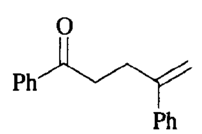
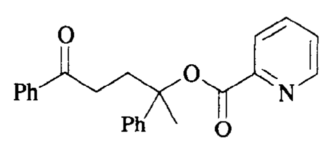
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$(PyCO_2)_3Mn$, DMF, rt, 24 h	 (40)	209
C_9 		$Mn(OAc)_3$, DMF, rt	 (44) +  (7) +  (6)	209
		$(PyCO_2)_3Mn$, DMF, rt	 (8) +  (14)	209

TABLE VIII. ALKENES AND β-KETOCARBOXYLIC ACIDS (*Continued*)

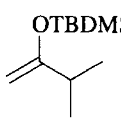
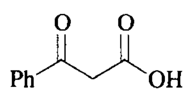
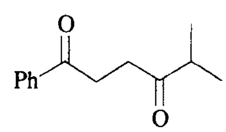
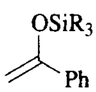
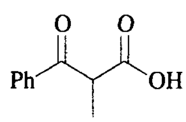
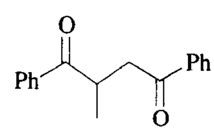
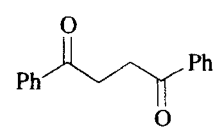
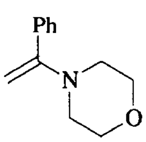
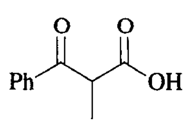
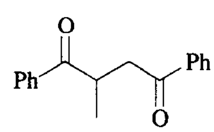
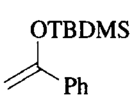
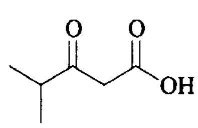
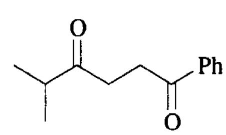
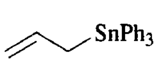
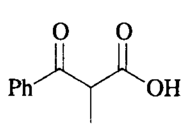
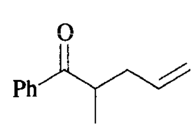
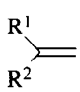
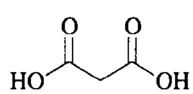
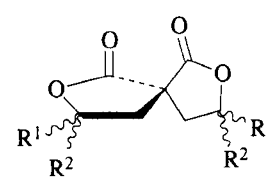
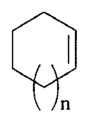
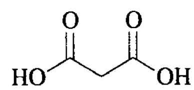
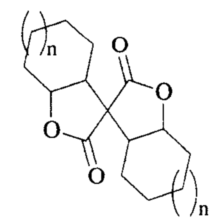
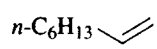
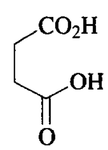
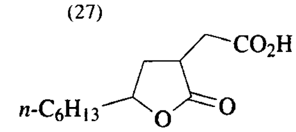
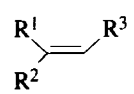
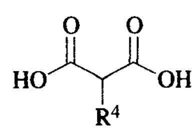
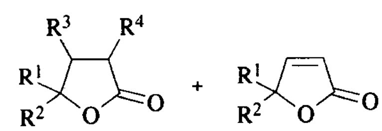
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$(PyCO_2)_3Mn$, DMF, rt	 (45)	209
		$(PyCO_2)_3Mn$, DMF, rt	 + 	209
C_{11} R = Me			(70) (47)	
C_{14} R_3 = *t*-BuMe$_2$			(68) (0)	
C_{12} 		$(PyCO_2)_3Mn$, DMF, rt, 24 h	 (66)	209
C_{14} 		$(PyCO_2)_3Mn$, DMF, rt	 (55)	209
C_{21} 		$(PyCO_2)_3Mn$, DMF, rt, 110 h	 (63)	209

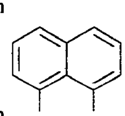
TABLE IX. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACIDS

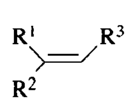
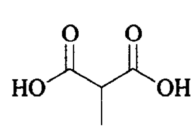
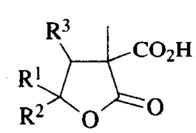
Substrate		Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2-C_{14} 			$Mn(OAc)_3$, AcOH		
R¹	R²				
n-Bu	H		70°, 2 h	9 : 47 : 44[a] (100)	145
n-C_6H_{13}	H		"	11 : 59 : 30[a] (100)	145
n-C_6H_{13}	H		reflux, 1 - 5 min	(4) (17) (19)[b]	144
t-Bu	H		70°, 2 h	2 : 48 : 50[a] (42)	145
Ph	Me		"	20 : 49 : 31[a] (81)	145
Ph	Me		reflux, 1 - 5 min	(10) (19) (39)[b]	144
CH_2Cl	H		70°, 2 h	9 : 60 : 31[a] (30)	145
Ph	Ph		"	(93)	145
Ph	Ph		reflux, 1 - 5 min	(84)	144
Me	Me		70°, 2 h	(51)	145
H	H		"	(29)	145
$(CH_2)_5$			"	(42)	145
$(CH_2)_5$			reflux, 1 - 5 min	(27)	144
Ph	H		"	(9) (30) (40)[b]	144
p-$MeOC_6H_4$	H		"	(84)	144

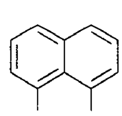
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH		
C_5 n = 0		70°, 2 h	0 : 92 : 8[a] (40)	145
C_6 n = 1		70°, 2 h	(16)	145
n = 1		reflux, 1-5 min	(27)	144
C_8 		$Mn(OAc)_3$, AcOH, AcOK, reflux	 (25)	128
C_8-C_{16} 		$Mn(OAc)_3$, AcOH, 100°, 3-5.5 min		146

R^1	R^3	R^2	R^4		
Ph	H	Ph	Br	(68)	(0)
Ph	H	Ph	Cl	(82)	(0)
4-$MeOC_6H_4$	H	4-$MeOC_6H_4$	Br	(0)	(82)
4-$MeOC_6H_4$	H	4-$MeOC_6H_4$	Cl	(19)	(63)
4-MeC_6H_4	H	4-MeC_6H_4	Br	(4)	(69)
4-MeC_6H_4	H	4-MeC_6H_4	Cl	(74)	(0)
4-$MeOC_6H_4$	H	Ph	Br	(0)	(67)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.

R^1	R^3	R^2	R^4		
4-$MeOC_6H_4$	H	Ph	Cl	(36)	(30)
Ph	H	Me	Br	(54)	(0)
Ph	H	Me	Cl	(46)	(0)
		H	Br	(40)	(0)
		H	Cl	(32)	(0)
Ph	H	H	Br	(28)	(0)
Ph	H	H	Cl	(28)	(0)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 100°, 2.5 - 10 min		146

R^1	R^3	R^2	
Ph	H	Ph	(78)
4-$MeOC_6H_4$	H	4-$MeOC_6H_4$	(70)
4-MeC_6H_4	H	4-MeC_6H_4	(88)
Ph	H	Me	(68)
		H	(13)
Ph	H	H	(48)
$(CH_2)_5$[c]	H		(56)
n-C_6H_{13}	H	H	(42)

[a] Denotes the diastereomeric ratio, *symm-syn* : *unsymm* : *symm-anti*.
[b] These are the yields of the individual diastereomers.
[c] $R^1 + R^2$.

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES

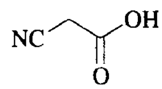
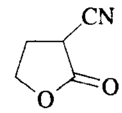
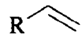
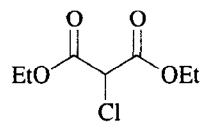
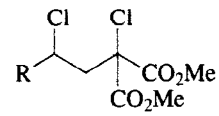
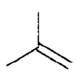
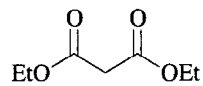
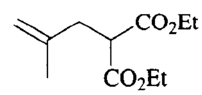
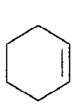
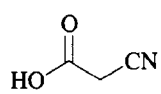
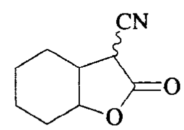
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
$CH_2{=}CH_2$		$Mn(OAc)_3$, AcOH, 70°, 10 - 15 min	 (4)	129
C_3-C_6				
		$Mn(OAc)_3$, LiCl, AcOH, 70-90°, 0.5 - 3 h		50
R				
n-Bu			(65)	
CN			(32)	
CO_2Me			(29)	
C_4				
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°	 (60)	64
C_6				
				
		$Mn(OAc)_3$, AcOH 23°, 15 min	(79)	147
		$Mn(OAc)_3$, AcOH, 70°, 10 - 15 min	6.8 : 1.0 : 1.0 : 1.9 (46)	129

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

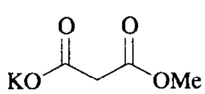
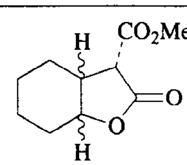
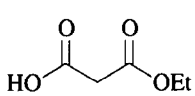
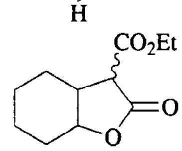
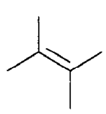
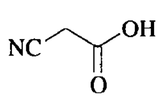
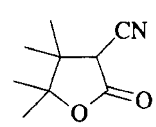
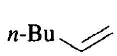
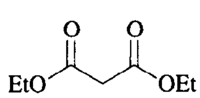
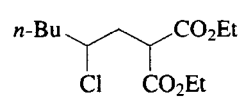
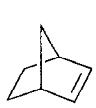
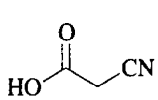
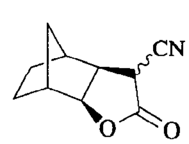
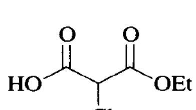
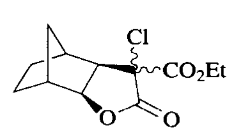
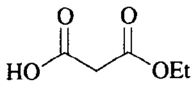
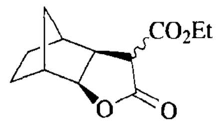
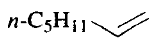
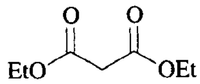
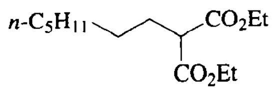
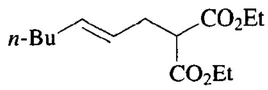
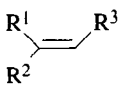
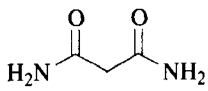
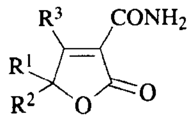
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 70°, 10 - 12 min	 1.0 : 1.3 (39)	129
		$Mn(OAc)_3$, AcOH, 23°, 4 - 6 h	 (75)	147
		$Mn(OAc)_3$, AcOH, 70°, 10 - 15 min	 (62)	129
		$Mn(OAc)_3$, LiCl, AcOH, 60°, 2 h	 (61)	63
C_7				
		$Mn(OAc)_3$, AcOH 23°, 15 min	 (81)	147
		$Mn(OAc)_3$, AcOH, 23°	 (88)	147

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, 23°, 4 - 6 h		(73)	147
		$Mn(OAc)_3$, AcOH, 90°		(50)	64
	"	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH		(—)	64
C_7-C_{20} 		$Mn(OAc)_3$, AcOH, reflux, 1 - 3 min			150

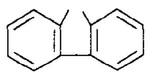
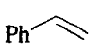
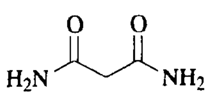
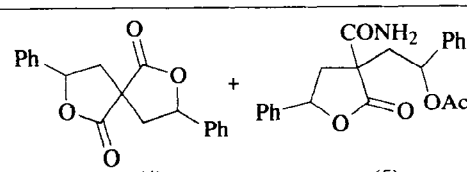
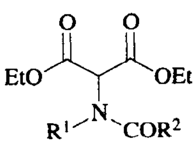
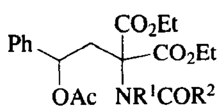
R^1	R^2	R^3	Yield (%)
Ph	Ph	H	(56)
Me	Ph	H	(38)
Ph	Ph	Ph	(69)
		CO_2H	(48)
$(CH_2)_5$		H	(26)

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8 		$Mn(OAc)_3$, AcOH, reflux, 1 - 3 min	 (4) + (5)		150
		$Mn(OAc)_3$, AcOH, 80°, 8 h			107

R^1	R^2	Yield (%)
Me	H	(88)
C_6H_4CO		(87)

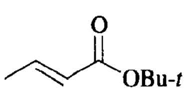
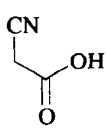
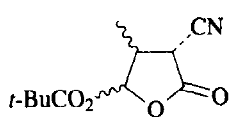
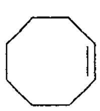
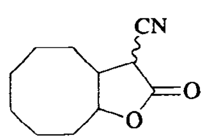
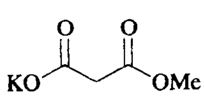
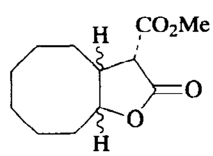
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, 70°, 10 - 15 min		1.6 : 1.0 (9)	129
	"	"		1.6 : 1.0 : 9.6 : 2.1 (66)	129
		$Mn(OAc)_3$, AcOH, 70°, 10 - 12 min		5.7 : 1.0 (67)	129

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

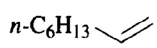
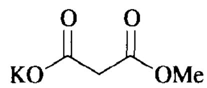
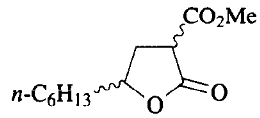
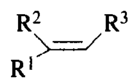
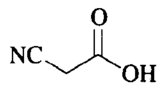
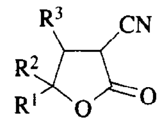
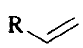
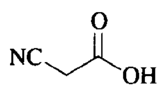
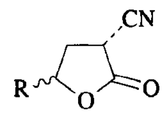
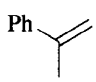
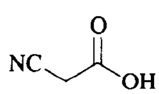
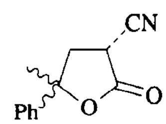
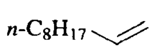
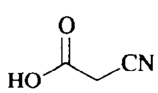
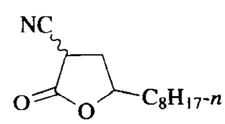
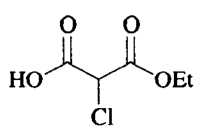
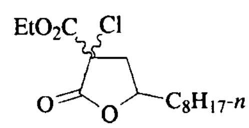
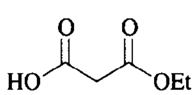
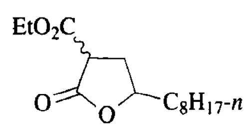
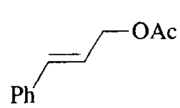
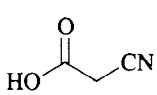
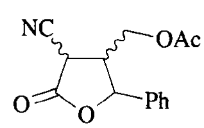
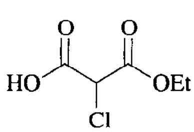
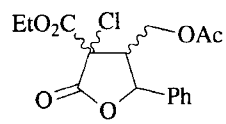
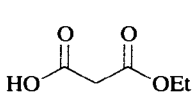
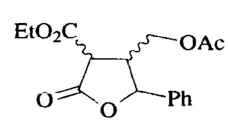
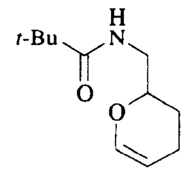
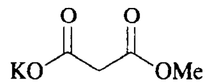
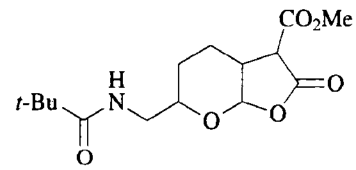
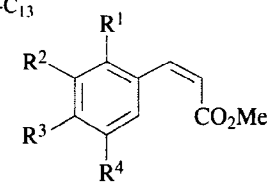
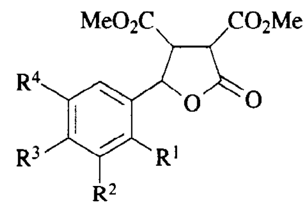
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 70°, 10 - 12 min	 1 : 1 (76)	129
C_8-C_9				
		$Mn(OAc)_3$, AcOH, AcOK, reflux		128
R^1 R^2 R^3				
n-C_6H_{13} H H			(60)	
Ph H H			(41)	
Ph Me H			(43)	
n-Pr H n-Pr			(49)	
Ph H Me			(51)	
		$Mn(OAc)_3$, AcOH, 70°, 10 - 15 min		129
C_8 R = n-C_6H_{13}			α : β 3.7 : 1.0 (61)	
C_{10} R = n-C_8H_{17}			α : β 3.3 : 1.0 (69)	
C_9				
		$Mn(OAc)_3$, AcOH, 70°, 10 - 15 min	 α : β 1.5 : 1.0 (70)	129

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		$Mn(OAc)_3$, AcOH 23°, 15 min	 (85)	147
		$Mn(OAc)_3$, AcOH, 23°	 (40)	147
		$Mn(OAc)_3$, AcOH, 23°, 4 - 6 h	 (74)	147
C_{11}				
		$Mn(OAc)_3$, AcOH 23°, 15 min	 (77)	147
		$Mn(OAc)_3$, AcOH, 23°	 (71)	147
		$Mn(OAc)_3$, AcOH, 23°, 4 - 6 h	 (78)	147

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 110°, 10 min	 (41)	149
C_{11}-C_{13} 	"	$Mn(OAc)_3$, AcOH, 70°, 15 min		148

R^1	R^2	R^3	R^4	Yield (%)
H	H	OMe	H	(63)
OMe	H	OMe	H	(80)
H	OMe	OMe	H	(66)
OMe	H	H	OMe	(60)
OMe	H	OMe	OMe	(75)
H	OMe	OMe	OMe	(73)
OMe	OMe	OMe	H	(80)

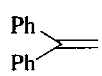
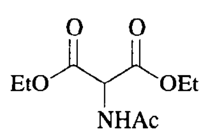
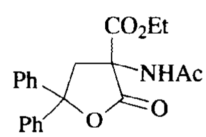
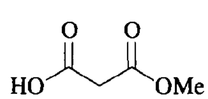
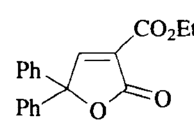
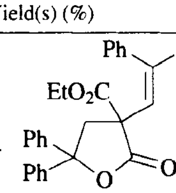
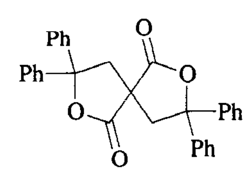
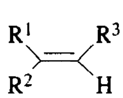
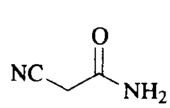
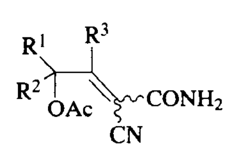
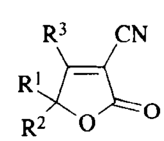
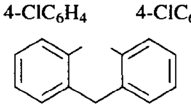
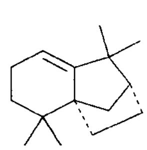
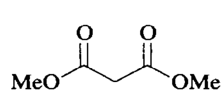
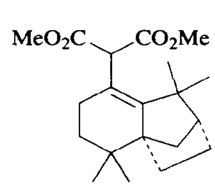
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 		$Mn(OAc)_3$, AcOH, 80°, 8 h	 (90)	107

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, reflux, 22 min	 (25) +  (12) +  (11)	146
C_{14}-C_{21} 		$Mn(OAc)_3$, AcOH, reflux, 1 min	 + 	151

R^1	R^2	R^3	Yield I (%)	Yield II (%)
Ph	Ph	H	(21)	(14)
4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	H	(24)	(15)
		Ph	(30)	(0)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 		$Mn(OAc)_3$, AcOH, 110°, 24 h [a]	 (—)	111

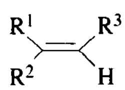
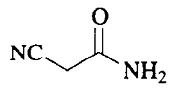
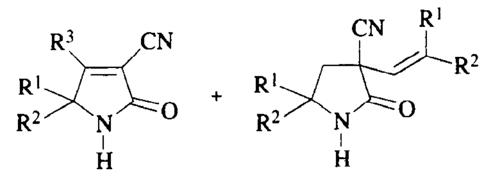
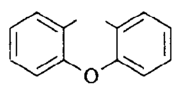
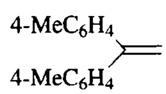
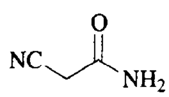
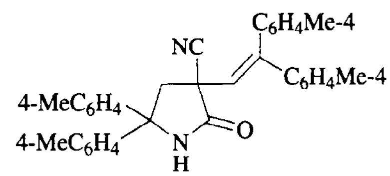
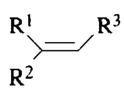
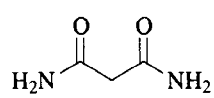
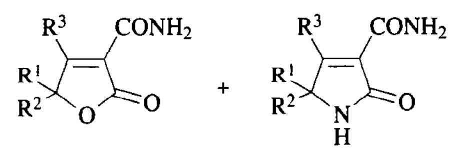
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}-C_{20} 		$Mn(OAc)_3$, AcOH, reflux, 1 min		151
R[1] / R[2] / R[3]				
$4\text{-}MeOC_6H_4$ / $4\text{-}MeOC_6H_4$ / H			(23) + (33)	
Ph / $4\text{-}MeOC_6H_4$ / H			(7) + (37)	
 / Ph			(14) + (0)	
C_{16} 		$Mn(OAc)_3$, AcOH, reflux, 1 min	 (44)	151
		$Mn(OAc)_3$, AcOH, reflux, 1 - 3 min		150
R[1] / R[2] / R[3]				
C_{16} 4-MeOPh / 4-MeOPh / H			(9) + (18)	
C_{22} 4-MeOPh / 4-MeOPh / Ph			(14) + (17)	

TABLE X. ALKENES OR CYCLOALKENES AND DICARBOXYLIC ACID DERIVATIVES (*Continued*)

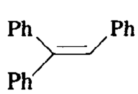
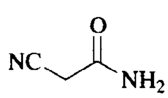
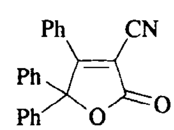
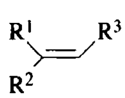
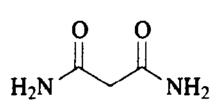
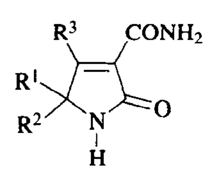
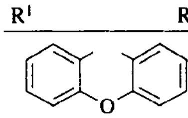
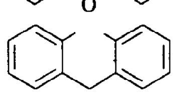
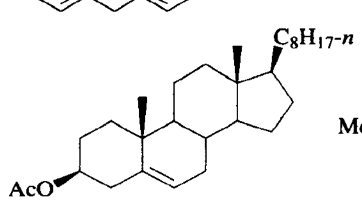
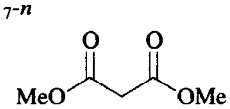
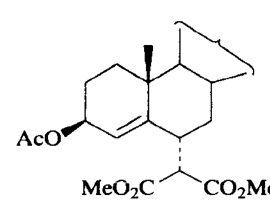
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 		$Mn(OAc)_3$, AcOH, reflux, 1 min	 (30)	151
		$Mn(OAc)_3$, AcOH, reflux, 1 - 3 min		150
R[1] / R[2] R[3]				
C_{20}  / Ph			(59)	
C_{21}  / Ph			(90)	
C_{29} 		$Mn(OAc)_3$, AcOH, 4 h	 (—)	111

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS

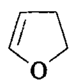
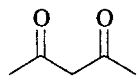
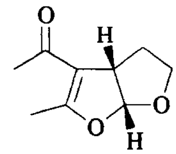
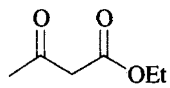
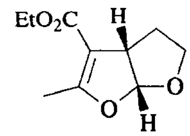
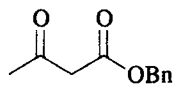
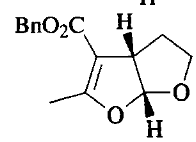
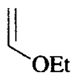
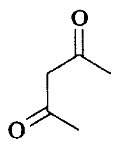
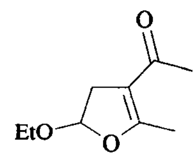
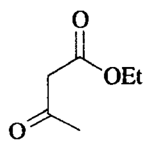
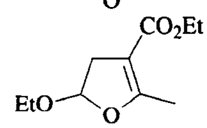
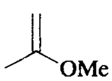
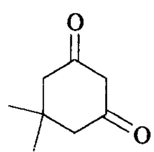
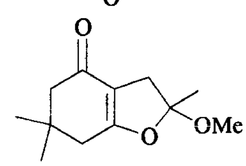
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4					
		$Mn(OAc)_3$, AcOH, 60°		(26)	142
		"		(53)	139, 142
		"		(56)	139, 142
		$Mn(OAc)_3$, AcOH, 45°, 30 min		(73)	137
		$Mn(OAc)_3$, AcOH, 40°, 10 min		(89)	137
		$Mn(OAc)_3$, AcOH, 23°, 10 min		(98)	137

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

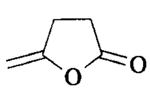
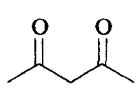
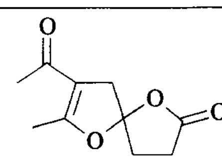
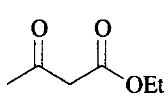
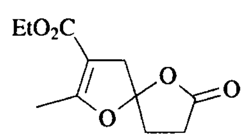
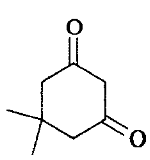
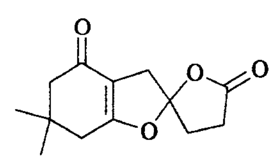
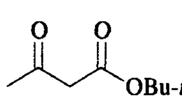
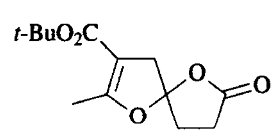
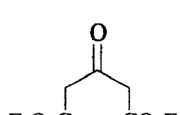
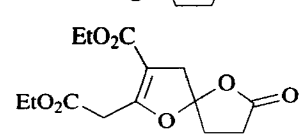
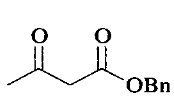
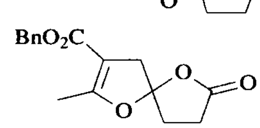
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_5					
		$Mn(OAc)_3$, AcOH, 65°		(56)	139, 141
		"		(47)	139, 141
		"		(64)	139, 141
		"		(31)	141
		"		(38)	139, 141
		"		(52)	141

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

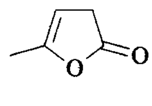
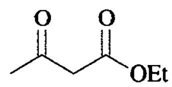
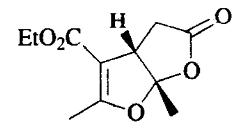
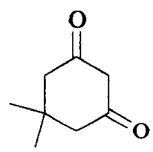
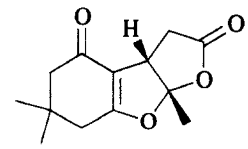
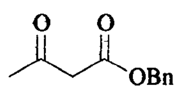
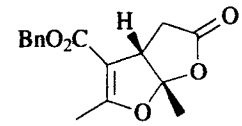
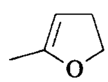
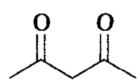
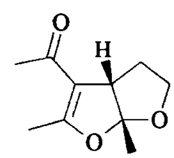
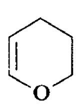
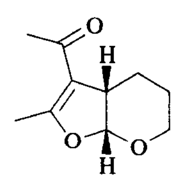
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, 60°		(28)	142
		"		(24)	142
		"		(15)	142
		"		(44)	142
	"	"		(38)	142

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

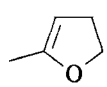
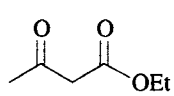
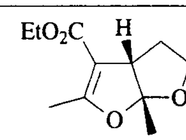
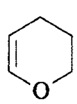
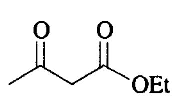
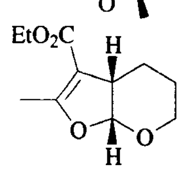
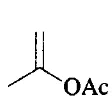
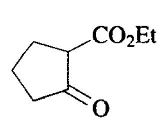
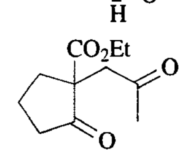
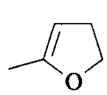
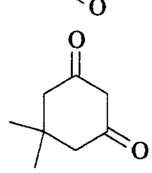
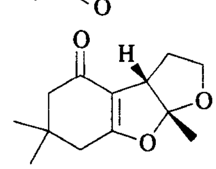
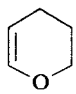
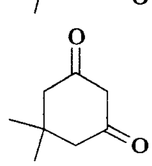
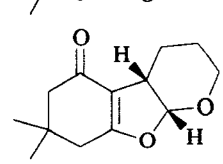
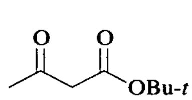
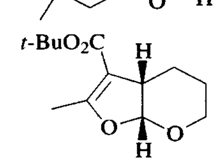
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, 60°		(51)	139, 142
		$Mn(OAc)_3$, AcOH, 60°		(47)	142
		$Mn(OAc)_3$, AcOH, 40°, 30 min		(64)	138
		$Mn(OAc)_3$, AcOH, 60°		(40)	139, 142
		$Mn(OAc)_3$, AcOH, 60°		(43)	139, 142
		$Mn(OAc)_3$, AcOH, 60°		(31)	142

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

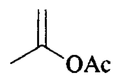
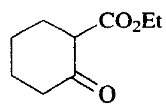
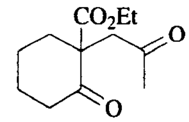
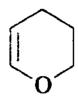
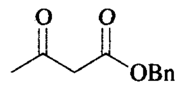
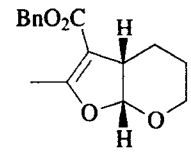
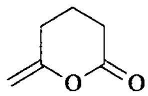
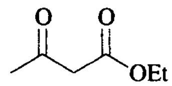
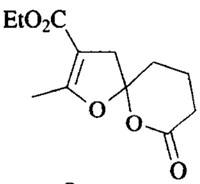
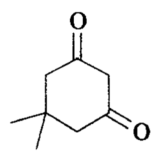
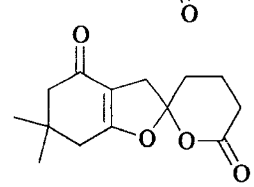
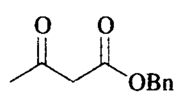
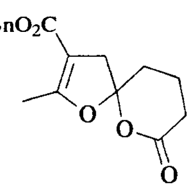
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 40°, 30 min	 (71)	138
		$Mn(OAc)_3$, AcOH, 60°	 (50)	142
C_6				
		$Mn(OAc)_3$, AcOH, rt	 (30)	141
		$Mn(OAc)_3$, AcOH, rt	 (36)	141
		$Mn(OAc)_3$, AcOH, rt	 (19)	141

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

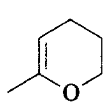
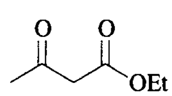
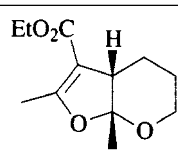
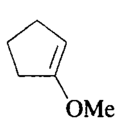
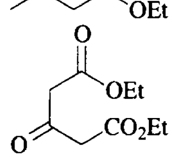
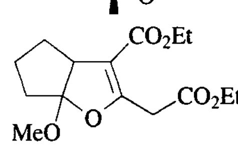
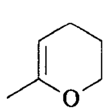
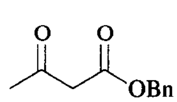
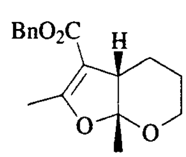
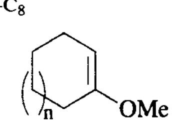
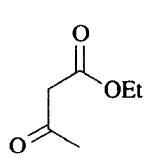
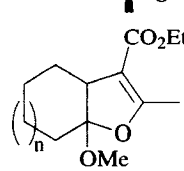
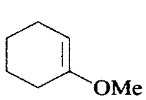
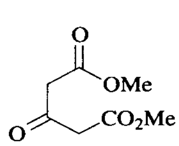
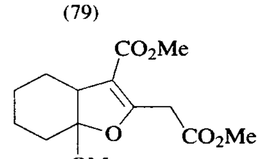
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 60°	 (39)	142
		$Mn(OAc)_3$, AcOH, 23°, 30 min	 (69)	137
		$Mn(OAc)_3$, AcOH, 60°	 (39)	142
C_6-C_8				
		$Mn(OAc)_3$, AcOH, 23°, 10 min		137
n = 0			(79)	
n = 1			(86)	
n = 2			(79)	
C_7				
		$Mn(OAc)_3$, AcOH, 23°, 20 min	 (71)	137

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

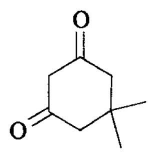
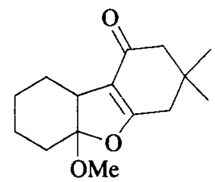
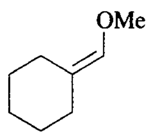
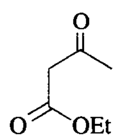
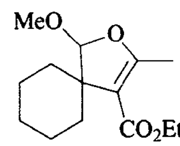
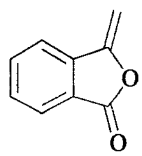
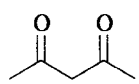
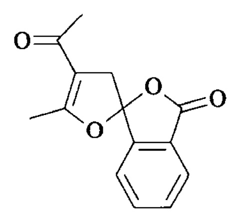
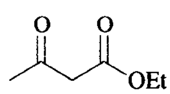
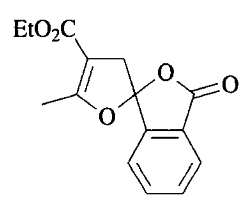
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$ AcOH, 23°, 10 min		(76)	137
C_8 		$Mn(OAc)_3$, AcOH, 23°, 25 min		(86)	138
C_9 		$Mn(OAc)_3$, AcOH, 65°		(91)	141
		$Mn(OAc)_3$, AcOH, 65°		(85)	141

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

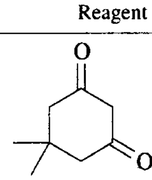
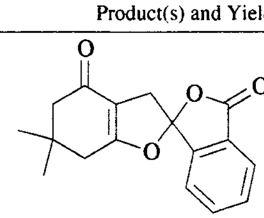
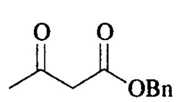
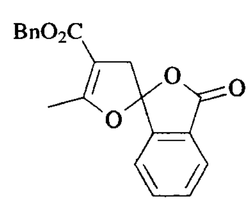
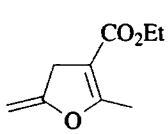
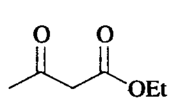
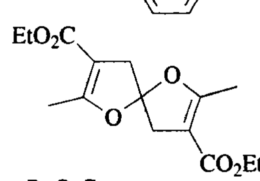
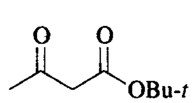
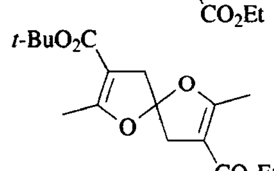
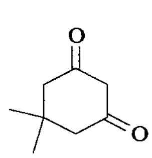
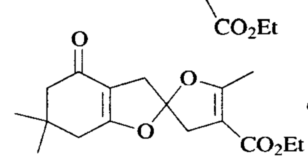
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, 65°		(87)	141
		"		(78)	141
		$Mn(OAc)_3$, AcOH, 60°		(37)	139, 143
		"		(11)	143
		"		(43)	139, 143

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

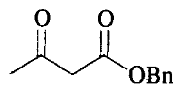
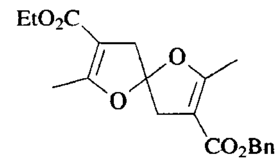
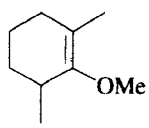
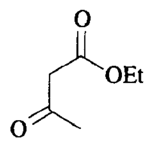
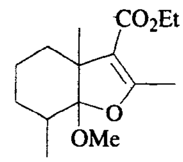
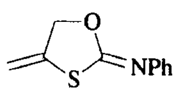
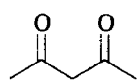
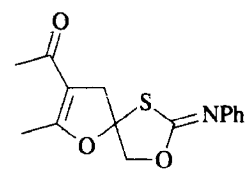
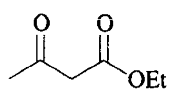
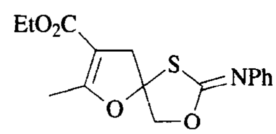
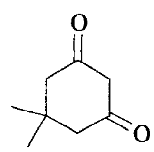
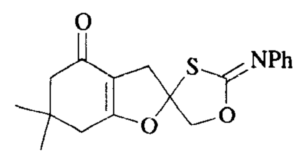
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 60°	 (40)	139, 143
		$Mn(OAc)_3$, AcOH, 60°, 30 min	 (—)	138
C_{10}				
		$Mn(OAc)_3$, AcOH, 23°	 (57)	140
		"	 (47)	140
		"	 (65)	140

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

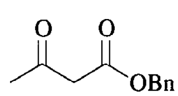
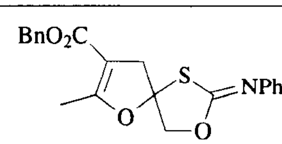
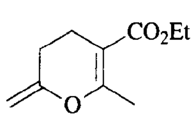
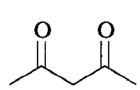
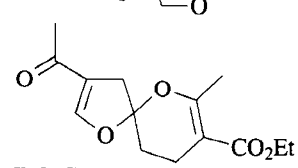
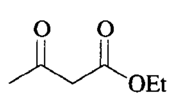
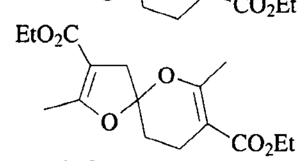
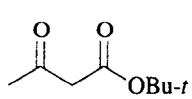
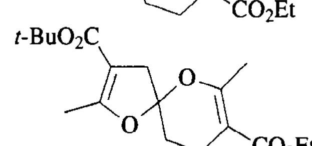
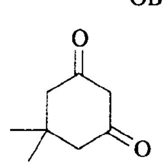
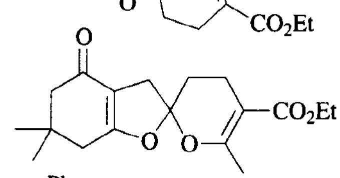
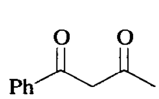
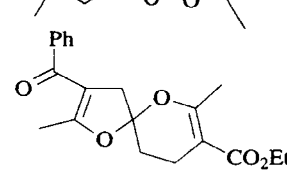
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 23°	 (46)	140
		$Mn(OAc)_3$, AcOH, 60°	 (66)	143
		"	 (58)	143
		"	 (44)	143
		"	 (69)	143
		"	 (33)	143

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

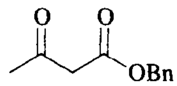
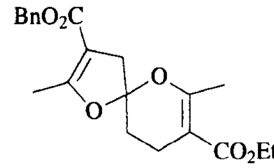
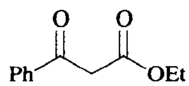
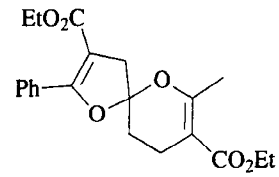
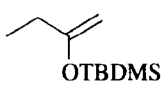
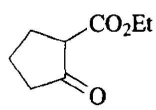
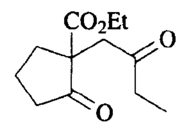
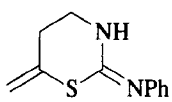
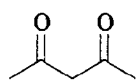
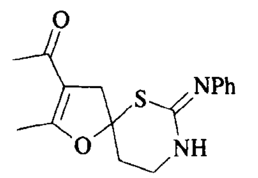
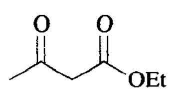
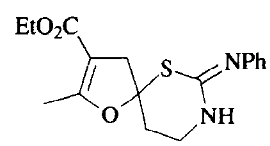
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 60°	 (61)	139, 143
		"	 (41)	143
		$Mn(OAc)_3$, AcOH, 40°, 30 min	 (46)	138
C_{11}				
		$Mn(OAc)_3$, AcOH, 23°	 (55)	140
		"	 (60)	140

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

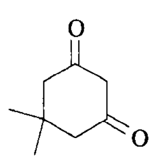
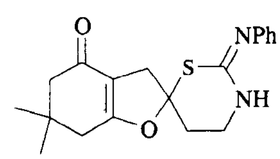
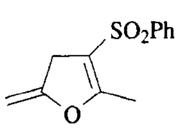
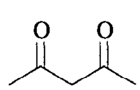
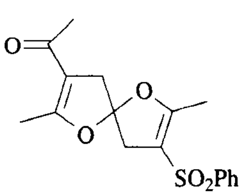
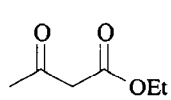
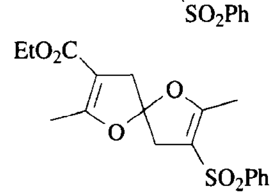
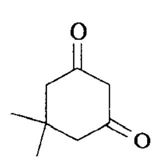
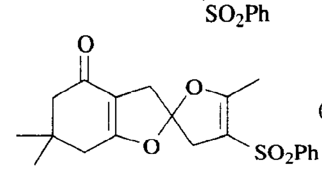
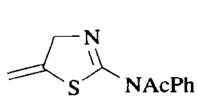
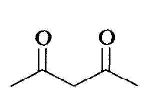
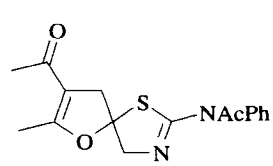
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 23°	 (62)	140
C_{12}				
		$Mn(OAc)_3$, AcOH, 60°	 (36)	143
		"	 (26)	139, 143
		"	 (30)	143
		$Mn(OAc)_3$, AcOH, 23°	 (58)	140

TABLE XI. ENOL ETHERS OR ENOL LACTONES AND β-DICARBONYL COMPOUNDS (*Continued*)

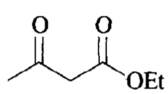
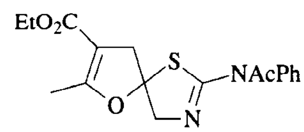
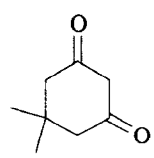
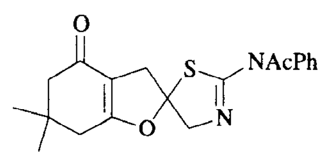
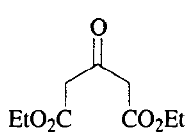
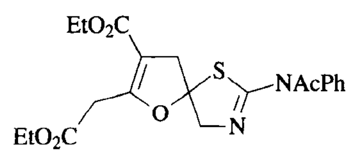
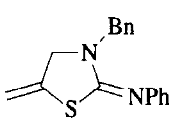
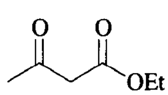
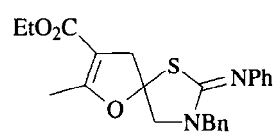
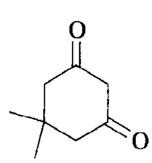
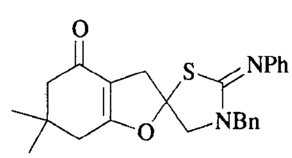
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 23°	 (48)	140
		"	 (76)	140
		"	 (32)	140
C_{17} 		"	 (48)	140
		"	 (59)	140

TABLE XII. ALKYNES AND CARBONYL COMPOUNDS

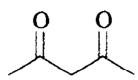
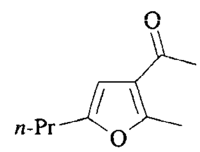
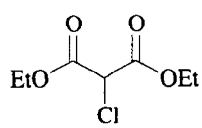
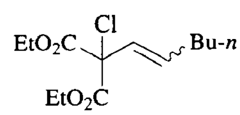
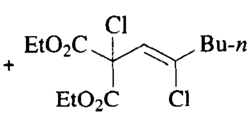
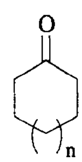
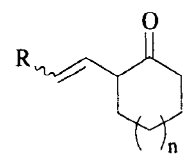
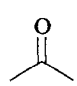
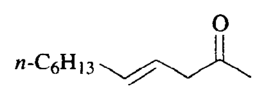
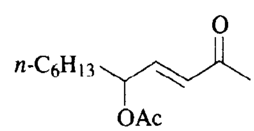
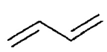
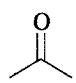
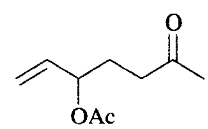
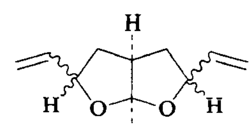
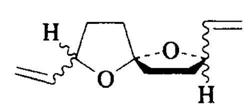
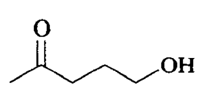
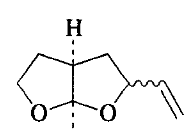
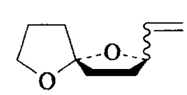
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5					
	n-PrC≡CH		$Mn(OAc)_3$, AcOH, 70°, 0.5 h	 (18)	152
C_6					
	n-BuC≡CH		$Mn(OAc)_3$, LiCl, AcOH	 +  3 : 2 (—)	50
	RC≡CH		$Mn(OAc)_3$, 80°, 0.5 - 1 h		49
	R	n			
C_6	n-Bu	0		(46)	
C_6	n-Bu	1		(42)	
C_7	n-C_5H_{11}	0		(52)	
C_8					
	n-C_6H_{13}C≡CH		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 2 h	 (13) +  (18)	44

TABLE XIII. 1,3 - ALKADIENES AND KETONES

	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 80°, 3 h	 (7) +	61
				 1 : 1 : 2[a] (—) +	
				 3 : 3 : 1 (—)	
			"	 (—) +	61
				 (—)	

[a] Ratio of exo-exo, exo-endo, and endo-endo stereoisomers.

TABLE XIV. 1,3 - ALKADIENES AND ACETIC ACID

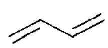
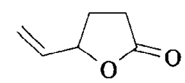
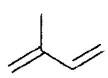
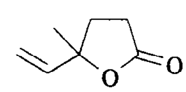
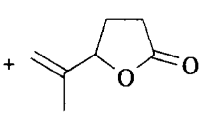
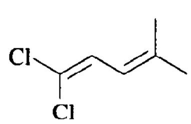
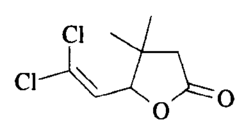
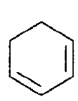
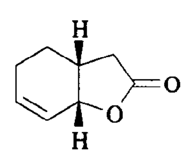
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
				
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, 140°, 3 h	(39)	200
	"	$Mn(OAc)_3$, AcOH, AcOK, reflux	(30)	128
C_5				
	"	"	 (37) +  (13)	128
C_6				
	"	$Mn(OAc)_3$, AcOH, AcOK, reflux, 100 h	 (28)	154
	AcOH, Ac_2O	1. $Mn(OAc)_3$ AcOH, Ac_2O, reflux, 15 min 2. KOH, EtOH, H_2O, 25°, 30 min 3. H_2SO_4, 60°, 8 h	 (8)	156

TABLE XIV. 1,3 - ALKADIENES AND ACETIC ACID (*Continued*)

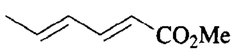
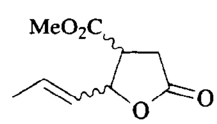
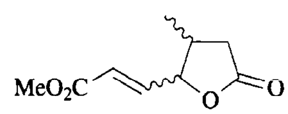
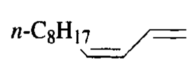
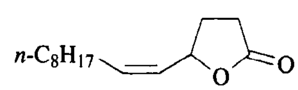
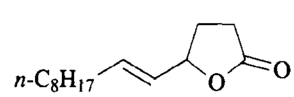
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	AcOH	$Mn(OAc)_3$, AcOH, AcOK, 135°	 *E* : *Z* 20 : 9 + (60)  *E* : *Z* 45 : 23	108
C_{12}				
	"	$Mn(OAc)_3$ AcOH, AcOK 115°, 6 h	 + (45) 56 : 44 	153

TABLE XV. NONCONJUGATED DIENES AND CARBONYL COMPOUNDS

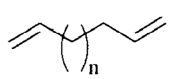
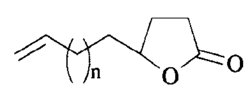
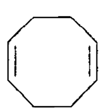
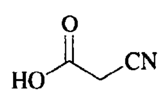
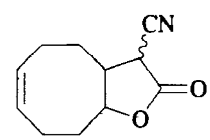
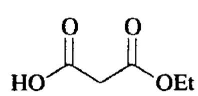
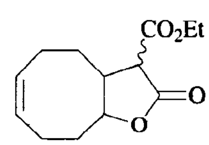
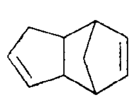
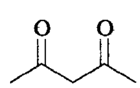
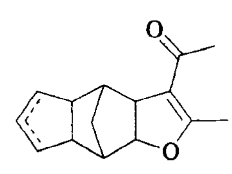
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
 C_6 n = 1 C_8 n = 3	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (24) (26)		128
C_8 		$Mn(OAc)_3$, AcOH 23°, 15 min		(83)	147
		$Mn(OAc)_3$, AcOH, 23°, 4 - 6 h		(58)	147
C_{10} 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 10 - 15 min		(66)	72

TABLE XV. NONCONJUGATED DIENES AND CARBONYL COMPOUNDS (*Continued*)

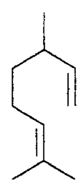
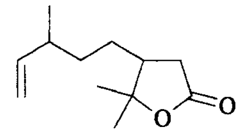
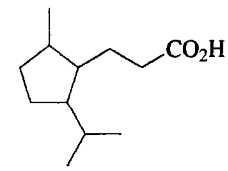
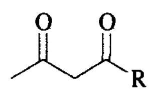
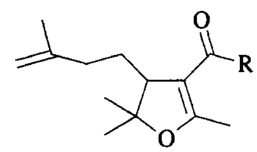
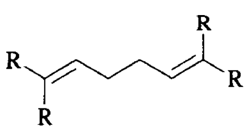
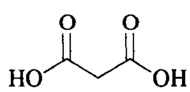
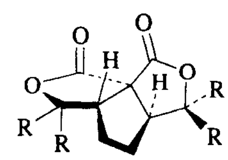
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, reflux, 10 min	 (—) +  (—)	82
		$Mn(OAc)_3$, AcOH, reflux, 10 min		82
	R = Me		(—)	
	R = OEt		(—)	
		$Mn(OAc)_3$, AcOH, 70°, 2 h		145
C_{10} R = Me			(40)	
C_{30} R = Ph			(12)	

TABLE XV. NONCONJUGATED DIENES AND CARBONYL COMPOUNDS (*Continued*)

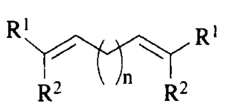
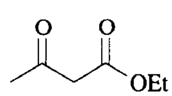
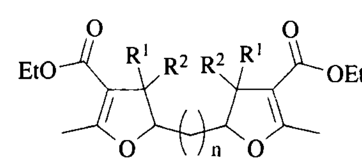
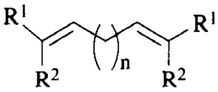
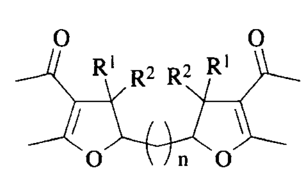
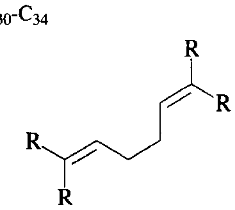
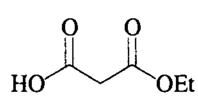
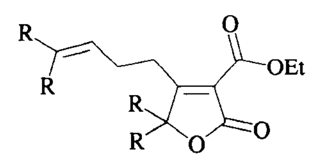
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29}-C_{34}				
		$Mn(OAc)_3$, AcOH reflux, 4 - 9 min		109
n / R^1 / R^2				
1 / Ph / Ph			(22)	
1 / p-ClC_6H_4 / p-ClC_6H_4			(17)	
1 / p-MeC_6H_4 / p-MeC_6H_4			(14)	
2 / Ph / Ph			(89)	
2 / p-ClC_6H_4 / p-ClC_6H_4			(71)	
2 / p-MeC_6H_4 / p-MeC_6H_4			(79)	
2 / p-$MeOC_6H_4$ / p-$MeOC_6H_4$			(62)	
	$Mn(acac)_3$[a]	$Mn(acac)_3$, AcOH, reflux, 1 - 3 min		109
n / R^1 / R^2				
1 / Ph / Ph			(13)	
1 / p-ClC_6H_4 / p-ClC_6H_4			(23)	
1 / p-MeC_6H_4 / p-MeC_6H_4			(71)	
2 / Ph / Ph			(71)	
2 / p-ClC_6H_4 / p-ClC_6H_4			(46)	
2 / p-MeC_6H_4 / p-MeC_6H_4			(29)	
2 / p-$MeOC_6H_4$ / p-$MeOC_6H_4$			(29)	

TABLE XV. NONCONJUGATED DIENES AND CARBONYL COMPOUNDS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{30}-C_{34}				
		$Mn(OAc)_3$, AcOH, reflux, 1 - 6 min		109
R				
Ph			(81)	
p-ClC_6H_4			(65)	
p-MeC_6H_4			(47)	
p-$MeOC_6H_4$			(33)	

[a] Monodihydrofurans were formed in 11 - 39% yields.

TABLE XVI. 1,3-ALKADIENES OR 1,3-CYCLOALKADIENES AND DICARBONYL COMPOUNDS

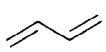
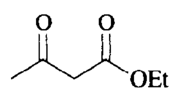
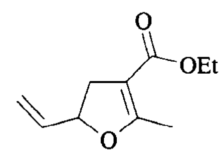
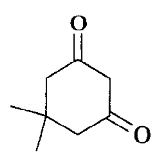
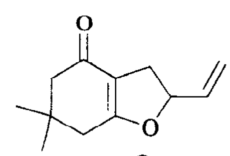
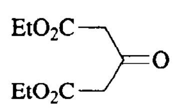
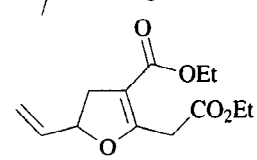
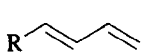
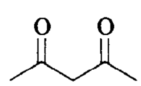
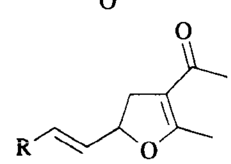
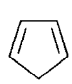
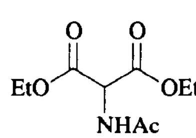
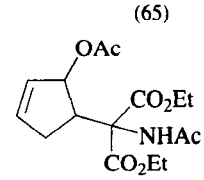
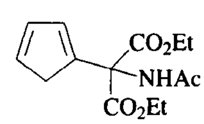
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 10 - 15 min	 (64)	72
		"	 (42)	72
		"	 (52)	72
		"		72, 74
C_4 R = H			(97)	
C_5 R = Me			(65)	
C_5 		$Mn(OAc)_3$, AcOH, 80°, 8 h	 (20) +  (10)	107

TABLE XVI. 1,3-ALKADIENES OR 1,3-CYCLOALKADIENES AND DICARBONYL COMPOUNDS (*Continued*)

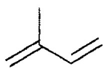
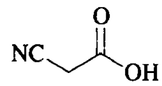
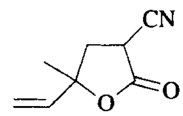
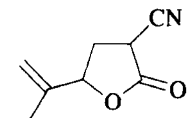
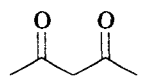
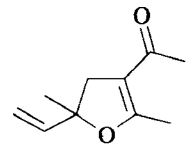
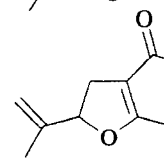
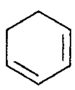
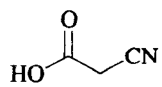
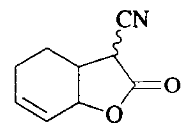
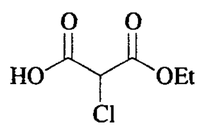
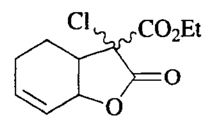
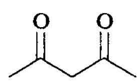
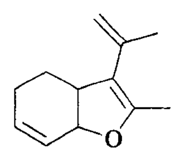
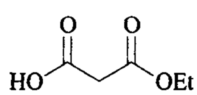
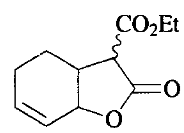
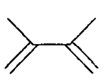
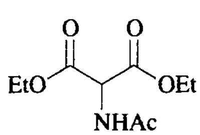
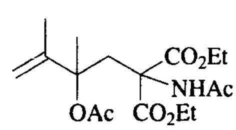
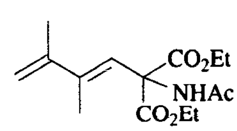
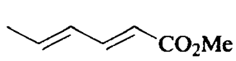
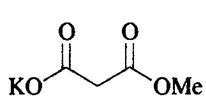
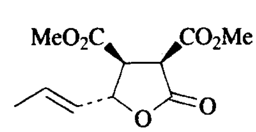
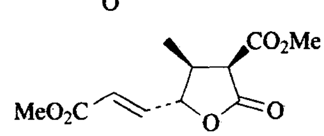
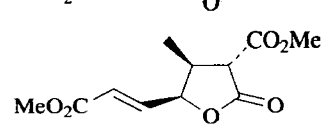
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, AcOK, reflux	 (39) +  (5)	128
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 10 - 15 min	 (70) +  (10)	72
C_6				
		$Mn(OAc)_3$, AcOH, 23°, 15 min	 (78)	147
		$Mn(OAc)_3$, AcOH, 23°	 (82)	147
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 10 - 15 min	 (32)	72
		$Mn(OAc)_3$, AcOH, 23°, 4 - 6 h	 (76)	147

TABLE XVI. 1,3-ALKADIENES OR 1,3-CYCLOALKADIENES AND DICARBONYL COMPOUNDS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 80°, 8 h	 (40) +  (28)	107
C_7				
		$Mn(OAc)_3$, AcOH, 70°	 **I** +  **II** +  **III** **I : II : III** 21 : 44 : 15 (63)	108

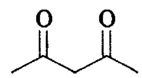
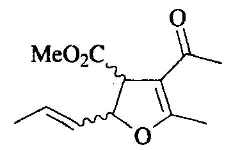
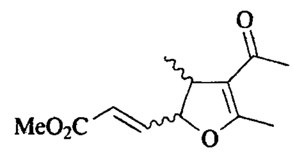
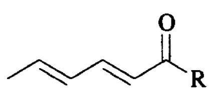
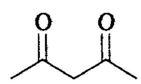
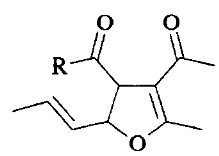
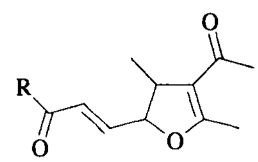
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 70°	 *E*:*Z* 36 : 12 +  *E*:*Z* 15 : 19 (57)	108
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 10 - 15 min	 I +  II	72
R = OMe			I (35) + II (7)	
R = Me			I (40) + II (8)	

TABLE XVI. 1,3-ALKADIENES OR 1,3-CYCLOALKADIENES AND DICARBONYL COMPOUNDS (*Continued*)

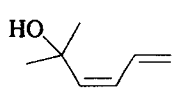
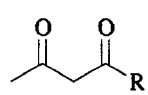
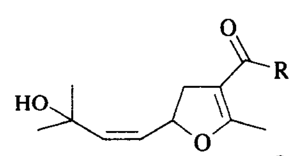
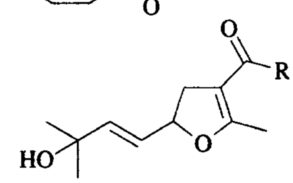
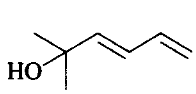
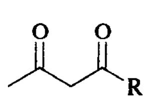
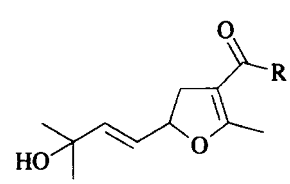
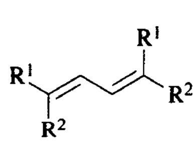
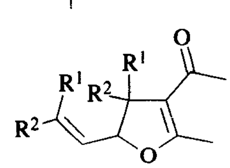
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 15 min	 I + 	73
	R = Me		I + II (56) I:II = 30:70	
	R = OEt		I + II (60) I:II = 40:60	
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 15 min	 R = Me (53) R = OEt (57)	73
	$Mn(acac)_3$	$Mn(acac)_3$, AcOH, reflux, 2 min		109
R^1 R^2				
Me Me			(72)	
Ph H			(85)	

TABLE XVI. 1,3-ALKADIENES OR 1,3-CYCLOALKADIENES AND DICARBONYL COMPOUNDS (*Continued*)

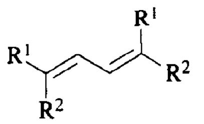
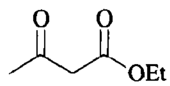
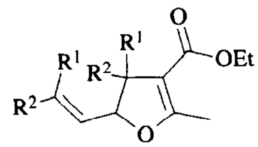
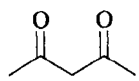
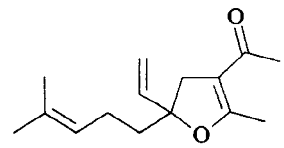
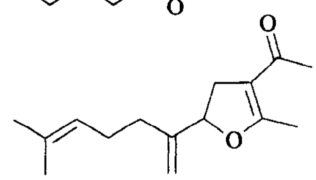
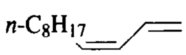
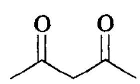
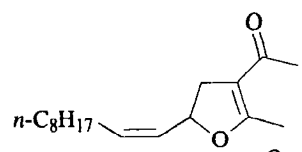
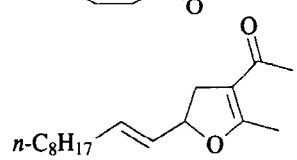
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
 R¹ R² C_8 Me Me C_{16} Ph H		$Mn(OAc)_3$, AcOH, reflux, 1 - 4 min	 (57) (49)	109
C_{10} 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 10 - 15 min	 (43) +  (8)	72
C_{12} 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 15 min	 + 80 : 20 (77) 	73

TABLE XVI. 1,3-ALKADIENES OR 1,3-CYCLOALKADIENES AND DICARBONYL COMPOUNDS (*Continued*)

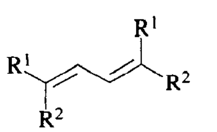
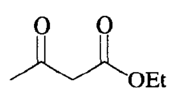
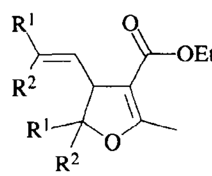
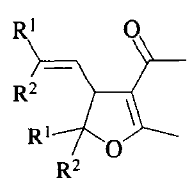
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}-C_{32}  R¹ R² Ph Ph *p*-ClC_6H_4 *p*-ClC_6H_4 *p*-MeC_6H_4 *p*-MeC_6H_4		$Mn(OAc)_3$, AcOH, reflux, 3 - 7 min	 (46) (29) (11)	109
R¹ R² Ph Ph *p*-ClC_6H_4 *p*-ClC_6H_4 *p*-MeC_6H_4 *p*-MeC_6H_4	$Mn(acac)_3$	$Mn(acac)_3$, AcOH, reflux, 2 min	 (19) (30) (38)	109

TABLE XVII. 1,3-ALKENYNES AND ACETIC ACID

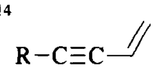
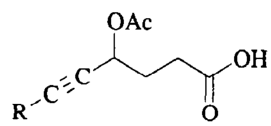
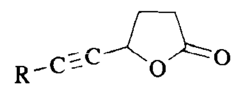
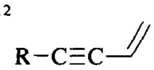
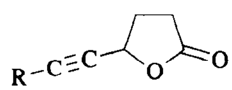
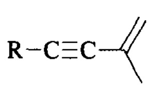
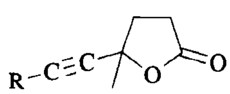
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_6-C_{14}					
	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, 115°, 10 min	 +		62
R					
Et			(27)	(17)	
n-Bu			(40)	(12)	
n-C_7H_{15}			(40)	(0)	
n-C_8H_{17}			(57)	(0)	
n-$C_{10}H_{21}$			(49)	(0)	
C_7-C_{12}					
	"	$Mn(OAc)_3$, AcOH, AcOK, 115°, 4 h			158, 153, 156
R					
$Me_2C(OMe)$			(33)		
n-Pr			(47)		
n-Bu			(50)		
n-C_7H_{15}			(34)		
n-C_8H_{17}			(51)		
C_8-C_9					
	"	"			156
R					
n-Pr			(30)		
n-Bu			(40)		
i-Bu			(52)		

TABLE XVIII. 1,3-ALKENYNES AND β-DICARBONYL COMPOUNDS

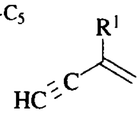
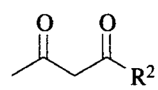
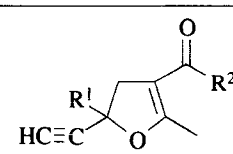
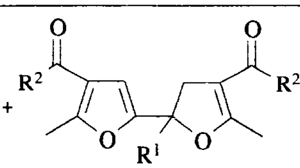
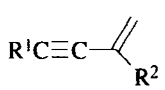
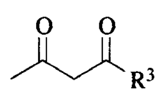
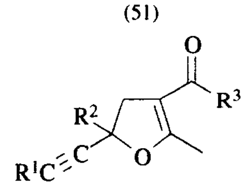
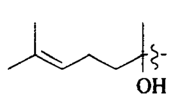
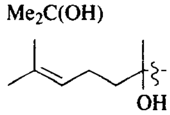
Substrate			Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4-C_5 				$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 70°, 15 min	 +		74, 76
R¹	R²						
H	Me				(4)	(14)	
H	OEt				(9)	(18)	
Me	OEt				(51)	(11)	
C_5-C_{12} 				"			75, 77, 161
R¹	R²	R³					
n-Bu	H	OEt			(68)		
n-Bu	H	Me			(36)		
CH_2OH	H	OEt			(50)		
i-PrCH(OH)	H	OEt			(59)		
i-PrCH(OH)	H	Me			(55)		
$Me_2C(OH)$	H	OEt			(54)		
$Me_2C(OMe)$	H	OEt			(50)		
$Me_2C(OAc)$	H	OEt			(22)		
	H	OEt			(48)		
$Me_2C(OH)$	Me	OEt			(66)		
$Me_2C(OH)$	Me	Me			(60)		
	Me	OEt			(50)		

TABLE XVIII. 1,3-ALKENYNES AND β-DICARBONYL COMPOUNDS (*Continued*)

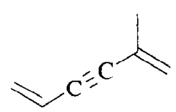
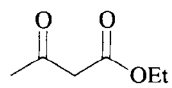
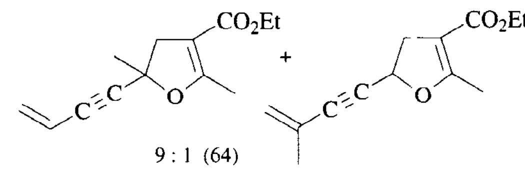
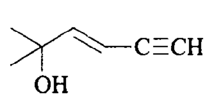
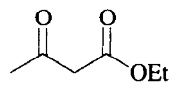
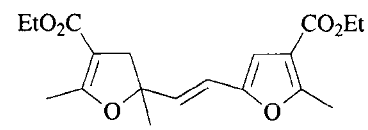
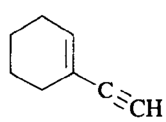
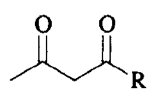
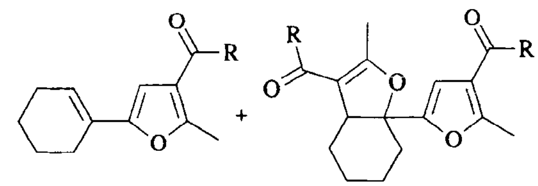
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_7			$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 70°, 15 min	 9 : 1 (64)		76
			$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 30°, 3 h		(36)	77
C_8			AcOH, 30°, 3 h			77
		R = Me	$Mn(OAc)_3$, (1 eq) $Cu(OAc)_2$, (1 eq)	(24)	(20)	
		R = OEt	"	(19)	(23)	
		R = Me	$Mn(OAc)_3$, (3 eq) $Cu(OAc)_2$, (3 eq)	(0)	(63)	
		R = OEt	"	(0)	(60)	

TABLE XVIII. 1,3-ALKENYNES AND β-DICARBONYL COMPOUNDS (*Continued*)

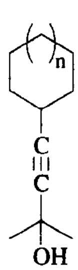
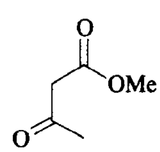
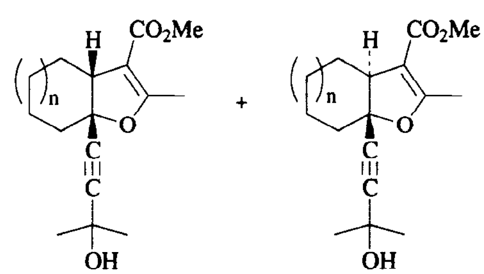
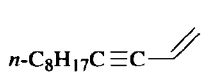
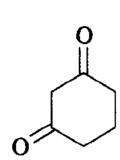
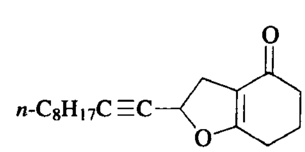
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
			$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 30°			57
C_{10}	n = 0		1 h	(47)	(0)	
C_{11}	n = 1		2.5 h	(25) 89 : 11		
C_{12}			$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 30°, 30 min		(78)	57

TABLE XIX. Co-COMPLEXED 1,3-ALKENYNES AND β-DICARBONYL COMPOUNDS

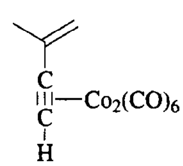
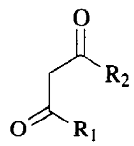
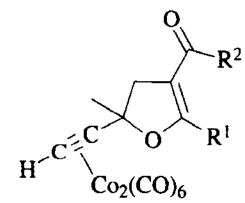
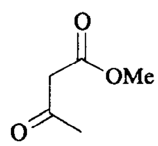
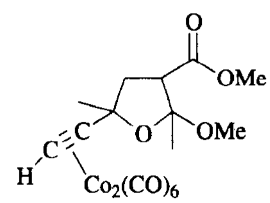
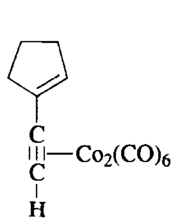
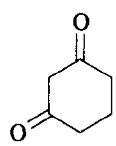
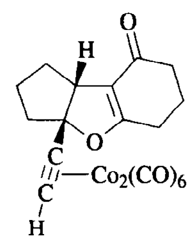
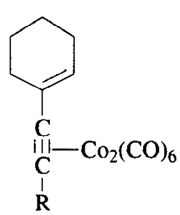
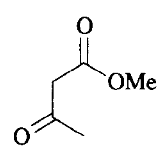
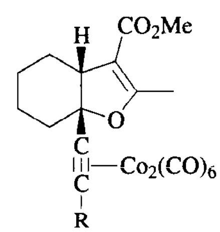
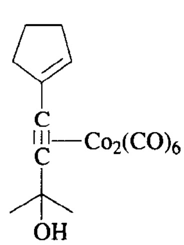
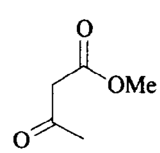
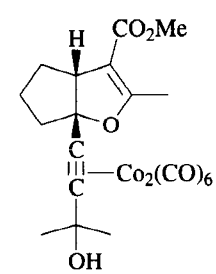
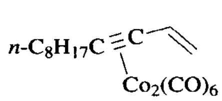
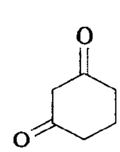
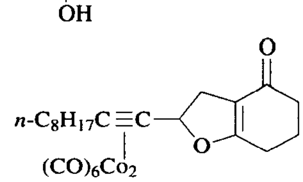
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		 R^1 / R^2 Me / OMe Me / Me $(CH_2)_3$	$Mn(OAc)_3$, AcOH, 30°, 30 min	 (65) + (8)[a] (52) + (6)[a] (46) + (10)[a]	57
			$Mn(OAc)_3$, MeOH, 30°, 30 min	 (46)	57
C_{13}			$Mn(OAc)_3$, AcOH, 30°, 1 h	 (28) + (10)[a]	57

TABLE XIX. Co-COMPLEXED 1,3-ALKENYNES AND β-DICARBONYL COMPOUNDS (*Continued*)

	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
			$Mn(OAc)_3$, AcOH, 30°, 2.5 h		57
C_{14}	R = H			(22) + (3)[a]	
C_{17}	R = $Me_2C(OH)$			(27) + (20)[a]	
C_{16}			$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 30°, 1 h	 (61) + (17)[a]	57
C_{18}			$Mn(OAc)_3$, AcOH, 30°, 30 min	 (41) + (27)[a]	57

[a] Decomplexation product.

TABLE XX. 1,3-ALKADIYNES AND β-DICARBONYL COMPOUNDS

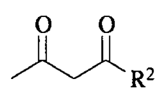
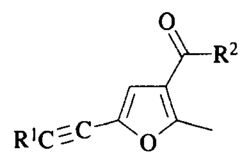
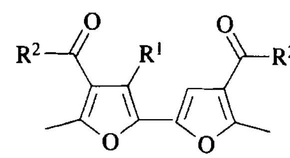
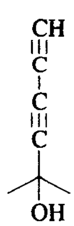
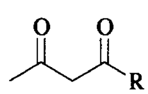
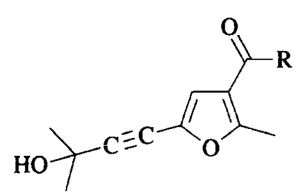
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_6-C_8					
$R^1C{\equiv}C{-}C{\equiv}CH$		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 30°, 3 h		+ 	163, 78
R^1	R^2				
Et	OEt		(13)	(5)	
n-Pr	Me		(29)	(28)	
n-Pr	OEt		(31)	(13)	
n-Bu	Me		(32)	(30)	
n-Bu	OEt		(30)	(14)	
C_7					
		"			78
	R = Me		(37)		
	R = OEt		(40)		

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS

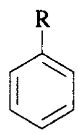
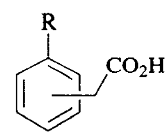
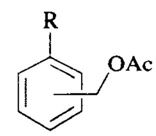
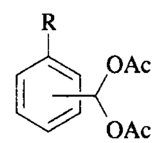
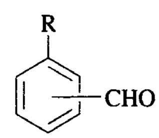
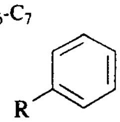
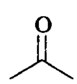
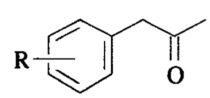
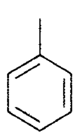
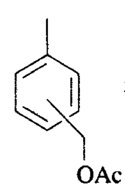
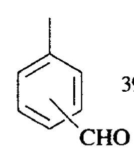
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	AcOH	$Mn(OAc)_3$, AcOH, 24 h	 I +  II +  III +  IV	27
			I / II / III / IV	
R = H		101°	(8) / (51) / (9) / (18)	
R = Cl		110°	(13) 40[a] / (21) 46[a] / (17) 30[a] / (11) 39[a]	
C_6-C_7 		$Mn(OAc)_3$, AcOH, reflux		34, 35
R = H		1.5 h	(40)	
R = Me		1 h	66 : 20 : 14[b] (51)	
R = OMe		45 min	84 : 3 : 13[b] (74)	
R = Cl		—	72 : 6 : 22[b] (25)	
R = F		105 min	71 : 10 : 19[b] (29)	
C_7 	AcOH	$Mn(OAc)_3$, AcOH, 110°, 24 h	 58 : 23 : 19[b] (67) +  39[a] (7)	27

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

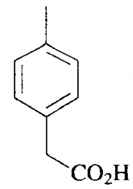
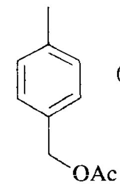
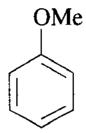
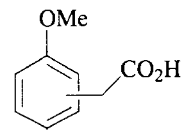
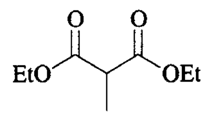
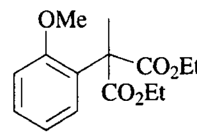
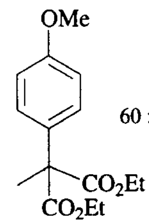
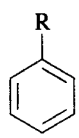
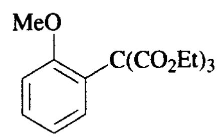
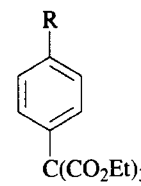
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	AcOH	$Mn(OAc)_3$, AcOH	 (—) +  (—)	33
	AcOH	$Mn(OAc)_3$, AcOH	 78 : 5 : 17[b] (75)	33
		$Mn(OAc)_3$, AcOH, 80°, 4 h	 +  60 : 40 (15)	165
	$HC(CO_2Et)_3$	$Mn(OAc)_3$ NaOAc, AcOH 60 - 65°, 2 d	 + 	37
C_7 R = OMe			(8) (12)	
C_8 R = NHCOMe			(0) (31)	

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

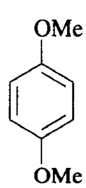
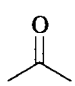
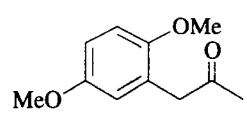
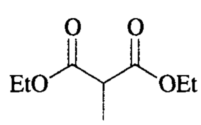
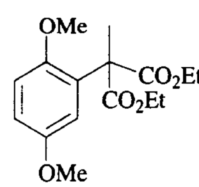
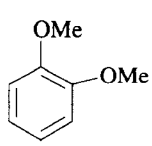
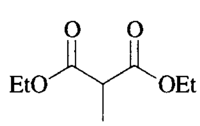
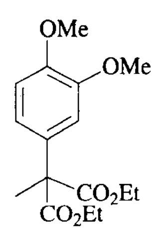
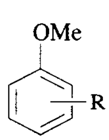
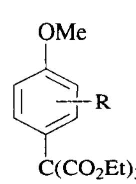
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		$Mn(OAc)_3$, AcOH, reflux, 40 min	 (39)	35
		$Mn(OAc)_3$, AcOH, 80°, 4 h	 (12)	165
		$Mn(OAc)_3$, AcOH, 80°, 4 h	 (20)	165
	$HC(CO_2Et)_3$	$Mn(OAc)_3$ NaOAc, AcOH 60 - 65°, 2d		37
R = 2-OMe			(35)	
R = 3-OMe			(28)	

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

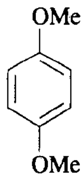
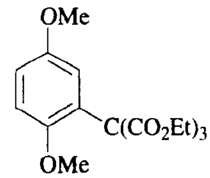
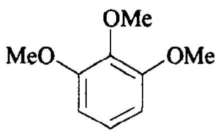
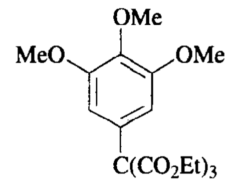
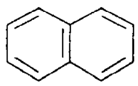
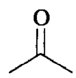
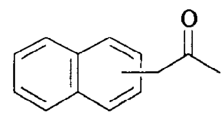
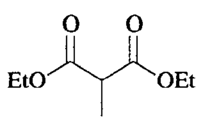
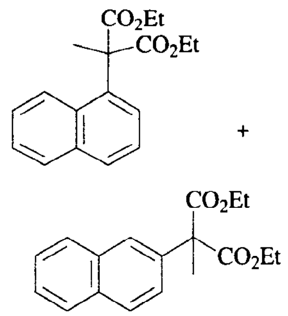
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	$HC(CO_2Et)_3$	$Mn(OAc)_3$ NaOAc, AcOH 60 - 65°, 2d	 (36)	37
C_9 	$HC(CO_2Et)_3$	$Mn(OAc)_3$ NaOAc, AcOH 60 - 65°, 2d	 (35)	37
C_{10} 		$Mn(OAc)_3$, AcOH, reflux, 25 min	 α : β 92 : 8 (77)	35
		$Mn(OAc)_3$, AcOH, 80°, 4 h	 91 : 9 (19)	165

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

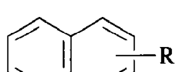
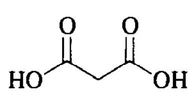
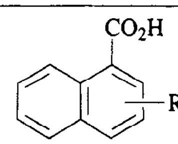
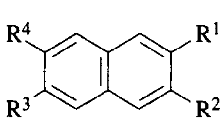
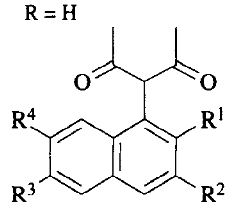
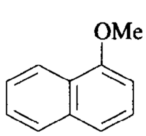
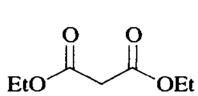
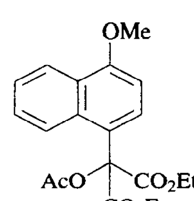
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}-C_{12}  R = 2,3-(MeO)$_2$; R = 1-Me; R = 2-Me; R = 1,8-Me$_2$; R = H		$Mn(OAc)_3$, AcOH reflux, 1 min	 R = 6,7-(MeO)$_2$; R = 4-Me; R = 2-Me; R = 4,5-Me$_2$; R = H	39
	$Mn(acac)_3$	$Mn(OAc)_3$, AcOH, 100°, 2-25 min		40
R^1 / R^2 / R^3 / R^4: MeO / H / H / H			(54)	
MeO / H / H / MeO			(52)	
MeO / H / MeO / H			(46)	
MeO / MeO / H / H			(41)	
H / H / H / H			(8)	
C_{11} 		$Mn(OAc)_3$, AcOH, 80°, 2 h	 (40)	38

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

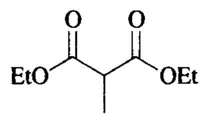
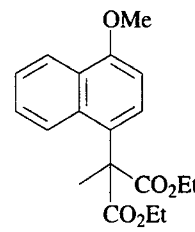
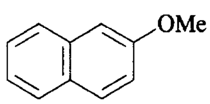
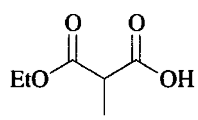
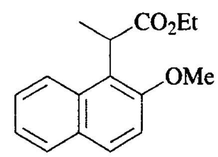
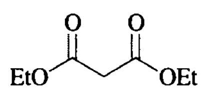
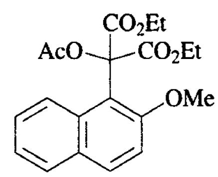
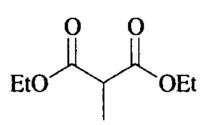
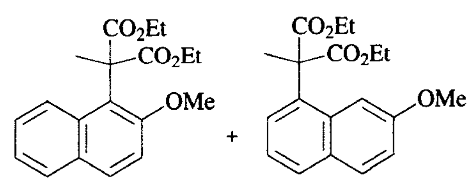
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, 80°, 3 h		(51)	38, 165
		$Mn(OAc)_3$, AcOH, 80°, 9 h		(35)	165
		$Mn(OAc)_3$, AcOH, 80°, 2 h		(12)	38
		$Mn(OAc)_3$, AcOH, 80°, 4 h	 83 : 13 (52)		165

TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

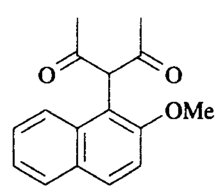
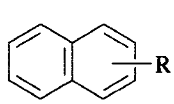
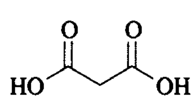
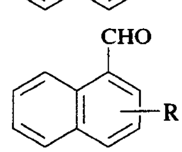
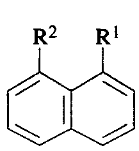
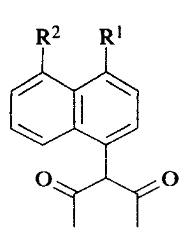
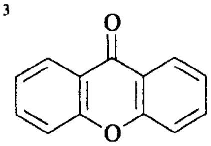
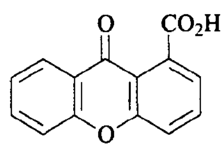
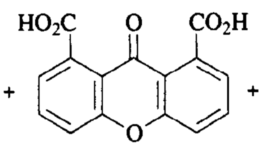
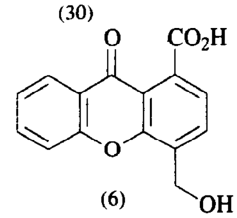
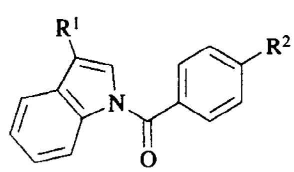
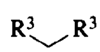
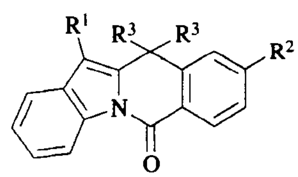
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Mn(acac)_3$	$Mn(acac)_3$, AcOH, 80°, 2.5 h		(48)	38
C_{11}-C_{12} 		$Mn(OAc)_3$, AcOH reflux, 1 min			39
R = 2,7-$(MeO)_2$			R = 2,7-$(MeO)_2$	(55)	
R = 1-MeO			R = 4-MeO	(46)	
R = 2-MeO			R = 2-MeO	(33)	
R = 1,5-$(MeO)_2$			R = 4,8-$(MeO)_2$	(58)	
R = 1,3-$(MeO)_2$			R = 2,4-$(MeO)_2$	(53)	
R = 2,6-$(MeO)_2$			R = 2,6-$(MeO)_2$	(34)	
R = 1,7-$(MeO)_2$			R = 4,6-$(MeO)_2$	(26)	
			R = 2,8-$(MeO)_2$	(22)	
	$Mn(acac)_3$	$Mn(OAc)_3$, AcOH, 100°, 2-25 min			40
R^1 / R^2					
MeO / H				(9)[c]	
Me / Me				(30)	
$(CH_2)_2$				(24)	
Me / H				(15)	

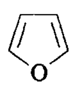
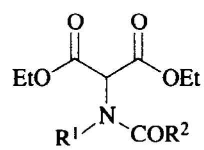
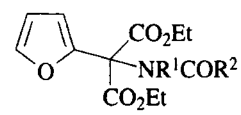
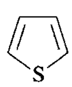
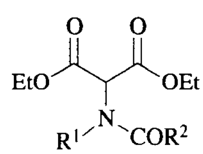
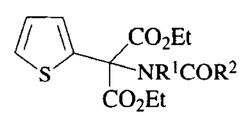
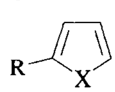
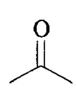
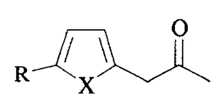
TABLE XXIA. ARENES AND CARBONYL COMPOUNDS (*Continued*)

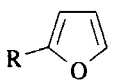
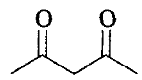
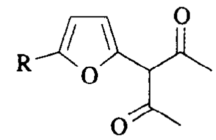
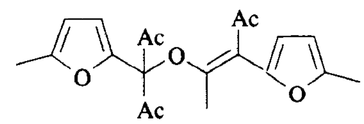
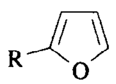
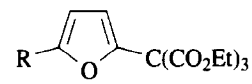
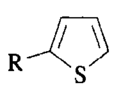
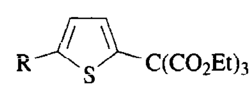
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, reflux, 40 min	 (30) +  (12) +  (6)	220
C_{16}-C_{23} 	 $R^3 = CO_2Me$	$Mn(OAc)_3$, AcOH, 80°, 24 h		221

R^1	R^2		R^1	R^2	
CO_2Me	H	(83)	CN	OMe	(62)
CO_2Me	H	(74)	COMe	H	(48)
CO_2Me	Ph	(81)	COMe	Me	(52)
CN	H	(59)	COMe	Ph	(42)
CN	Me	(57)			

[a] Content (%) of *ortho* isomer.
[b] Ratio of *o* : *m* : *p* isomers.
[c] An α-overoxidation product was also formed (40%).

TABLE XXIB. HETEROCYCLES AND CARBONYL COMPOUNDS

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		$Mn(OAc)_3$, 65°, 12 h		107
	R¹ / R²			
	H / Me		(70)	
	H / H		(74)	
	Me / Ph		(64)	
	C_6H_4CO		(82)	
		$Mn(OAc)_3$, 65°, 12 h		107
	R¹ / R²			
	H / Me		(60)	
	C_6H_4CO		(85)	
C_4-C_5				
		$Mn(OAc)_3$, AcOH, 70 - 80°		166
R / X				
H / O			(35)	
Me / O			(50)	
H / S			(40)	

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, 80°, 1 h	 I +  II	166
			I / II	
R = H			(5) / (0)	
R = Me			(14) / (15)	
	$HC(CO_2Et)_3$	$Mn(OAc)_3$, AcOH, AcONa, 60 - 65°, 1 d		37
C_4 R = H			(92)	
C_6 R = COMe			(48)	
	$HC(CO_2Et)_3$	$Mn(OAc)_3$, AcOH, AcONa, 60 - 65°, 1 d		37
C_4 R = H			(55)	
C_6 R = COMe			(53)	

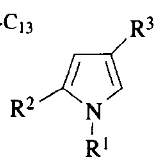
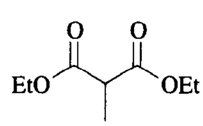
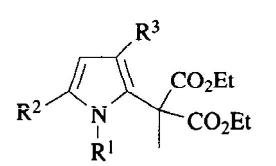
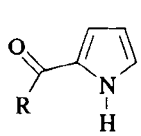
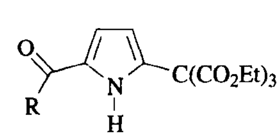
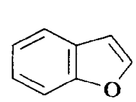
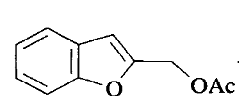
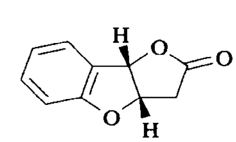
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5-C_{13} 		$Mn(OAc)_3$, AcOH, AcONa, 70°, 4 - 6 h		167
R^1 / R^2 / R^3				
H / CHO / H			(80)	
Me / CO_2Me / H			(60)	
Me / COMe / H			(64)	
Me / 4-MeC_6H_4CO / H			(70)	
H / PhCO / H			(83)	
Me / H / COMe			(19)	
H / H / CO_2Me			(24)	
	$HC(CO_2Et)_3$	$Mn(OAc)_3$, AcOH, AcONa, 60 - 65°, 1 d		37
C_6 R = Me			(61)	
C_{11} R = Ph			(86)	
C_8 	AcOH	$Mn(OAc)_3$, AcOH, Ac_2O, reflux	 (42) +  (21)	132

TABLE XXIB. HETEROCYCLES AND CARBONYL COMPOUNDS (*Continued*)

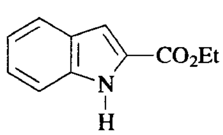
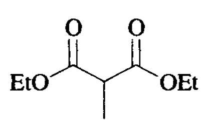
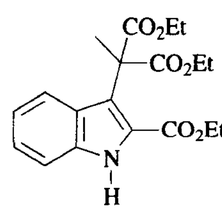
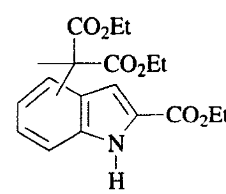
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		$Mn(OAc)_3$, AcOH, AcONa 70°, 4-6 h	 (64) +  (8)	167

TABLE XXII. NITROALKYLATION REACTIONS

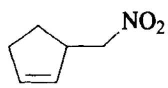
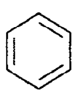
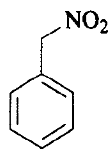
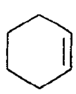
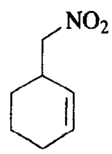
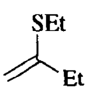
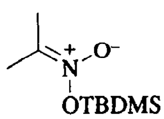
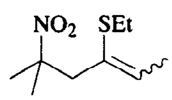
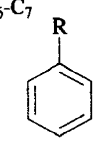
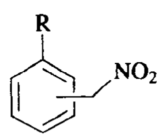
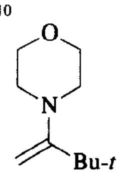
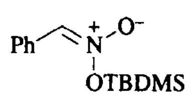
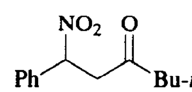
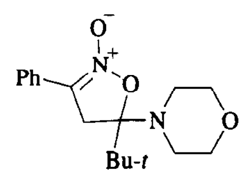
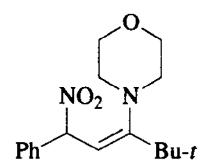
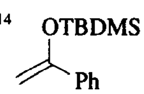
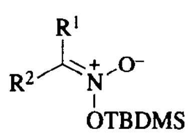
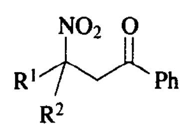
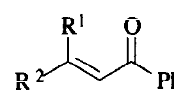
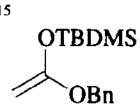
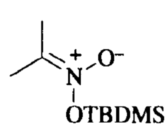
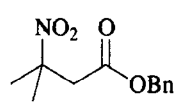
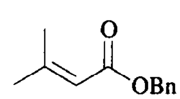
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_5 	CH_3NO_2	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, reflux, 1-4 h		(11)	79
C_6 	CH_3NO_2	$Mn(OAc)_2$, Pt anode, AcOH, $LiBF_4$, 83°, 3 h		(73)	169
	CH_3NO_2	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, reflux, 1-4 h		(38)	79
		$Mn(pic)_3$, DMF, rt		(30)	118
C_6-C_7 	CH_3NO_2				
R = H		$Mn(OAc)_3$, AcOH, 83°	(78)		36
R = Me			(66)[a]		
R = OMe			(77)[a]		
R = Cl			(20)[a]		
R = H		$Mn(OAc)_3$, AcOH, reflux	(14)		168
R = Me			(55)		

TABLE XXII. NITROALKYLATION REACTIONS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10} 		Mn(pic)$_3$, DMF, rt	 (46) +  (19) +  (7)		118
C_{14} 		Mn(pic)$_3$, DMF, rt, 24 h	 +		118
	R^1 R^2				
	Me Me		(74)	(11)	
	Me H		(0)	(69)	
	Ph Me		(30)	(0)	
	Ph H		(0)	(70)	
C_{15} 		Mn(pic)$_3$, DMF, rt	 (46) +	 (12)	118

[a] The product was a mixture of *o* (60 - 70 %) and *m* and *p* (30 - 40 %) isomers.

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES

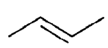
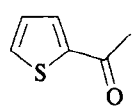
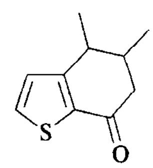
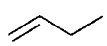
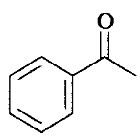
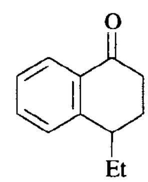
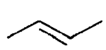
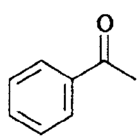
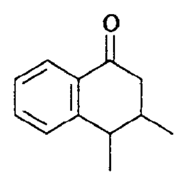
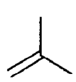
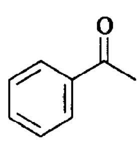
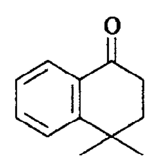
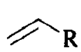
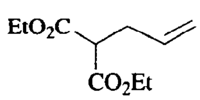
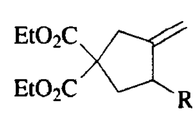
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		$Mn(OAc)_3$, AcOH, 85°	 (43)	170
		$Mn(OAc)_3$, AcOH, 85°	 (49)	170
		$Mn(OAc)_3$, AcOH, 85°	 (40)	170
		$Mn(OAc)_3$, AcOH, 85°	 (43)	170
C_4-C_6 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 75°, 24 h		80
R = OAc			(40)	
R = *n*-Bu			(35)	
R = CH_2TMS			(89)	

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES (*Continued*)

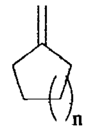
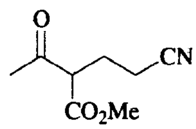
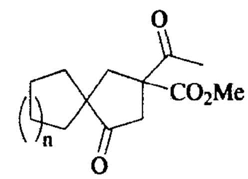
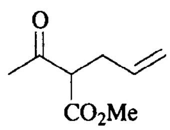
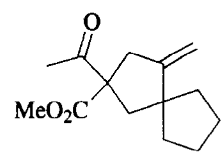
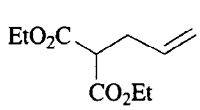
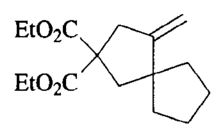
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 				
n = 0		$Mn(OAc)_3$, EtOH, TFA, 25°, 18 h	(30)	171
n = 0		$Mn(OAc)_3$, $Mn(OAc)_2$, EtOH, TFA, 25°, 28 h	(51)	
n = 1		$Mn(OAc)_3$, EtOH, 25°, 6 h	(39)	
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 16 h	 (75)	80
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 75°, 24 h	 (100)	80

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES (*Continued*)

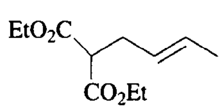
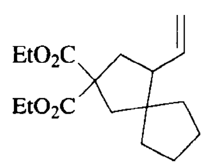
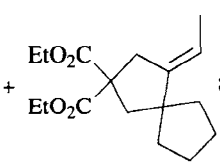
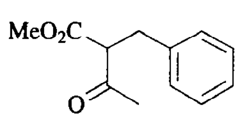
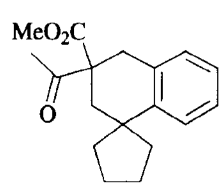
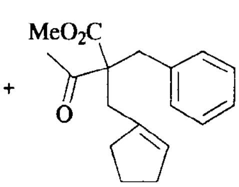
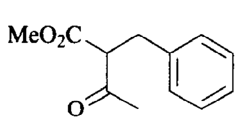
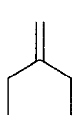
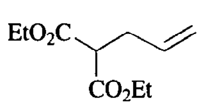
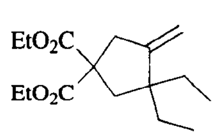
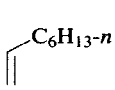
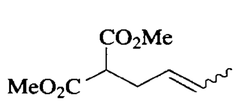
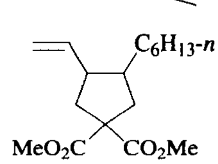
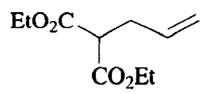
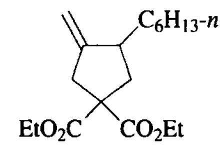
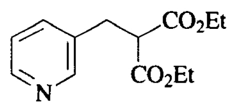
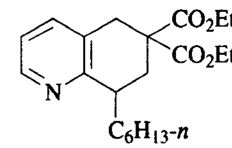
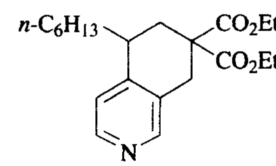
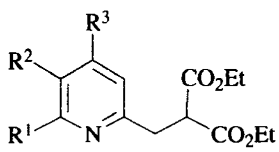
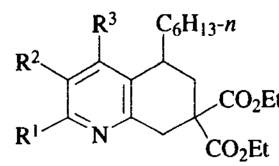
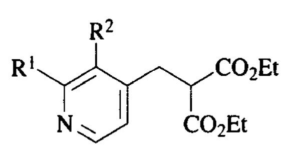
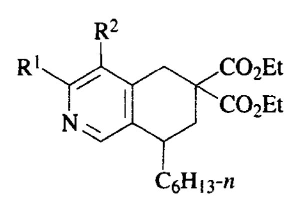
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 70°, 38 h	 +  8:1 (49)	80
		$Mn(OAc)_3$, AcOH, 25°, 1 h	 +  **I** 1.4:1 (77)	80
		$Mn(OAc)_3$, AcOH, 25°, 9 h	**I** (79)	80
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 75°, 24 h	 (86)	80
C_8 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 90°, 6 h	 (81)	81

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES (*Continued*)

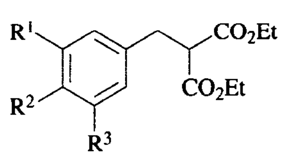
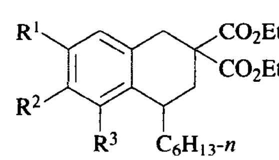
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 90°, 6 h	 (80)	81
		$Mn(OAc)_3$,	 I +  II	172
		AcOH, 70°, 8 h	I + II (95) I:II = 1.4:1	
		MeCN, CF_3CO_2H, 20°, 12 h	I + II (95) I:II = 1.1:1	
		$Mn(OH)_3$, AcOH, 70°, 12 h		172

R^1	R^2	R^3	Yield (%)
H	H	H	(90)
H	Et	H	(89)
Me	H	Me	(61)
CH=CHCH=CH		H	(85)

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OH)_3$, AcOH, 70°, 12 h		172

R^1	R^2	Yield (%)
H	H	(83)
CH=CHCH=CH		(88)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH 60°, 12 h		173

R^1	R^2	R^3	Yield (%)
H	H	H	(90)
H	Cl	H	(86)
H	F	H	(85)
H	CO_2Me	H	(85)
F	H	H	(89)
MeO	H	H	(83)
NO_2	H	H	(80)
Me	H	H	(85)

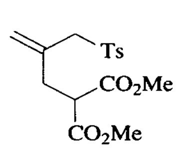
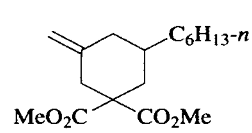
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 90°, 6 h	 (35)	81

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES (*Continued*)

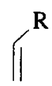
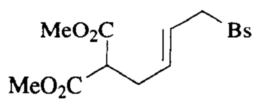
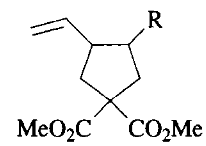
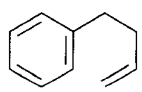
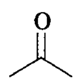
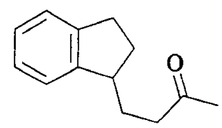
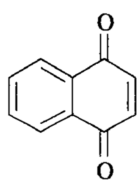
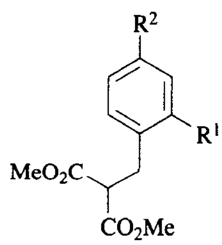
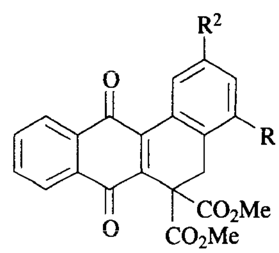
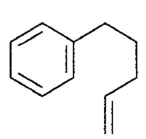
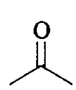
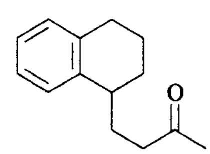
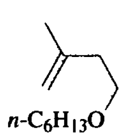
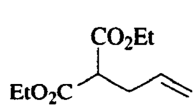
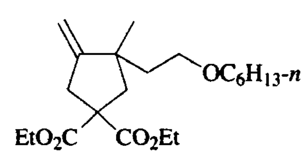
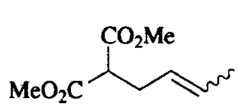
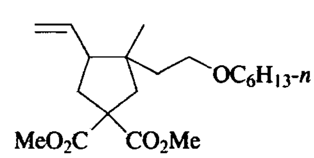
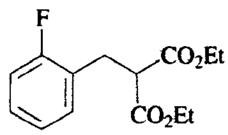
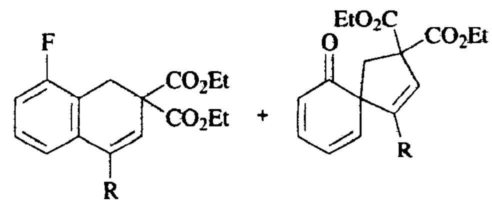
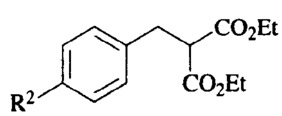
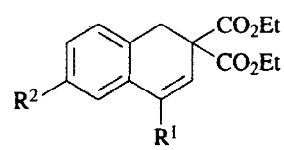
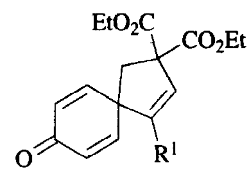
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 90°, 6 h		81
C_8 R = n-C_6H_{13}			(62)	
C_9 R = CH_2Ts			(77)	
C_{10} 		$Mn(OAc)_3$, AcOH	 (—)	170
		$Mn(OAc)_3$, AcOH, 80°, 8 h		177
	R^1 R^2			
	H H		(59)[a]	
	H Me		(51)	
	H OMe		(58)	
	H Br		(51)	
	Me Me		(35)	
	Me H		(32)	

TABLE XXIIIA. ADDITION-CYCLIZATION REACTIONS - ALKENES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		$Mn(OAc)_3$, AcOH	 (70)	170
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 90°, 6 h	 (60)	81
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 90°, 6 h	 (60)	81

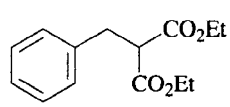
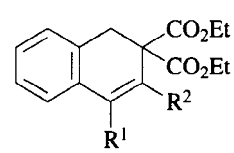
[a] Analogous results were obtained with 1,4-dihydroquinones as substrates.

TABLE XXIIIB. ADDITION-CYCLIZATION REACTIONS - ALKYNES

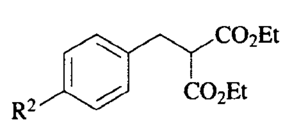
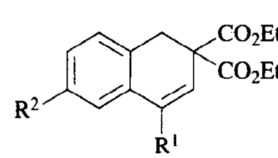
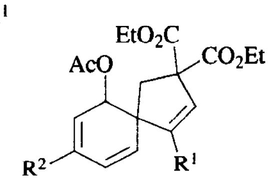
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
RC≡CH		$Mn(OAc)_3$, AcOH		174
C_3 R = CH_2OH			(12) (65)	
C_8 R = n-C_6H_{13}			(6) (77)	
C_3-C_8 $R^1C≡CH$		$Mn(OAc)_3$, AcOH	 I +  II	174

R^1	R^2	I	II
n-C_6H_{13}	OMe	(10)	(79)
CH_2OH	OMe	(13)	(48)
n-C_6H_{13}	F	(28)	(66)
TMS	F	(32)	(62)
Ph	F	(13)	(69)
Ph	i-Pr	(85)	(0)
Ph	H	(92)	(0)

TABLE XXIIIB. ADDITION-CYCLIZATION REACTIONS - ALKYNES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3-C_{14} $R^1C≡CR^2$		$Mn(OAc)_3$, AcOH, 70°, 6-24 h		30

R^1	R^2	Yield
n-C_6H_{13}	H	(92)
CO_2Et	H	(50)
TMS	H	(91)
Ph	H	(95)
CH_2OH	H	(70)
Ph	Ph	(67)
Et	Et	(19)
CO_2Et	CO_2Et	(20)
CO_2Me	Me	(12)
n-Pr	n-Pr	(23)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5-C_8 $R^1C≡CH$		$Mn(OAc)_3$, AcOH	 I +  II	174

R^1	R^2	I	II
n-C_6H_{13}	CF_3	(65)	(12)
TMS	CF_3	(41)	(6)
Ph	CF_3	(63)	(18)
Ph	CO_2Me	(60)	(31)

TABLE XXIIIB. ADDITION-CYCLIZATION REACTIONS - ALKYNES (*Continued*)

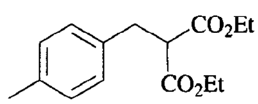
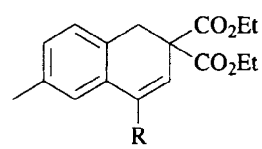
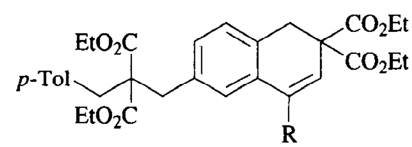
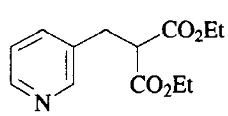
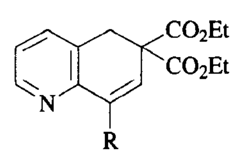
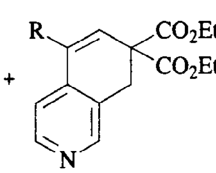
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
RC≡CH		$Mn(OAc)_3$, AcOH	 I +  II	174
R			I II	
TMS			(37) (52)	
Ph			(23) (67)	
n-C_6H_{13}			(41) (55)	
C_8				
HC≡CR		$Mn(OAc)_3$, AcOH, 60°, 12 h	 + 	172
R				
n-C_6H_{13}			1.8 : 1 (80)	
Ph			1.9 : 1 (74)	

TABLE XXIIIC. ADDITION-CYCLIZATION REACTIONS - ALKADIENES

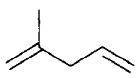
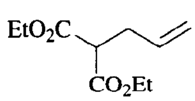
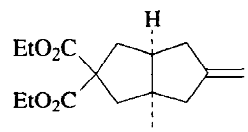
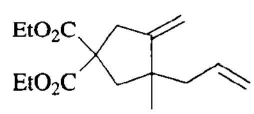
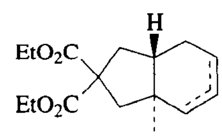
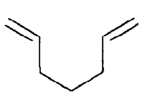
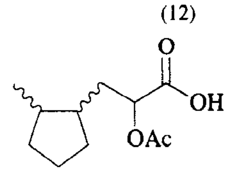
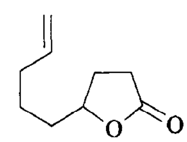
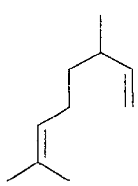
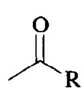
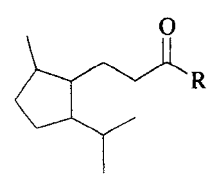
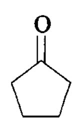
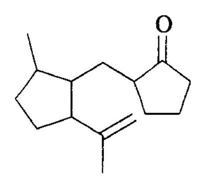
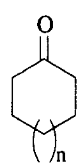
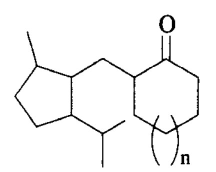
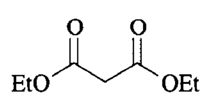
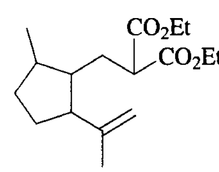
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 75°, 24 h	 (12) +  (12) +  (7)	80
C_7 	AcOH	$Mn(OAc)_3$, AcOH, AcOK, reflux	 (48) +  (13)	117
C_{10} 		$Mn(OAc)_3$		82
	R = Me	reflux, 24 h	(—)	
	R = Ph	dioxane, 12 h	(—)	

TABLE XXIIIC. ADDITION-CYCLIZATION REACTIONS - ALKADIENES (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 110°, 15 min	 (—)	82
		$Mn(OAc)_3$, dioxane		82
	n = 0	110°, 30 h,	(—)[a]	
	n = 1	12 h	(57)[a]	
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, reflux, 10 min	 (—)	82

[a] An α,β-unsaturated enone was also formed.

TABLE XXIV. INTRAMOLECULAR CYCLIZATIONS OF 2-SUBSTITUTED 3-KETOESTERS

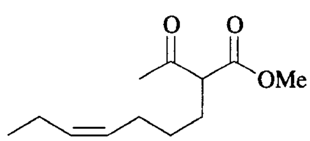
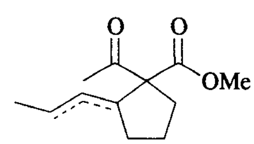
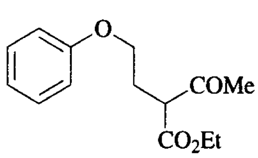
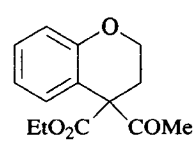
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 50°, 1 h	 (67)	83
C_{14}		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 3-4 h	 (92)	181

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE)

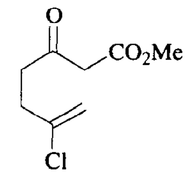
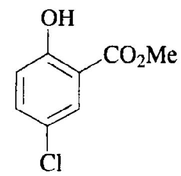
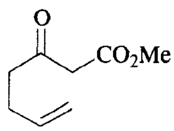
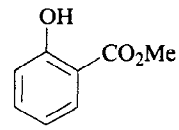
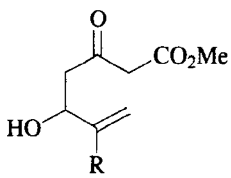
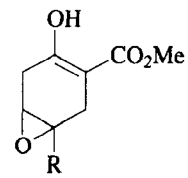
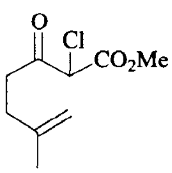
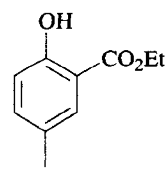
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (10)	84
				
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, 50°, 50 min	(94)	89
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	(78)	84, 90
		$Mn(OAc)_3$, AcOH, 25°, 3h		84
C_8	R = H		(30)	
C_9	R = Me		(50)	
C_9		1. $Mn(OAc)_3$, $Cu(OAc)_2$, AcOH 2. AcOH, TFA, 120°, 10 h	 (71)	84

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

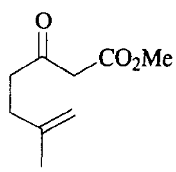
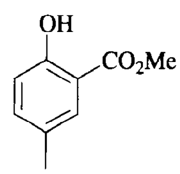
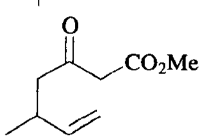
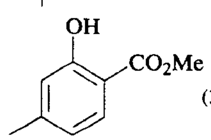
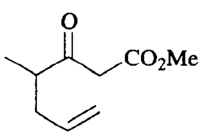
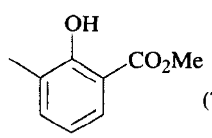
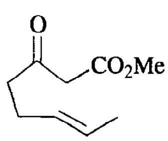
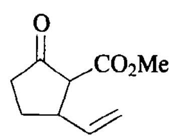
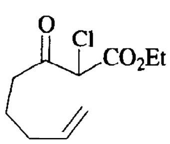
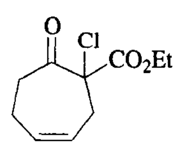
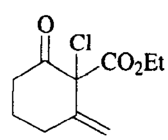
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $Mn(OAc)_3$, LiCl, AcOH 2. AcOH, LiCl, 100°, 24 h	 (70)	84
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (38)	84
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (78)	84
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 1 h	 (21)	85
C_{10}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°	 (50) +  (18)	88

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

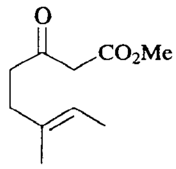
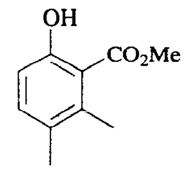
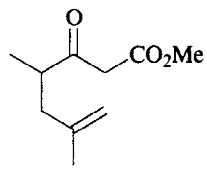
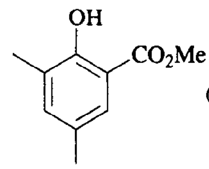
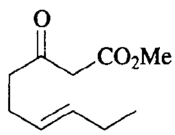
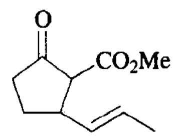
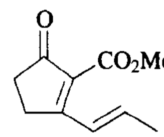
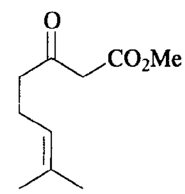
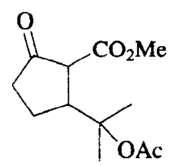
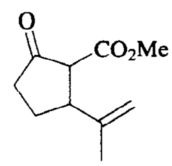
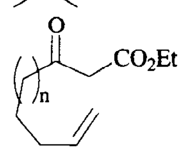
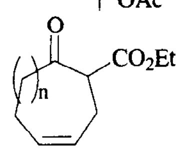
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $Mn(OAc)_3$, LiCl, AcOH 2. AcOH, LiCl, 100°, 24 h	 (40)	84
	1. $Mn(OAc)_3$, LiCl, AcOH 2. AcOH, LiCl, 100°, 24 h	 (91)	84
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 1 h	 (36) +  (10)	85
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 1 h	 (10) +  (8)	85
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 44 h		88
C_{10} n = 1		(13)	
C_{11} n = 2		(17)	

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

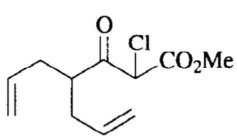
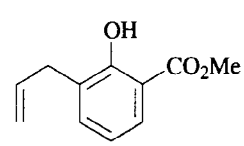
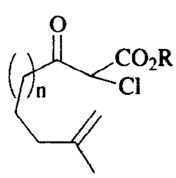
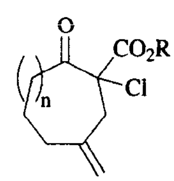
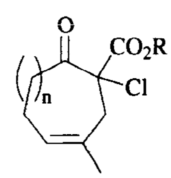
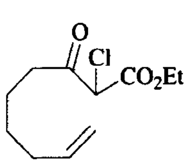
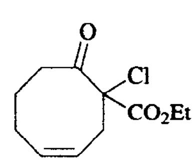
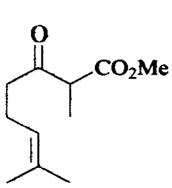
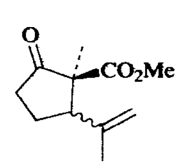
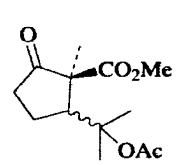
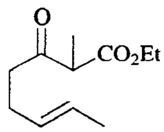
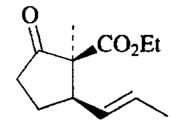
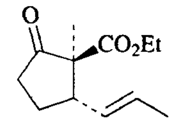
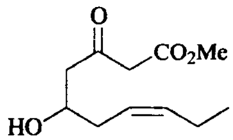
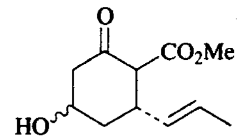
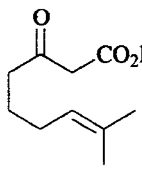
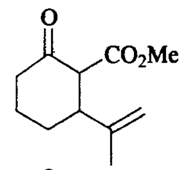
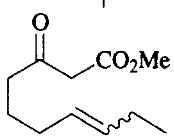
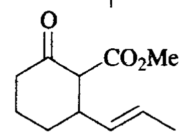
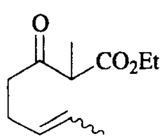
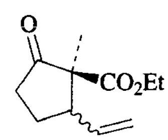
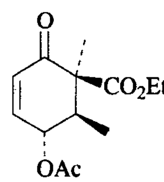
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 30 h	 (24)	86
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°	 + 	87
n R			
1 Et		(49) (20)	
2 Me		(20) (49)	
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°	 (47)	88
	$Mn(OAc)_3$, $Cu(OAc)_2$ AcOH, 60°, 1 h	 + 	85
		β : α 3 : 2 (27) β : α 3 : 2 (20)	

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (29) +  (11)	90
	Mn($OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 1 h	 α-OH (41) β-OH (9)	85
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 60°, 1 h	 (41)	85
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH		83
Z	50°, 1 h	(71)	
E	25°, 26 h	(64)	
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 4 d	 β : α 2.5 : 1 (39) +  (7)	83

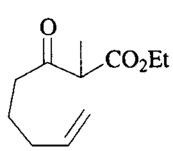
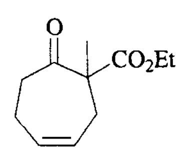
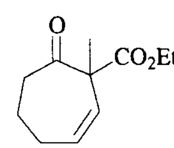
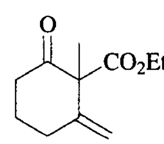
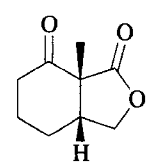
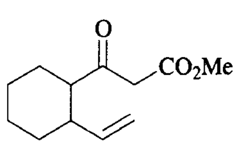
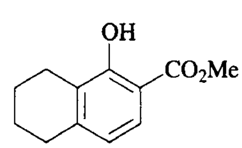
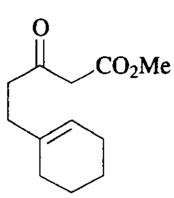
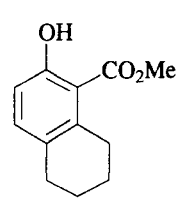
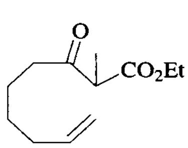
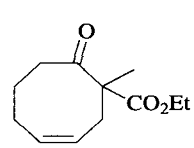
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°	 +  +  3 : 1 : 1 (46) +  (5)	88, 87
C_{12}			
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (46)	80
	1. $Mn(OAc)_3$, LiCl, AcOH 2. AcOH, LiCl, 100°, 24 h	 (37)	80
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°	 (38)	88

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

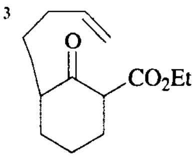
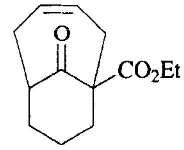
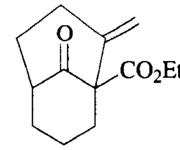
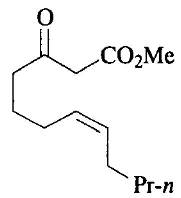
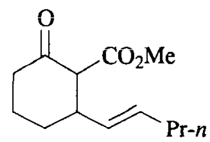
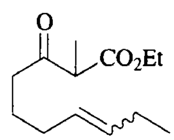
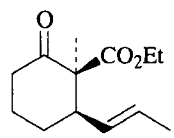
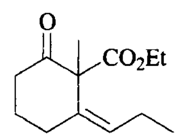
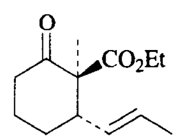
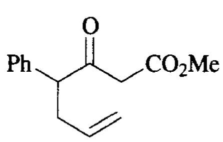
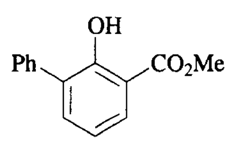
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 50°, 18 h	 (18) +  (18)	83
	$Mn(OAc)_3$, $Cu(OAc)_2$ AcOH, 60°, 1 h	 (75)	85
	$Mn(OAc)_3$, $Cu(OAc)_2$ AcOH, rt, 17 h	 I +  II +  III	83
		I / II / III	
Z		(56) (14) (3)	
E		(43) (10) (10)	
C_{14}			
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (20)	84

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

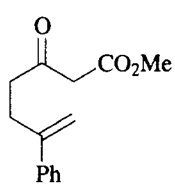
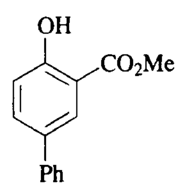
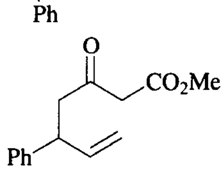
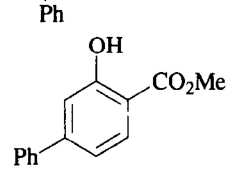
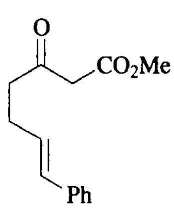
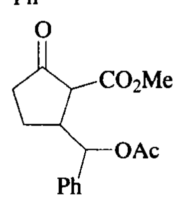
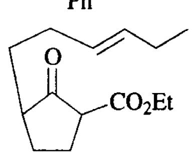
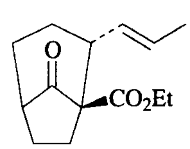
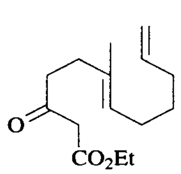
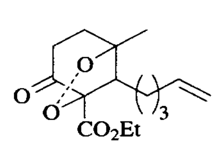
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $Mn(OAc)_3$, LiCl, AcOH 2. AcOH, LiCl, 100°, 24 h	 (44)	84
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (11)	84
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, 50°, 50 min	 (70)	89
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 24 h	 (78)	83
C_{15}			
	$Mn(OAc)_3$, O_2, AcOH, rt, 18 h	 (25)	56

TABLE XXVA. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (D-MODE) (*Continued*)

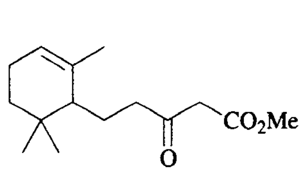
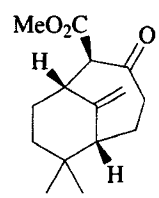
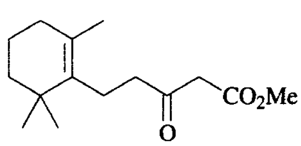
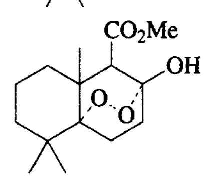
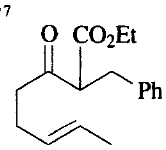
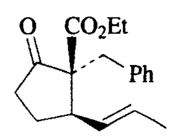
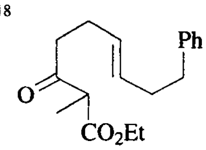
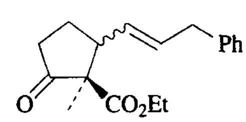
Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Mn(OAc)_3$, AcOH, 58°, 15 min		(60)	180
	$Mn(OAc)_3$, AcOH, rt, 24 h		(30)	180
C_{17} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH		(50)	90
C_{18} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 50°		α : β 3 :1 (64)	91

TABLE XXVB. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (T-MODE)

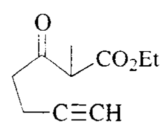
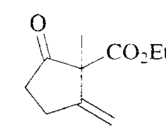
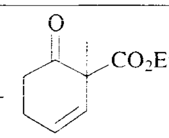
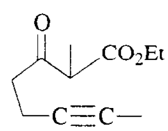
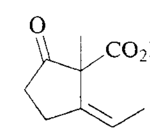
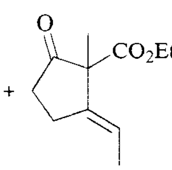
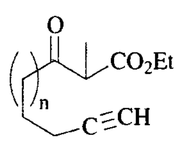
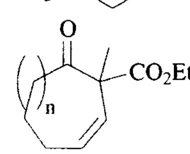
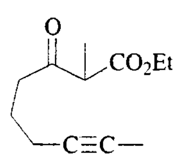
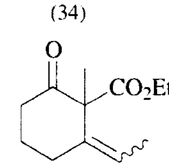
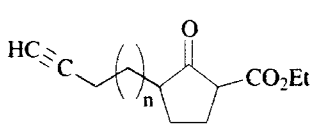
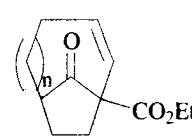
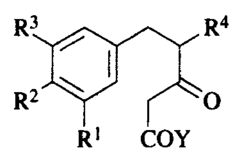
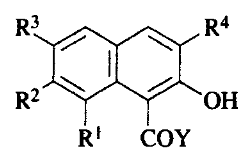
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$Mn(OAc)_3$, EtOH, 25°, 21 h	 (20) +  (12)	99
C_{11} 	$Mn(OAc)_3$, EtOH, 25°, 4.5 h	 (18) +  (48)	99
	$Mn(OAc)_3$ -anhydr., EtOH		87
C_{11} n = 1		(35)	
C_{12} n = 2		(34)	
C_{12} 	$Mn(OAc)_3$ -anhydr., EtOH	 E : Z 2.5 : 1 (59)	87
	$Mn(OAc)_3$ -anhydr., EtOH		87
C_{12} n = 1		(6)	
C_{13} n = 2		(13)	

TABLE XXVC. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 3-KETOESTERS (B-MODE)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}-C_{14}			
	1. $Mn(OAc)_3$, AcOH, 40°- 70° 2. SiO_2, C_6H_6, reflux		182

R^1	R^2	R^3	R^4	Y	Product(s) and Yield(s) (%)
H	H	H	H	OEt	(24)
H	H	H	Me	OEt	(30)
H	F	H	Me	OMe	(10)
OMe	H	H	Me	OMe	(41)
H	H	OMe	Me	OMe	(36)

TABLE XXVI. INTRAMOLECULAR CYCLIZATIONS OF *O*-SUBSTITUTED 3-KETOESTERS

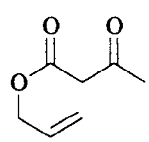
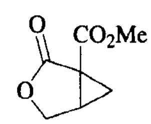
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, 75°	 (57)	92

TABLE XXVII. INTRAMOLECULAR CYCLIZATIONS OF 4-SUBSTITUTED 1,3-DIKETONES

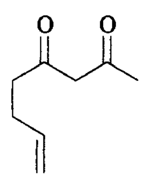
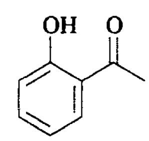
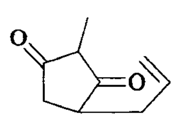
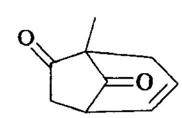
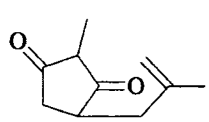
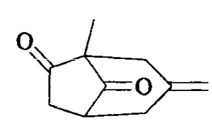
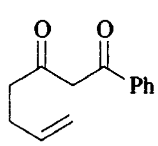
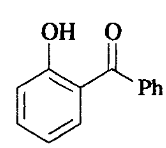
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, 50°, 50 min		(96)	89
C_9		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 18 h		(38)	83
C_{10}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 18 h		(48)	83
C_{13}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH		(47)	84

TABLE XXVIII. INTRAMOLECULAR CYCLIZATIONS OF 2-SUBSTITUTED 1,3-DIKETONES

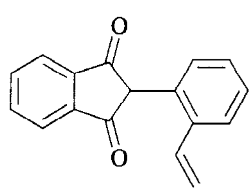
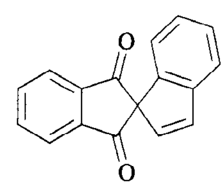
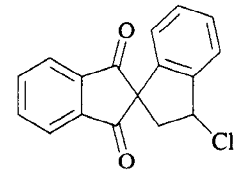
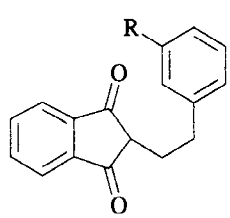
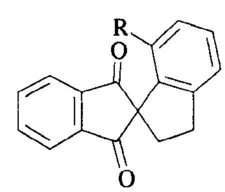
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 30 min		(72)	93
		$Mn(OAc)_3$, $Cu(OAc)_2$, $CHCl_3$, rt, 30 min		(68)	93
		$Mn(OAc)_3$, AcOH, 95-100°, 2 h			29
C_{18}	R = OMe		(32)		
C_{24}	R = OBn		(25)		

TABLE XXIX. INTRAMOLECULAR CYCLIZATIONS OF *O*-SUBSTITUTED MALONIC ESTERS

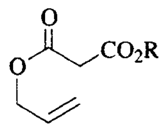
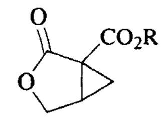
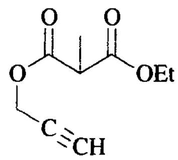
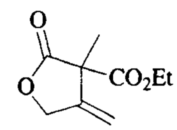
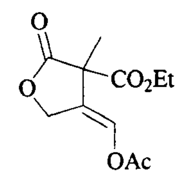
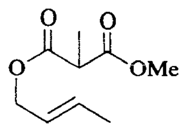
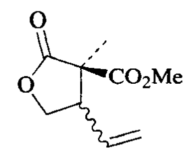
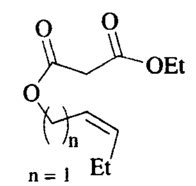
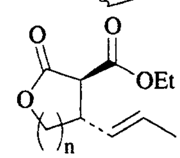
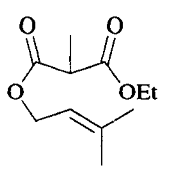
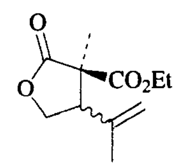
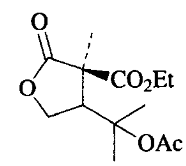
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, reflux		92, 96
C_7	R = Me		(42)	
C_9	R = $CH_2CH=CH_2$		(43)	
C_9		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcONa, reflux	 (38) +  (33)	96
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, reflux	 70 : 30 (54)	92, 96
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 50°, 3.5 h		83
C_{10}	n = 1		(18)	
C_{11}	n = 2		(27)	
C_{11}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcONa, reflux	 (30) +  (17)	96

TABLE XXIX. INTRAMOLECULAR CYCLIZATIONS OF *O*-SUBSTITUTED MALONIC ESTERS (*Continued*)

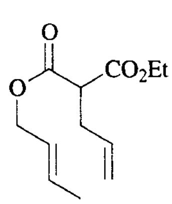
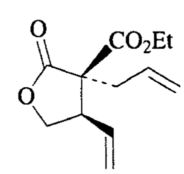
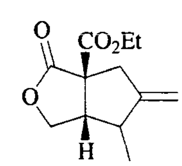
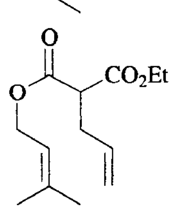
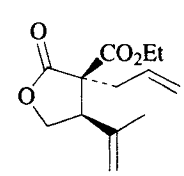
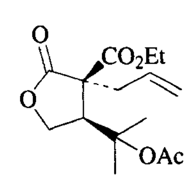
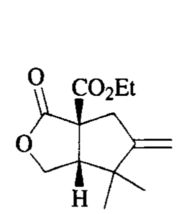
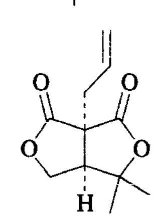
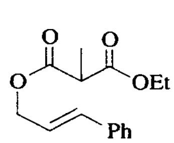
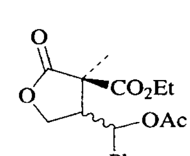
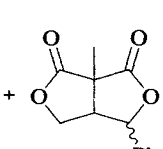
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (43) +  (18)	94
C_{13}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (31) +  (9) +  (26) +  (11)	94
C_{15}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcOK, reflux	 (43) +  (20)	92, 96

TABLE XXIX. INTRAMOLECULAR CYCLIZATIONS OF *O*-SUBSTITUTED MALONIC ESTERS (*Continued*)

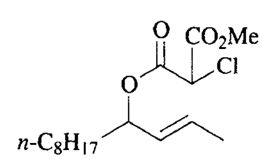
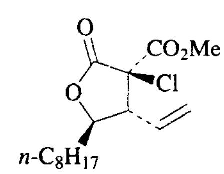
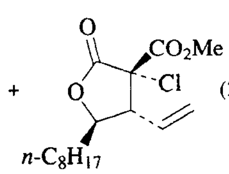
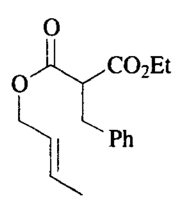
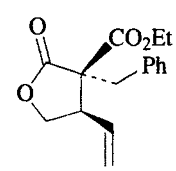
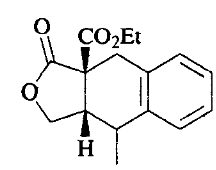
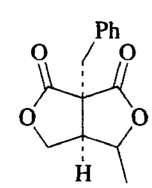
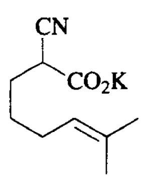
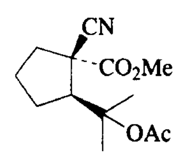
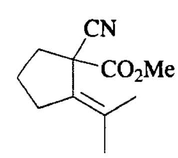
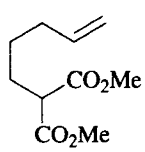
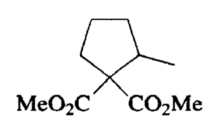
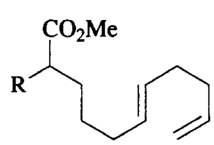
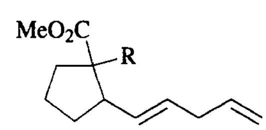
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, 75°, 2.5 h	 (62) +  (20)	95
C_{16} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (56) +  (24) +  (10)	94

TABLE XXXA. INTRAMOLECULAR CYCLIZATIONS OF *C*-SUBSTITUTED MALONIC ESTER DERIVATIVES (D-MODE)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		1. $Mn(OAc)_3$, AcOH, 70° 2. CH_2N_2	 (17)[a] +  (9)	178
		$Mn(OAc)_3$, EtOH, 55°	 (40)	99
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 55°		97
C_{13}	R = CN	2 d	(35)	
C_{14}	R = CO_2Me	3 d	(65)	

[a] A tandem cyclization product was also formed (17%).

TABLE XXXB. INTRAMOLECULAR CYCLIZATIONS OF *C*-SUBSTITUTED MALONIC ESTERS (B-MODE)

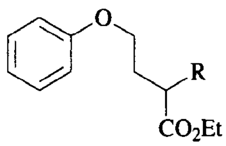
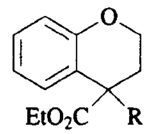
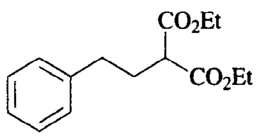
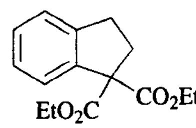
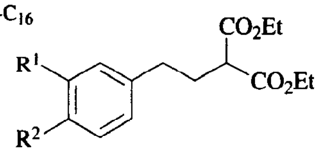
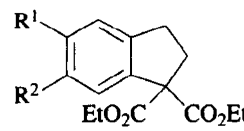
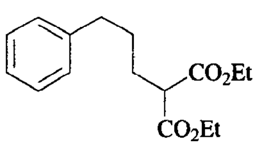
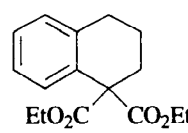
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 3-4 h		181
C_{13}	R = CN		(8)	
C_{15}	R = CO_2Et		(90)	
C_{15}		$Mn(OAc)_3$, AcOH, AcONa, 70°, 8 h	 (39)	181
C_{15}-C_{16}		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 3-24 h		181
	R^1 R^2			
	H H		(39)	
	OMe H		(47)	
	H OMe		(30)	
C_{16}		$Mn(OAc)_3$, AcOH, AcONa, 70°, 3 h	 **I** (85)	181
		$Mn(OAc)_3$ anhydr., AcOH, 60°, 6 h	**I** (89)	222

TABLE XXXB. INTRAMOLECULAR CYCLIZATIONS OF *C*-SUBSTITUTED MALONIC ESTERS (B-MODE) (*Continued*)

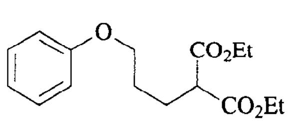
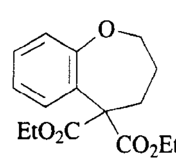
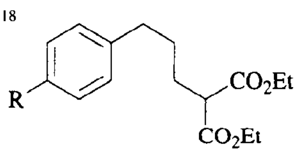
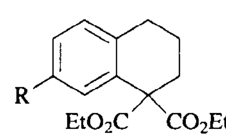
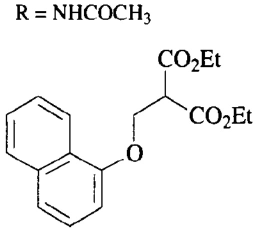
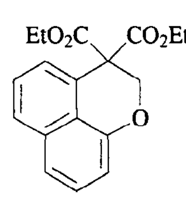
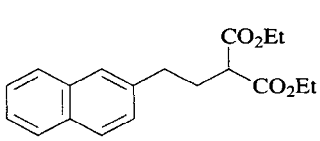
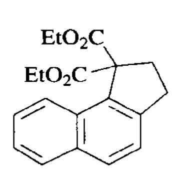
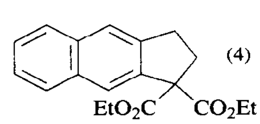
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 7 h	 (15)	181
C_{16}-C_{18}		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 3-10 h		181
	R = NO_2		(85)	
	R = OMe		(80)	
	R = $NHCOCH_3$		(88)	
C_{18}		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 3 h	 (91)	181
		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 4 h	 (90) +  (4)	181

TABLE XXXB. INTRAMOLECULAR CYCLIZATIONS OF *C*-SUBSTITUTED MALONIC ESTERS (B-MODE) (*Continued*)

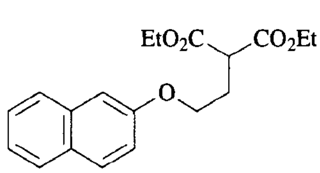
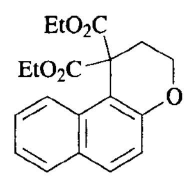
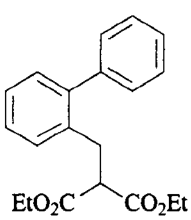
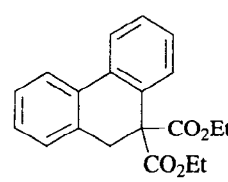
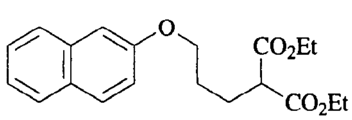
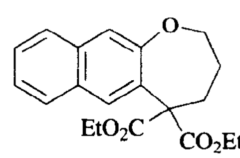
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 3 h		(90)	181
C_{20}		$Mn(OAc)_3$, AcOH, AcONa, 70°, 3 h		(93)	181
		$Mn(OAc)_3$, AcOH, AcONa, 70-80°, 5 h		(70)	181

TABLE XXXI. INTRAMOLECULAR CYCLIZATIONS OF *N*-SUBSTITUTED AMIDES

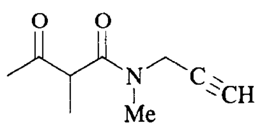
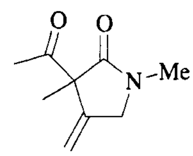
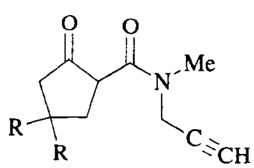
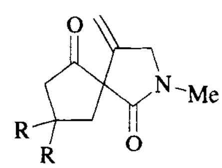
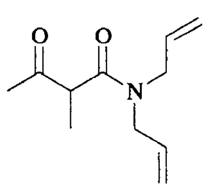
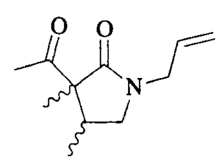
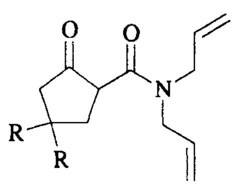
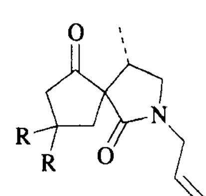
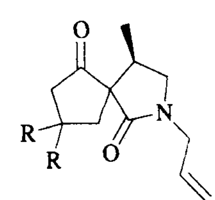
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_9		$Mn(OAc)_3$-anhydr., EtOH, rt, 1 h	 (40)		179
		$Mn(OAc)_3$-anhydr., EtOH, rt, 1 h			179
C_{10}	R = H		(60)		
C_{12}	R = Me		(55)		
C_{11}		$Mn(OAc)_3$-anhydr., EtOH, rt, 1 h	 (40)		179
		$Mn(OAc)_3$-anhydr., EtOH, rt, 1 h	 +		179
C_{12}	R = H		(47)	(3)	
C_{14}	R = Me		(47)	(3)	

TABLE XXXI. INTRAMOLECULAR CYCLIZATIONS OF *N*-SUBSTITUTED AMIDES (*Continued*)

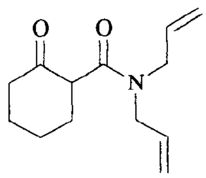
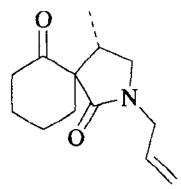
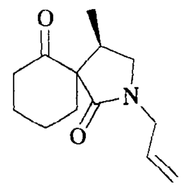
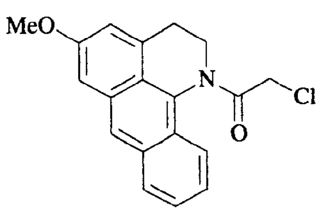
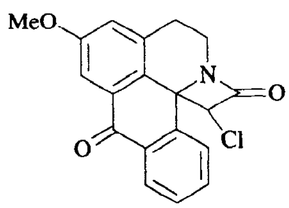
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		$Mn(OAc)_3$-anhydr., EtOH, rt, 1 h	 (30) +  (10)	179
C_{19}		$Mn(OAc)_3$, AcOH, 50°, 5 h	 (21)	223

TABLE XXXII. TANDEM CYCLIZATIONS (DD-MODE)

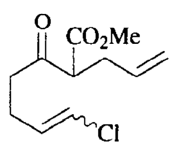
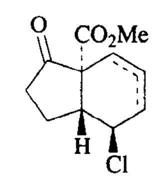
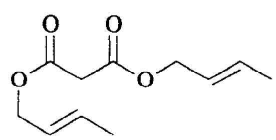
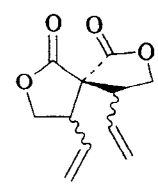
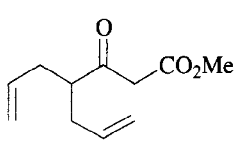
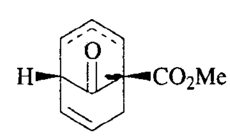
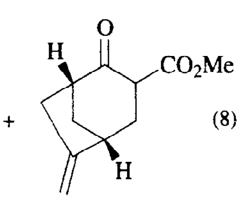
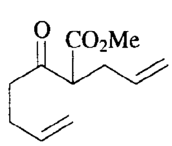
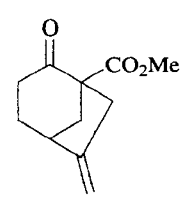
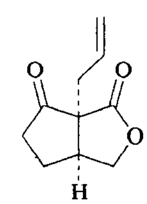
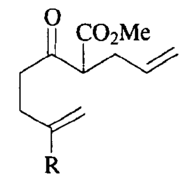
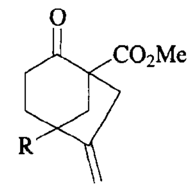
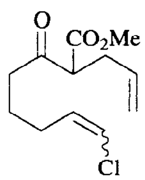
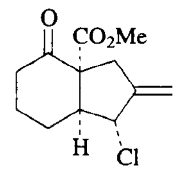
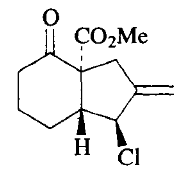
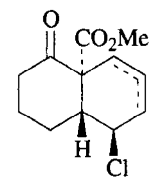
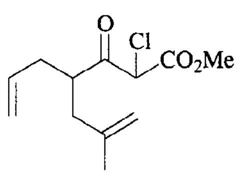
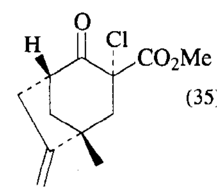
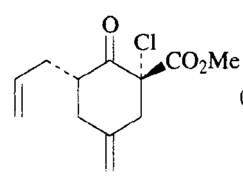
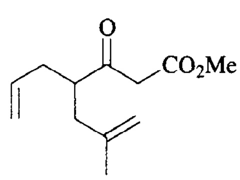
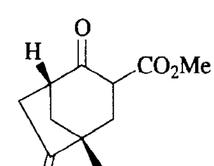
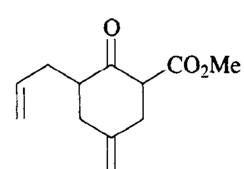
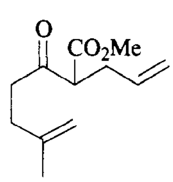
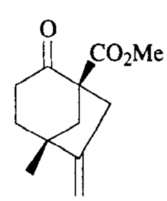
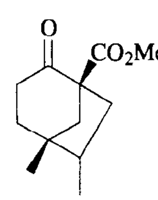
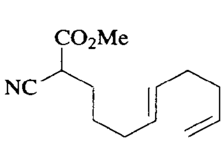
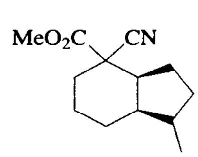
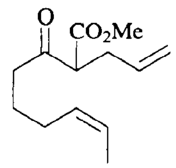
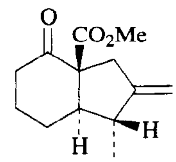
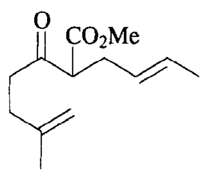
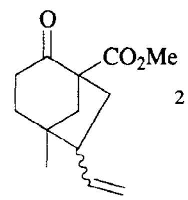
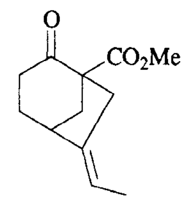
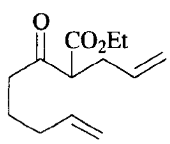
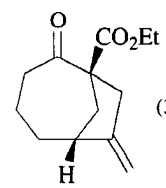
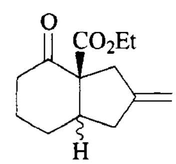
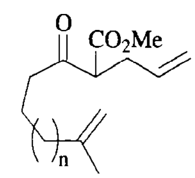
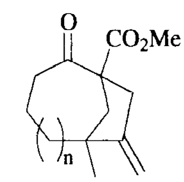
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 20 h	 1 : 1 (53)	103
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcONa, reflux	 38 : 54 : 8[a] (66)	96
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 38 h	 (11) +  (8)	86
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 5 h	 (48) +  (18)	100

TABLE XXXII. TANDEM CYCLIZATIONS (DD-MODE) (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}-C_{15} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 26 h	 R = Cl (72); R = $OPO(OEt)_2$ (77); R = CH_2TMS (30)	101
C_{12} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 12 h	 +  +  2 : 4 : 1 : 1 (66)	103
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 14 h	 (35) +  (33)	86

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 10.5 h	 +  6 : 1 (41)		86
		 +		
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 26 h	(86)	(0)	100, 102
	$Mn(pic)_3$, $Cu(OAc)_2$, AcOH, 25°	(0)	(15)	102
	$Mn(OAc)_3$, $Cu(pic)_2$, AcOH, 25°	(76)	(4)	102
	$Mn(OAc)_3$, AcOH, 25°	(14)	(24)	102
C_{13} 	$Mn(OAc)_3$, EtOH, 55°, 2d	 4 : 1 : 1.1 : 1.2 (35)		97

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 13 h	 (67)	100
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 2 : 1 (65) +  (5)	100
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (32) +  α (8) β (4)	88
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH		87
C_{13} n = 1		(68)	
C_{14} n = 2		(70)	

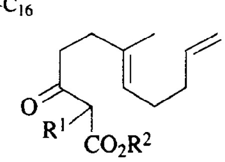
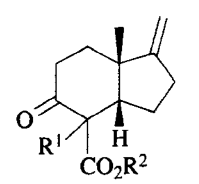
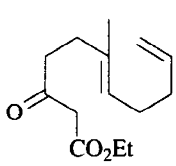
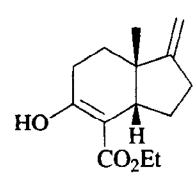
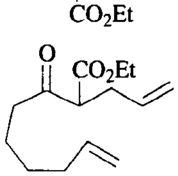
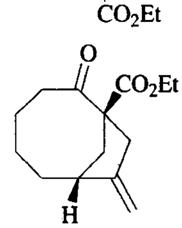
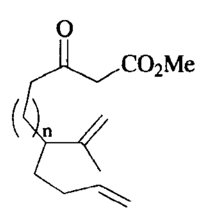
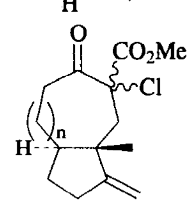
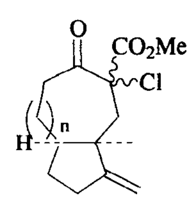
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}-C_{16} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 25°, 2 - 5 d	 R^1 / R^2: H / Me (44); Me / Et (46); Cl / Et (48)	101
C_{14} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 4 h	 (41)	98
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (11)[b]	88
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 + 	87
C_{14} n = 1		(45) (20)	
C_{15} n = 2		(57) (19)	

TABLE XXXII. TANDEM CYCLIZATIONS (DD-MODE) (*Continued*)

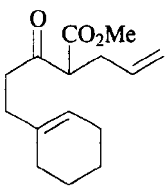
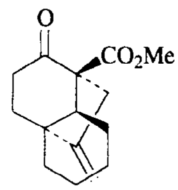
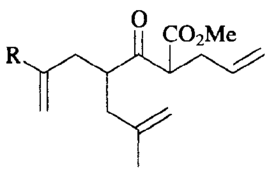
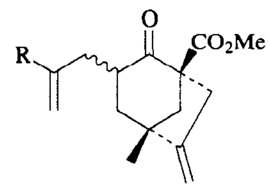
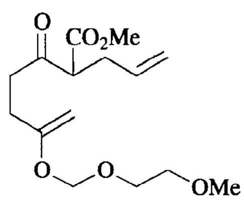
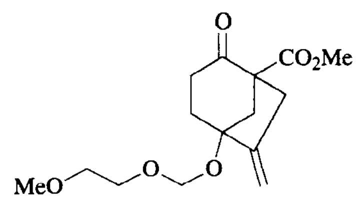
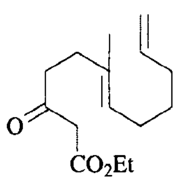
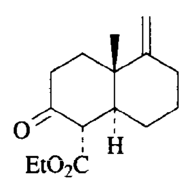
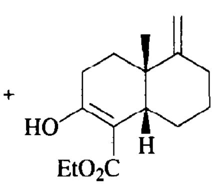
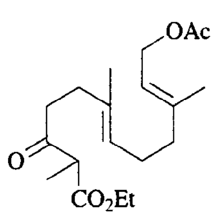
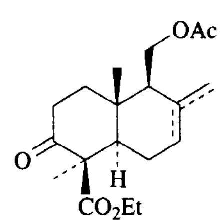
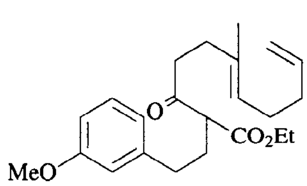
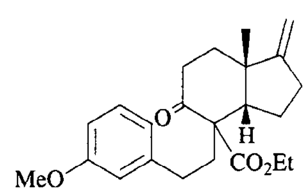
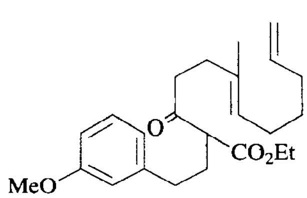
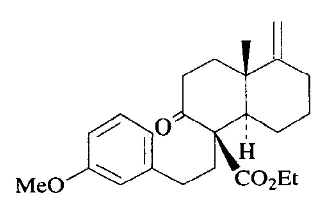
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (73)	100
	 R = H R = Cl	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 12 h	 α : β 1 : 3 (52) α (55), β (36)	86
		$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, 60°, 13 h	 (52)	99
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 7 h	 (43) +  (12)	56

TABLE XXXII. TANDEM CYCLIZATIONS (DD-MODE) (*Continued*)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}		$Mn(OAc)_3$, AcOH, 25°, 30 min	 exo (48) endo (15)	91
C_{23}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 7 h	 (50)	98
C_{24}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 4 h	 (57)	56

[a] Ratio of stereoisomers anti-symm : unsymm : syn-symm.
[b] A monocyclization product was also formed (17%).

TABLE XXXIII. TANDEM CYCLIZATIONS (DB-MODE)

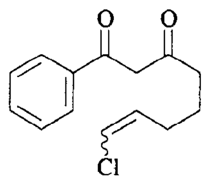
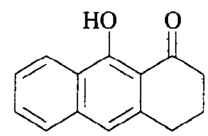
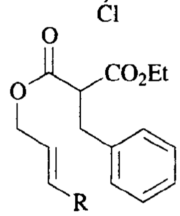
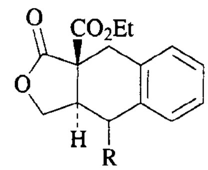
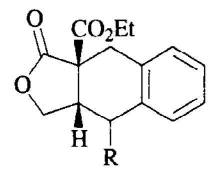
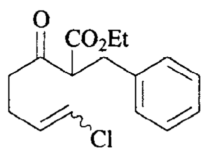
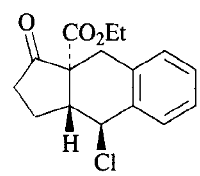
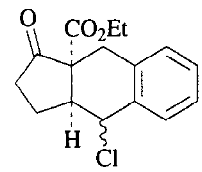
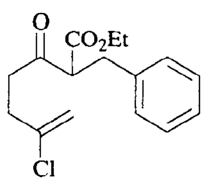
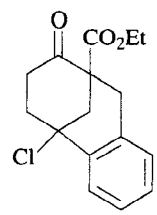
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}		$Mn(OAc)_3$, AcOH, 35°, 15 h	 (79)	103
		$Mn(OAc)_3$, AcOH	 + 	94
C_{15}	R = H		(23) (15)	
C_{16}	R = Me		(57) (20)	
C_{16}		$Mn(OAc)_3$, AcOH, rt, 20 h	 (55) +  (17)	103
		$Mn(OAc)_3$, AcOH, rt, 20 h	 (64)	103

TABLE XXXIII. TANDEM CYCLIZATIONS (DB-MODE) (*Continued*)

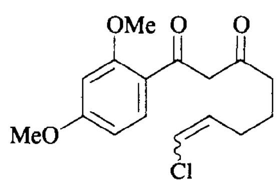
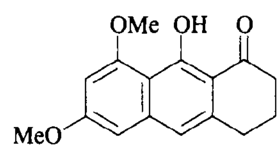
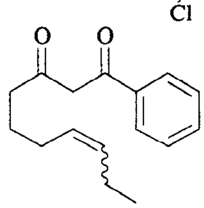
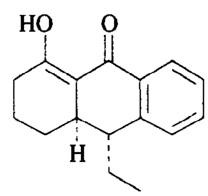
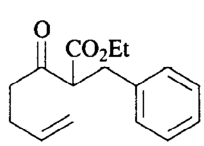
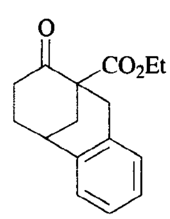
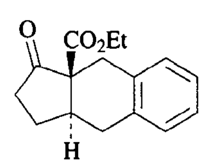
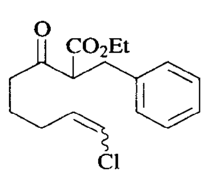
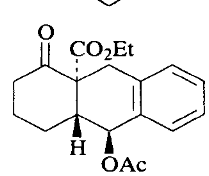
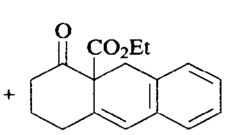
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. $Mn(OAc)_3$, AcOH, AcOK, 35°, 17 h 2. K_2CO_3, MeOH	 (43)	103
		$Mn(OAc)_3$, AcOH		90
	Z		(58)	
	E		(85)	
		$Mn(OAc)_3$, AcOH	 +  9 : 3 (55)	90
C_{17}		$Mn(OAc)_3$, AcOH, 35°, 28 h	 (54) +  (15)	103

TABLE XXXIII. TANDEM CYCLIZATIONS (DB-MODE) (*Continued*)

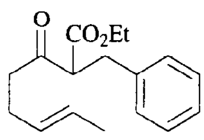
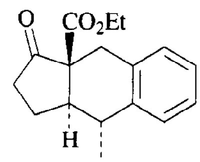
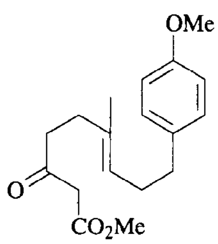
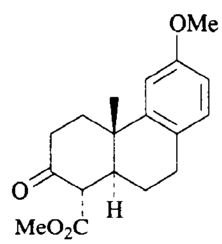
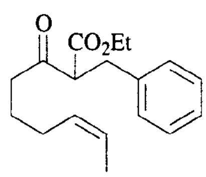
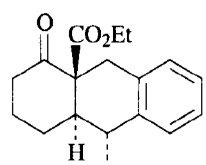
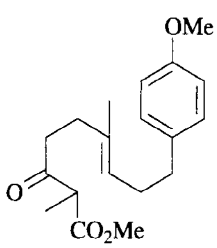
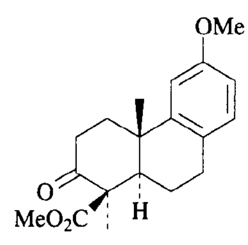
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
		Mn(OAc)$_3$, AcOH, 25°, 24 h		(74)	90
C_{18}		Mn(OAc)$_3$, AcOH, 20°, 1 h		(70)	85
		Mn(OAc)$_3$, AcOH, 25°, 24 h		(83)	90
C_{19}		Mn(OAc)$_3$, AcOH, 20°, 1 h		(50)	85

TABLE XXXIII. TANDEM CYCLIZATIONS (DB-MODE) (*Continued*)

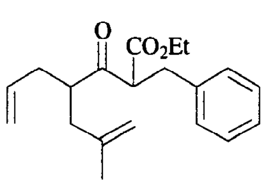
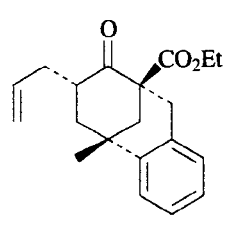
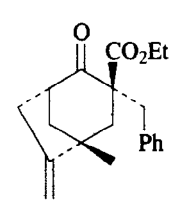
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{20}		Mn(OAc)$_3$, Cu(OAc)$_2$, AcOH, rt, 14 h	 + 	3 : 2 (33)	86

TABLE XXXIV. TANDEM CYCLIZATIONS (TD-MODE)

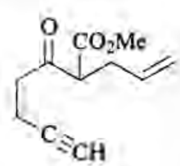
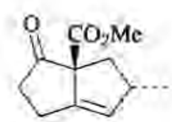
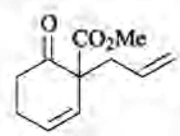
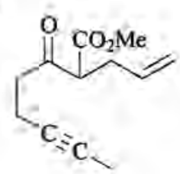
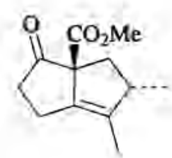
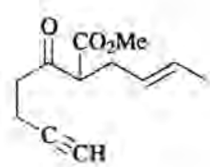
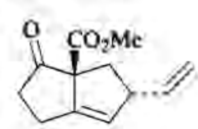
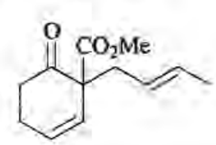
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	$Mn(OAc)_3$ - anhydr., EtOH, 25°, 8 h	 +  2 : 1 (20)	99
C_{12} 	$Mn(OAc)_3$ - anhydr., EtOH, 25°, 27 h	 (35)	99
	$Mn(OAc)_3$ - anhydr., $Cu(OAc)_2$, EtOH, 25°, 23 h	 (32) +  (15)	99

TABLE XXXV. TANDEM CYCLIZATIONS (TB-MODE)

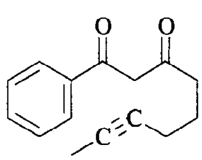
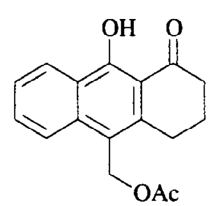
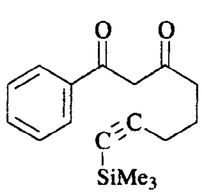
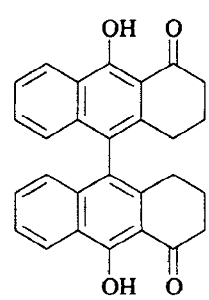
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		$Mn(OAc)_3$, AcOH, 35°, 17 h	 (81)	103
C_{17}		$Mn(OAc)_3$, AcOH, 35°, 17 h	 (71)	103

TABLE XXXVI. TANDEM CYCLIZATIONS (DC-MODE)

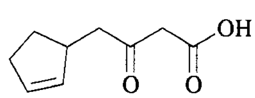
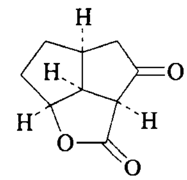
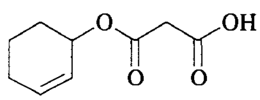
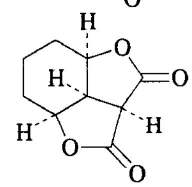
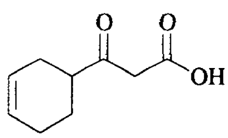
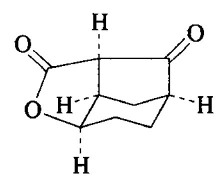
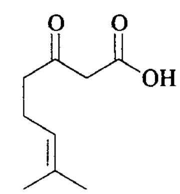
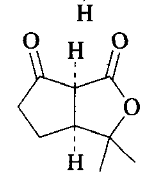
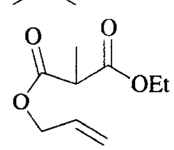
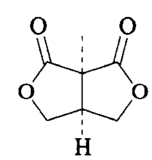
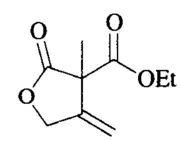
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		$Mn(OAc)_3$, AcOH, 23°, 1 h	 (52)	183
		$Mn(OAc)_3$, AcOH, 40°, 24 h	 (64)	183
		$Mn(OAc)_3$, AcOH, 23°, 24 h	 (61)	183
		$Mn(OAc)_3$, AcOH, 23°, 20 min	 (80)	183
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcONa, reflux	 (53) +  (20)	96

TABLE XXXVI. TANDEM CYCLIZATIONS (DC-MODE) (*Continued*)

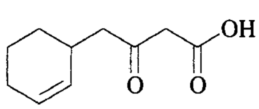
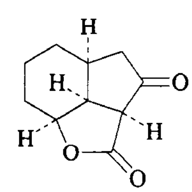
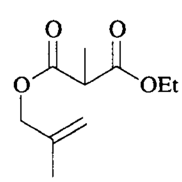
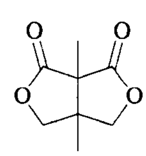
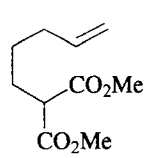
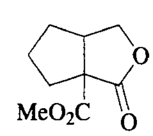
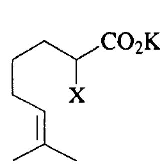
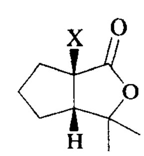
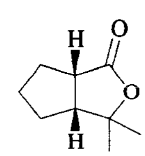
	Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10}		$Mn(OAc)_3$, AcOH, 23°, 20 min	 (63)		183
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, AcONa, reflux	 (21)		96
		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, 55°, 28 h	 (48)		99
		$Mn(OAc)_3$, AcOH, 25°	 +		178
C_{10}	X = CN		(14)	(0)	
C_{11}	X = CO_2Me		(41)	(3)	

TABLE XXXVI. TANDEM CYCLIZATIONS (DC-MODE) (*Continued*)

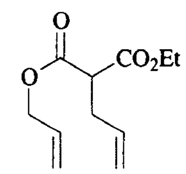
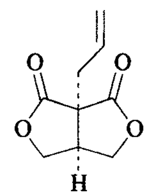
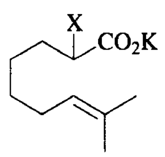
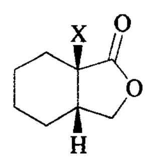
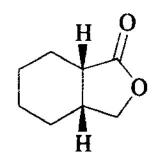
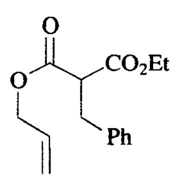
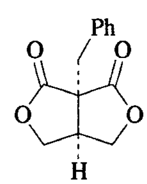
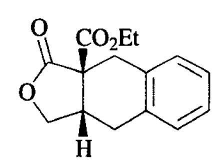
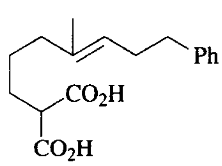
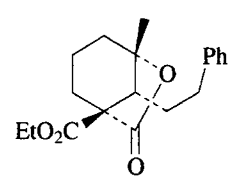
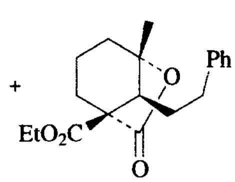
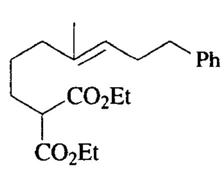
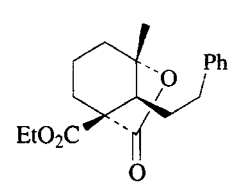
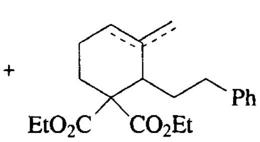
Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C_{11} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (47)			94
	$Mn(OAc)_3$, AcOH, 70°		+		178
C_{11} X = CN		(50)		(0)	
C_{12} X = CO_2Me		(48)[a]		(8)	
C_{15} 	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	 (40)	+	 (19)	94
C_{17} 	1. $Mn(OAc)_3$, AcOH 2. $MeCHN_2$	 (40)	+	 (20)	91

TABLE XXXVI. TANDEM CYCLIZATIONS (DC-MODE) (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
C_{21} 			+		91
	$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH	(61)		(33)	
	$Mn(OAc)_3$, AcOH	(40)		endo : exo 4 : 1 (55)	

[a] The product contained 20% of the *E* isomer.

TABLE XXXVII. TANDEM CYCLIZATIONS (DN-MODE)

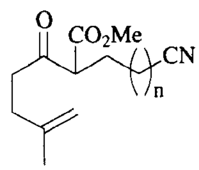
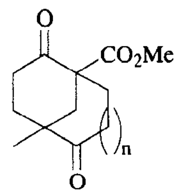
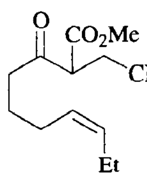
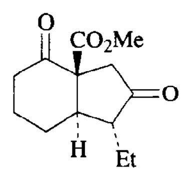
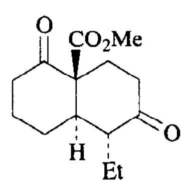
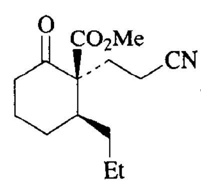
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		Mn(OAc)$_3$, AcOH, 25°, 24 h		171
C_{11}	n = 0		(51)	
C_{12}	n = 1		(8)	
C_{13}				
		Mn(OAc)$_3$, AcOH, 25°, 22 h	(40)	171
		Mn(OAc)$_3$, EtOH, TFA, 25°, 21 h	(57)	
		Mn(OAc)$_3$, EtOH, 25°, 18 h	 (13) +  (4)	171

TABLE XXXVIII. POLYCYCLIZATION REACTIONS (DDDD-MODE)

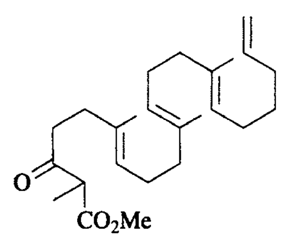
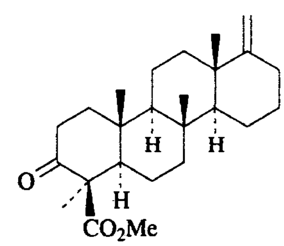
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25}		$Mn(OAc)_3$, $Cu(OAc)_2$, AcOH, rt, 20 h	 (31)	104

TABLE XXXIX. CARBON MONOXIDE TRAPPING REACTIONS

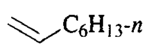
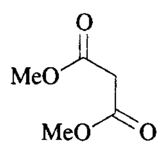
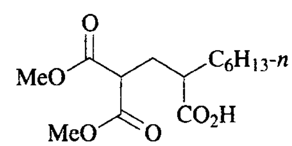
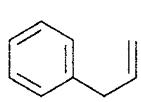
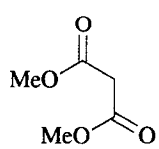
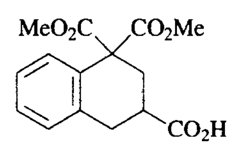
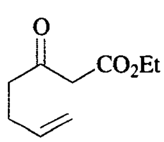
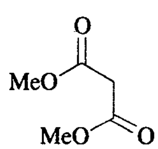
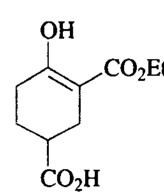
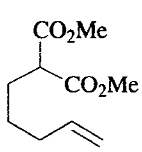
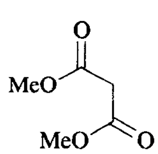
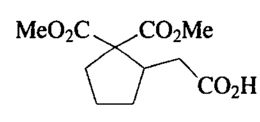
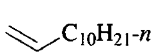
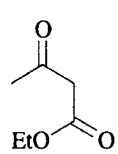
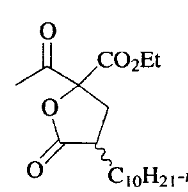
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8			$Mn(OAc)_3$, AcOH CO, 70°, 10 h		(43)	188
C_9			$Mn(OAc)_3$, AcOH CO, 70°, 15 h		(37)	188
			$Mn(OAc)_3$, AcOH CO, 70°, 13 h		(55)	188
C_{10}			$Mn(OAc)_3$, AcOH CO, 70°, 10 h		(50)	188
C_{12}			$Mn(OAc)_3$, AcOH CO, 70°, 10 h		56 : 44 (44)	188

TABLE XLA. INTERMOLECULAR REACTIONS WITH ELECTROCHEMICALLY GENERATED $Mn(OAc)_3$

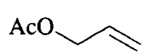
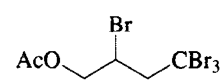
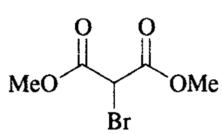
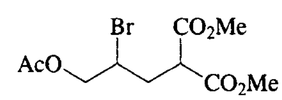
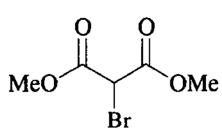
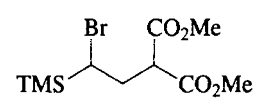
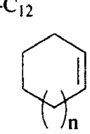
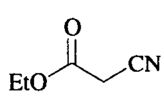
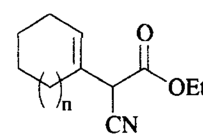
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	CBr_4	$Mn(OAc)_2$, anode, AcOH, AcOK, 40°	 (96)	190
		$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (80)	205
		$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (40)	205
C_5-C_{12} 		$Mn(OAc)_2$ (cat.), anode, AcOH, AcONa, EtOAc, 40°		203
n				
0			(64)	
1			(60)	
2			(51)	
3			(60)	
7			(50)	

TABLE XLA. INTERMOLECULAR REACTIONS WITH ELECTROCHEMICALLY GENERATED $Mn(OAc)_3$ (*Continued*)

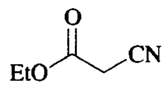
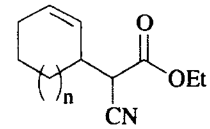
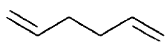
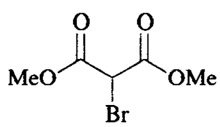
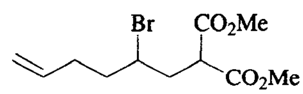
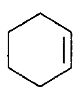
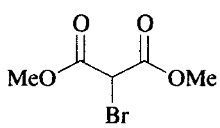
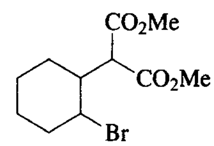
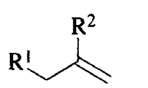
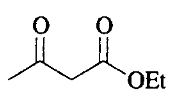
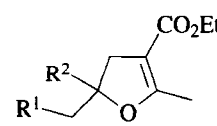
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_2$ (cat.), anode, $Cu(OAc)_2$, AcOH, AcONa, EtOAc, 40°	 n: 0 (44); 1 (53); 2 (54); 3 (47); 7 (49)	203, 204
C_6 		$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (75)	205
		$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (42)	205
C_6-C_8 		$Mn(OAc)_2$ (cat.), anode, AcOH, EtOAc, AcONa, 40°		204
R^1 = *n*-Pr, R^2 = H			(86)	
R^1 = *n*-C_5H_{11}, R^2 = H			(80)	
R^1 = *t*-Bu, R^2 = Me			(82)	

TABLE XLA. INTERMOLECULAR REACTIONS WITH ELECTROCHEMICALLY GENERATED $Mn(OAc)_3$ (*Continued*)

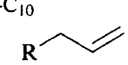
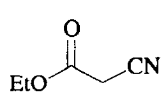
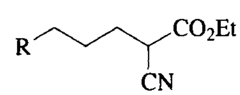
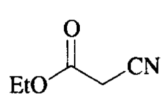
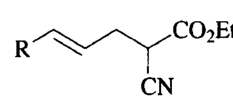
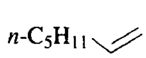
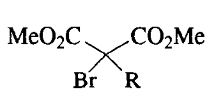
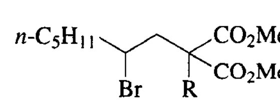
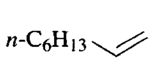
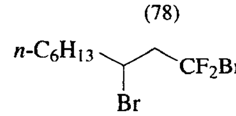
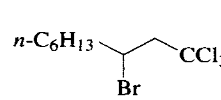
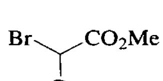
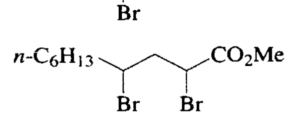
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6-C_{10} 		$Mn(OAc)_2$ (cat.), anode, AcOH, EtOAc, AcONa, 40°		203, 204
R = *n*-Pr			(62)	
R = *n*-C_5H_{11}			(54)	
R = *n*-C_7H_{15}			(56)	
		$Mn(OAc)_2$, anode, $Cu(OAc)_2$,AcOH, AcONa, EtOAc, 40°		203, 204
R = *n*-Pr			(45)	
R = *n*-C_5H_{11}			(55)	
R = *n*-C_7H_{15}			(58)	
C_7 		$Mn(OAc)_2$ - anode, AcOH, AcOK, 40°		
	R = Br		(61)	190,
	R = H		(78)	205
C_8 	CF_2Br_2	$Mn(OAc)_2$ - anode, AcOH, AcOK, rt	 (40)	190
	$BrCCl_3$	$Mn(OAc)_2$ - anode, AcOH, AcOK, 40°	 (95)	190
		$Mn(OAc)_2$ - anode, AcOH, AcOK, 40°	 (52)	190

TABLE XLA. INTERMOLECULAR REACTIONS WITH ELECTROCHEMICALLY GENERATED $Mn(OAc)_3$ (*Continued*)

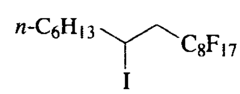
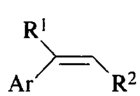
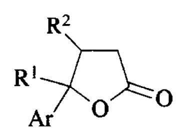
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	$C_8F_{17}I$	$Mn(OAc)_2$ - anode, AcOH, AcOK, rt	 (80)	190
C_8-C_{14}				
	AcOH, Ac_2O	$Mn(OAc)_2$, (cat.), anode, $Cu(OAc)_2$, AcOH, Ac_2O, AcONa, 95 - 97°		204
Ar / R^1 / R^2				
Ph / H / H			(80)	
Ph / Me / H			(75)	
Ph / H / Ph			(61)	
p-ClC_6H_4 / H / H			(58)	
p-MeC_6H_4 / H / H			(81)	
Ph / H / CO_2Et			(84)	
Ph / H / CH_2OH			(78)	

TABLE XLB. ADDITION-CYCLIZATIONS WITH ELECTROCHEMICALLY GENERATED $Mn(OAc)_3$

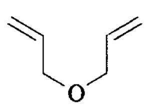
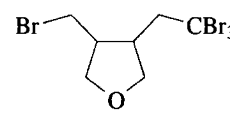
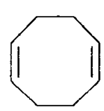
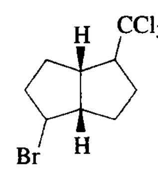
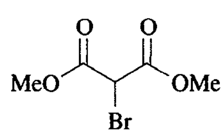
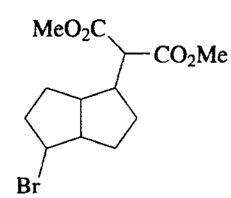
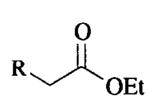
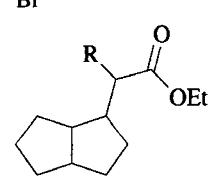
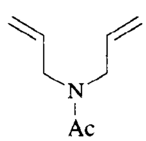
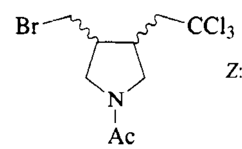
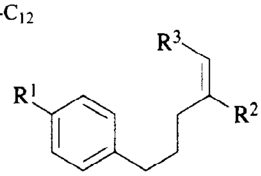
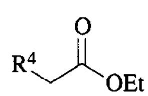
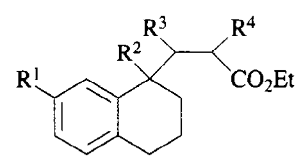
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	CBr_4	$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (72)	190
C_8 	$BrCCl_3$	$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (83)	190
		$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 (85)	205
		$Mn(OAc)_2$ (cat.), anode, AcOH, EtOAc, 20 - 25°		204
	R = CN		(76)	
	R = CO_2Et		(78)	

TABLE XLB. ADDITION-CYCLIZATIONS WITH ELECTROCHEMICALLY GENERATED $Mn(OAc)_3$ (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
	$BrCCl_3$	$Mn(OAc)_2$ (cat.), anode, AcOH, AcOK, 40°	 *Z*:*E* 4.5:1 (60)	190
C_{11}-C_{12} 		$Mn(OAc)_2$ (cat.), anode, AcOH, EtOAc		204

R[1]	R[2]	R[3]	R[4]	Yield (%)
H	H	H	CN	(70)
Me	H	H	CN	(58)
F	H	H	CN	(53)
H	Me	H	CN	(60)
H	H	Me	CN	(37)
H	H	H	CO_2Et	(79)
Me	H	H	CO_2Et	(61)
F	H	H	CO_2Et	(60)
H	Me	H	CO_2Et	(73)
H	H	Me	CO_2Et	(39)

TABLE XLI. SONOCHEMICAL REACTIONS

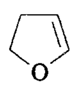
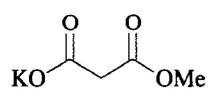
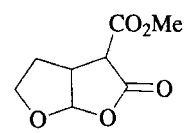
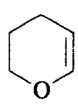
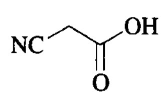
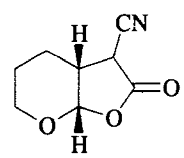
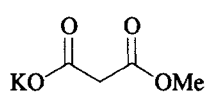
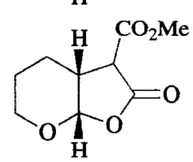
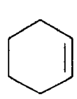
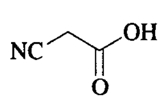
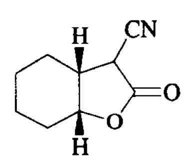
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 				
		Mn(OAc)$_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	(67)	191
		Mn(OAc)$_3$ (cat.), ultrasound, AcOH, 0°, 1.5 h	(41)	
C_5 		Mn(OAc)$_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 (65)	191
				
		Mn(OAc)$_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	(80)	191
		Mn(OAc)$_3$ (cat.), ultrasound, AcOH, 0°, 1.5 h	(39)	
C_6 		Mn(OAc)$_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 (65)	191

TABLE XLI. SONOCHEMICAL REACTIONS (*Continued*)

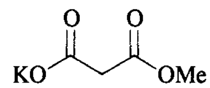
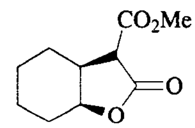
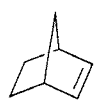
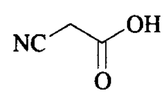
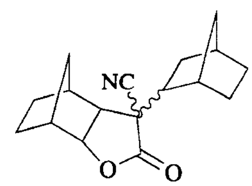
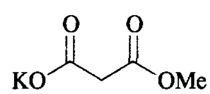
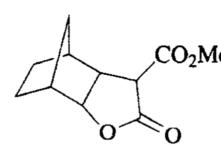
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
				
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	(78)	191
		$Mn(OAc)_3$ (cat.), ultrasound, AcOH, 0°, 1.5 h	(22)	
C_7 		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 (50)	191
				
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	(75)	191
		$Mn(OAc)_3$ (cat.), ultrasound, AcOH, 0°, 1.5 h	(34)	

TABLE XLI. SONOCHEMICAL REACTIONS (*Continued*)

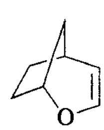
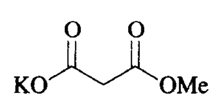
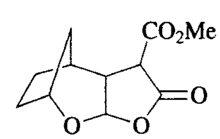
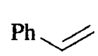
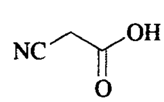
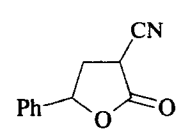
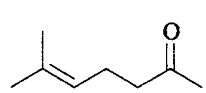
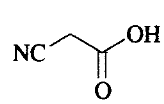
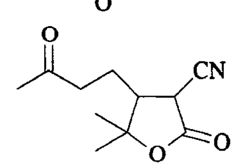
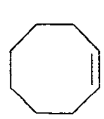
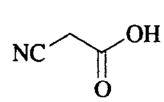
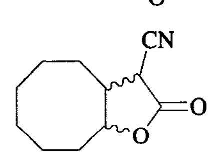
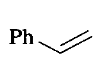
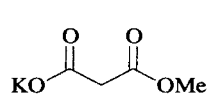
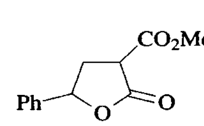
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	 (81)	191
C_8 		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 (55)	191
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 (73)	191
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 *E* : *Z* 9 : 1 (65)	191
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	 (62)	191

TABLE XLI. SONOCHEMICAL REACTIONS (*Continued*)

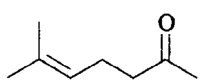
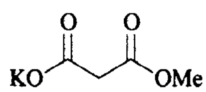
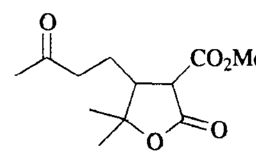
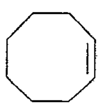
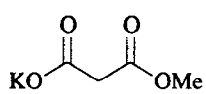
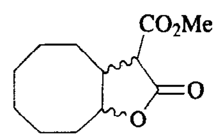
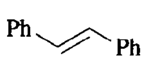
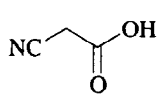
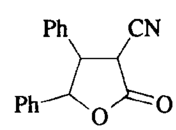
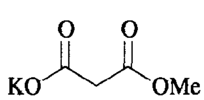
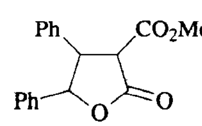
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	 (75)	191
			 I	191
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	I *E* : *Z* 7 : 3 (70)	
		$Mn(OAc)_3$ (cat.), ultrasound, AcOH, 0°, 1.5 h	I (39)	
C_{14} 		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 120 min	 (45)	191
		$Mn(OAc)_3$, ultrasound, AcOH, AcOK, 0°, 15 - 25 min	 (71)	191

TABLE XLIIA. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTERMOLECULAR ADDITIONS

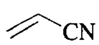
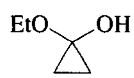
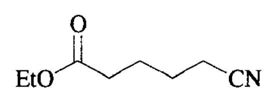
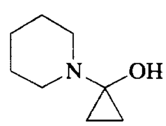
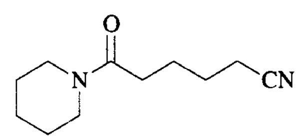
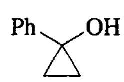
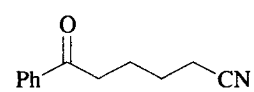
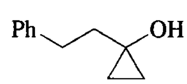
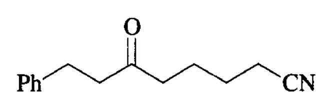
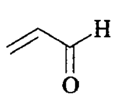
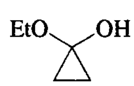
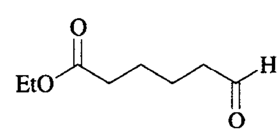
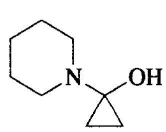
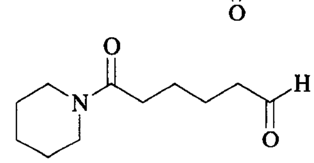
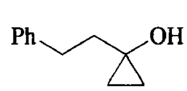
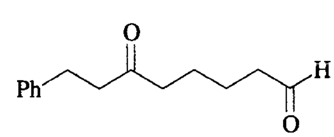
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		$Mn(pic)_3$, DMF, 0°, 1 - 2 h	 (72)	23
		"	 (75)	23
		"	 (47)	23
		"	 (52)	23
		"	 (47)	23
		"	 (48)	23
		"	 (46)	23

TABLE XLIIA. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTERMOLECULAR ADDITIONS *(Continued)*

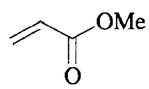
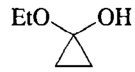
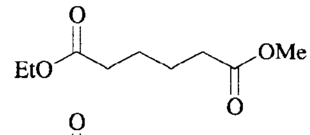
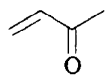
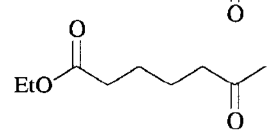
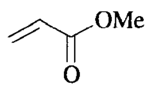
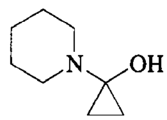
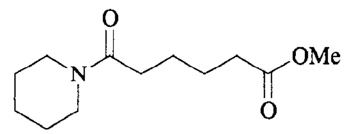
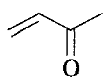
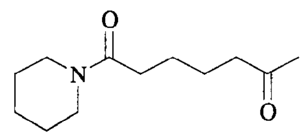
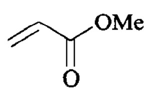
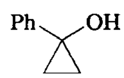
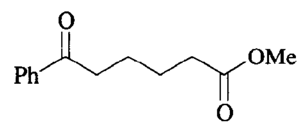
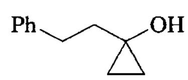
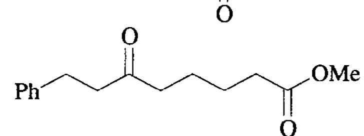
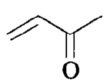
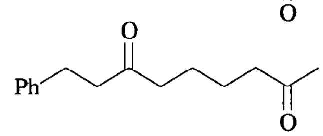
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4			Mn(pic)$_3$, DMF, 0°, 1 - 2 h		(44)	23
		"	"		(51)	23
			"		(49)	23
		"	"		(52)	23
			"		(57)	23
			"		(60)	23
		"	"		(43)	23

TABLE XLIIA. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTERMOLECULAR ADDITIONS *(Continued)*

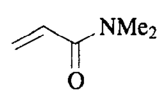
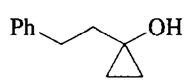
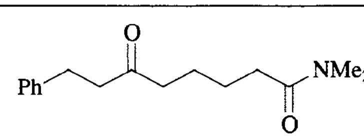
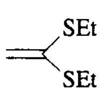
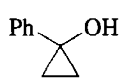
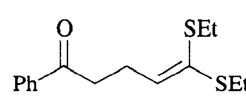
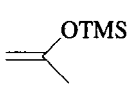
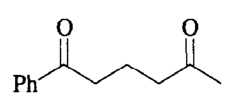
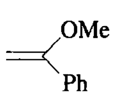
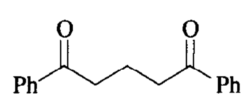
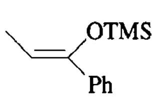
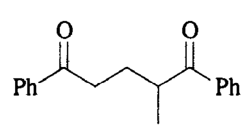
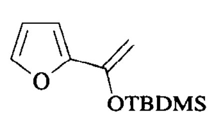
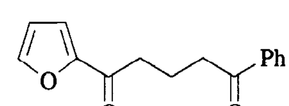
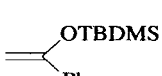
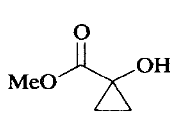
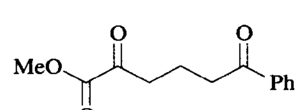
	Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_5			Mn(pic)$_3$, DMF, 0°, 1 - 2 h		(27)	23
C_6			Mn(pic)$_3$, DMF, 0°, 0.5 - 5 h		(71)	23
		"	"		(14)	22, 23
C_9		"	"		(72)	22, 23
C_{12}		"	"		(41)	22, 23
		"	"		(80)	23
C_{14}			"		(29)	23

TABLE XLIIA. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTERMOLECULAR ADDITIONS (*Continued*)

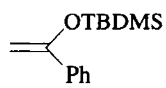
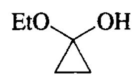
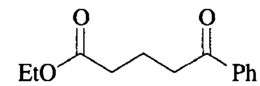
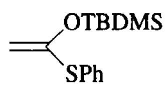
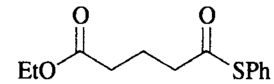
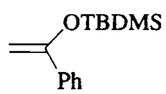
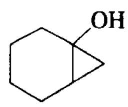
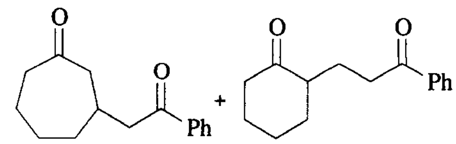
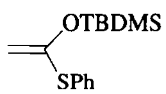
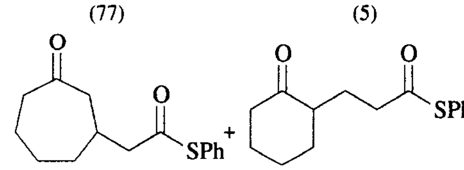
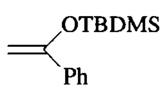
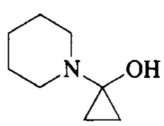
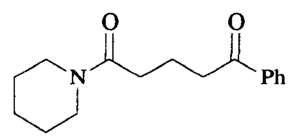
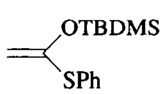
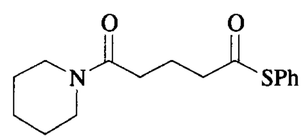
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		Mn(Pic)$_3$, DMF, 0°, 0.5 - 5 h	 (85)	22, 23
	"	"	 (63)	22, 23
		"	 (77) (5)	22, 23
	"	"	 (64) (10)	22, 23
		"	 (65)	23
	"	"	 (46)	23

TABLE XLIIA. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTERMOLECULAR ADDITIONS (*Continued*)

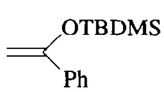
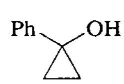
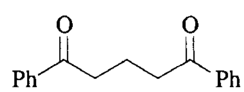
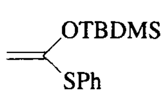
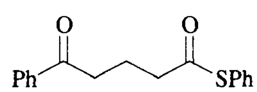
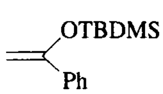
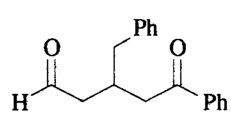
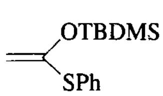
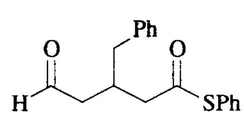
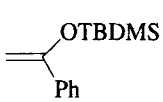
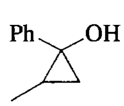
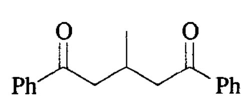
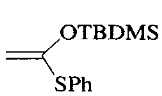
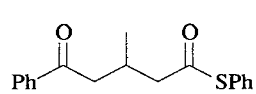
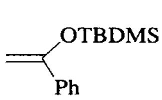
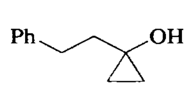
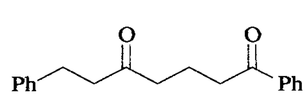
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		Mn(pic)$_3$, DMF, 0°, 0.5 - 5 h	 (89)	22, 23
	"	"	 (66)	22, 23
		"	 (78)	22, 23
	"	"	 (33)	22, 23
		"	 (78)	22, 23
	"	"	 (66)	22, 23
		"	 (80)	22, 23

TABLE XLIIA. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTERMOLECULAR ADDITIONS (*Continued*)

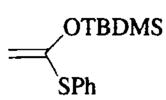
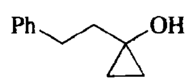
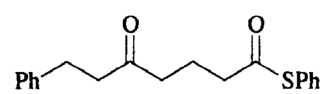
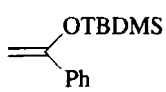
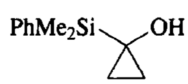
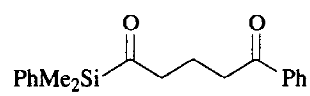
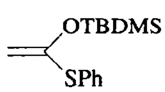
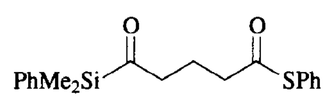
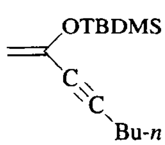
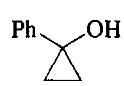
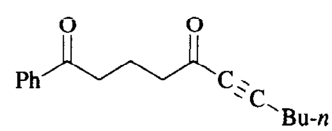
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
		$Mn(pic)_3$, DMF, 0°, 0.5 - 5 h		(59)	22, 23
		"		(60)	23
	"	"		(61)	23
		"		(88)	22, 23

TABLE XLIIB. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTRAMOLECULAR ADDITIONS

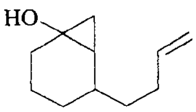
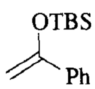
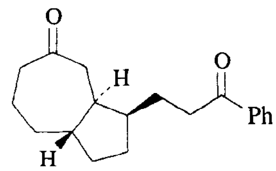
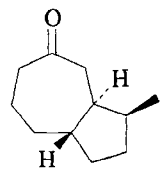
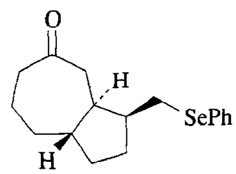
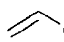
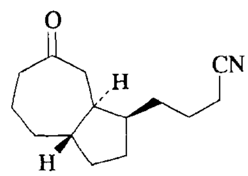
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{11} 		Mn(pic)$_3$, DMF, 0°		(81)	192
	n-Bu$_3$SnH	"		(75)	192
	PhSeSePh	"		(68)	192
	 CN, *n*-Bu$_3$SnH	"		(66)	192

TABLE XLIIB. CYCLOPROPANOL DERIVED ALKYL RADICALS: INTRAMOLECULAR ADDITIONS (*Continued*)

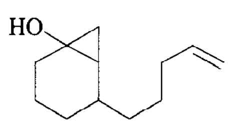
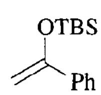
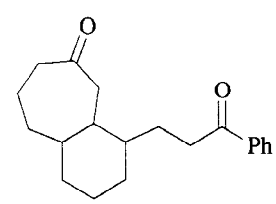
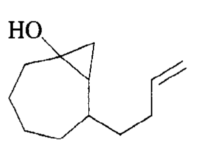
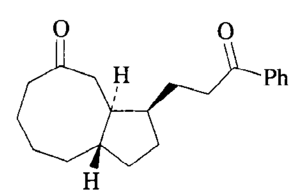
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}					
		Mn(pic)$_3$, DMF, 0°		(64)	192
	"	"		(63)	192

TABLE XLIIC. CYCLOBUTANOL DERIVED ALKYL RADICALS: INTRAMOLECULAR ADDITIONS

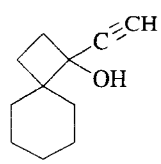
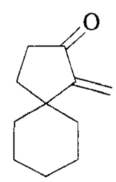
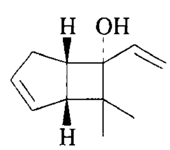
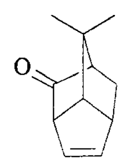
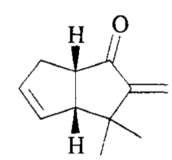
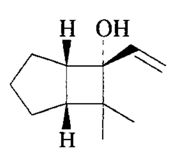
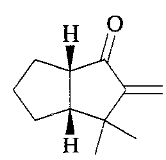
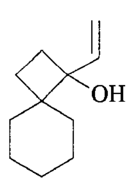
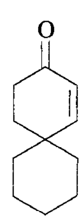
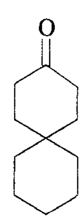
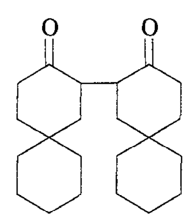
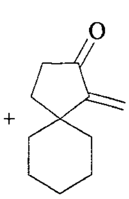
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	$Mn(OAc)_3$, EtOH, 25°, 12 h	 (45)	24
	$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, reflux, 1 h	 (44) +  (22)	24
	$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, 25°, 3 h	 (83)	24
	$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, reflux, 40 min	 (30) +  (24) +  (22) +  (6)	24

TABLE XLIIC. CYCLOBUTANOL DERIVED ALKYL RADICALS: INTRAMOLECULAR ADDITIONS (*Continued*)

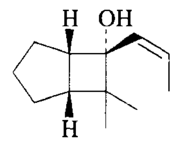
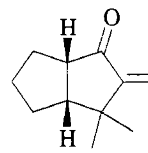
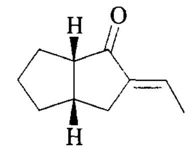
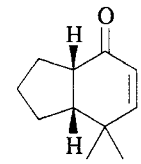
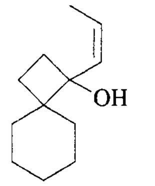
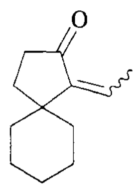
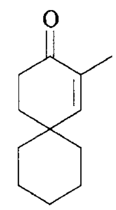
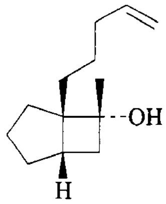
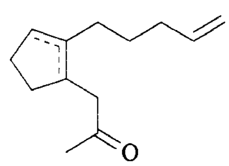
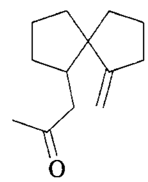
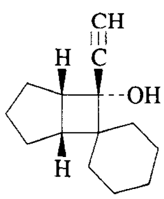
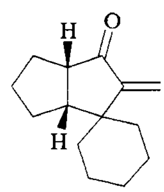
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		1. $Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, reflux, 0.5 h 2. Et_3N, Et_2O	 (34) +  (29) +  (10)	24
		$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, reflux, 30 min	 *Z* (8) *E* (22) +  (24)	24
C_{13}		$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, 25°, 4 h	 +  1 : 4 (69)	24
C_{14}		$Mn(OAc)_3$, EtOH, reflux, 20 min	 (40)	24

TABLE XLIIC. CYCLOBUTANOL DERIVED ALKYL RADICALS: INTRAMOLECULAR ADDITIONS (*Continued*)

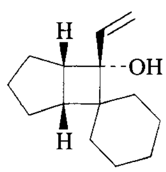
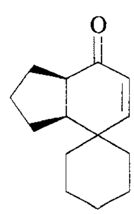
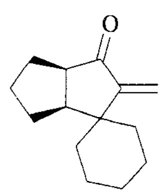
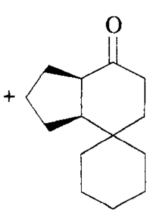
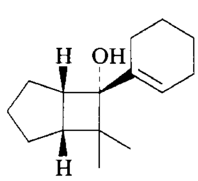
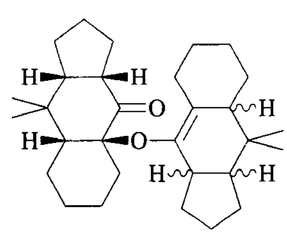
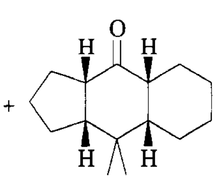
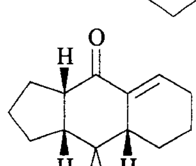
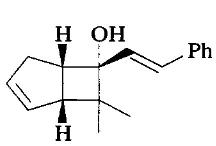
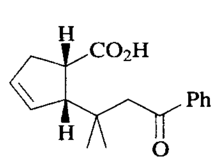
	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, reflux, 40 min	 (26) +  (22) +  (17)	24
C_{15}		$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, 25°, 11 h	 (40) +  (21) +  (14)	24
C_{17}		$Mn(OAc)_3$, $Cu(OAc)_2$, EtOH, 25°, 12 h	 (25)	24

TABLE XLIII. Cr(0) COMPLEX-DERIVED ALKYL RADICALS

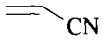
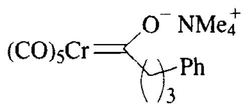
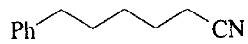
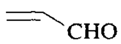
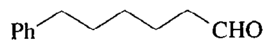
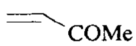
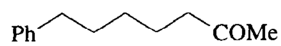
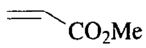
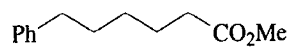
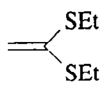
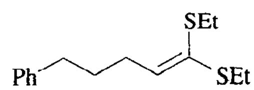
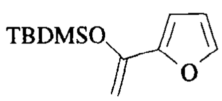
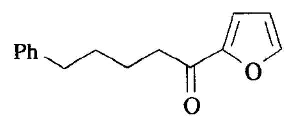
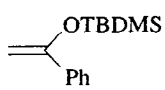
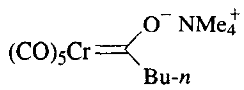
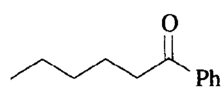
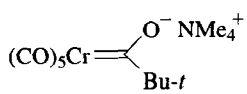
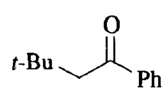
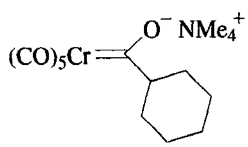
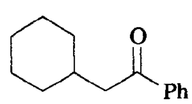
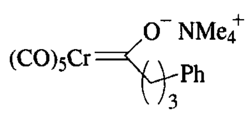
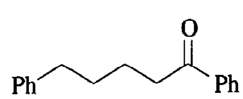
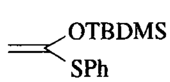
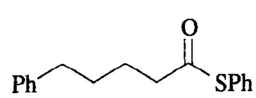
Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		Mn(pic)$_3$, DMF, 0°, 1 h	 (24)[a] (28)[b] (68)[c]	25
	"	"	 (48)[c]	25
C_4 	"	"	 (47)[c]	25
	"	"	 (77)[c]	25
C_6 	"	"	 (64)	25
C_{18} 	"	"	 (61)	25
C_{20} 		"	 (68)	25

TABLE XLIII. Cr(0) COMPLEX-DERIVED ALKYL RADICALS (*Continued*)

Substrate	Reagent	Conditions	Product(s) and Yield(s) (%)	Refs.
		Mn(pic)$_3$, DMF, 0°, 1 h	 (64)	25
		"	 (64)	25
		"	 (74)	25
	"	"	 (33)	25

[a] The trapping agent was 9,10-dihydroanthracene.
[b] The trapping agent was $(TMS)_3SiH$.
[c] The trapping agent was Bu_3SnH.

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The Vilsmeier Reaction of Fully Conjugated Carbocycles and Heterocycles

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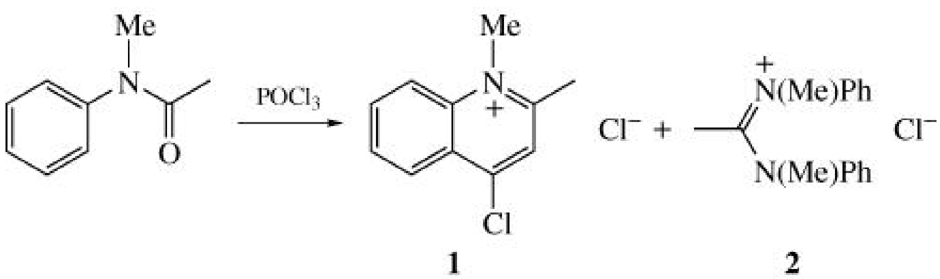
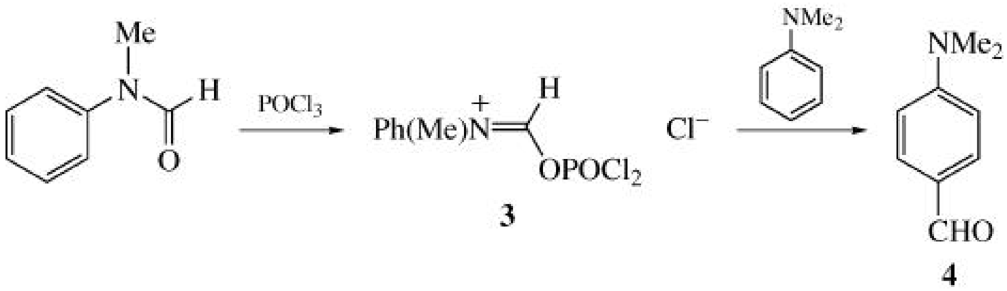
1. Introduction

In 1925 Fischer, Müller, and Vilsmeier (1) published a paper describing the reaction between phosphoryl chloride and *N*-methylacetanilide, giving a number of products, including the quinolinium salt **1** and the salt **2** (Eq. 1). The probable course of the reaction was given in a paper by Vilsmeier and Haack in 1927, (2) and they made the important discovery that the reagent obtained from *N*-methylformanilide and phosphoryl chloride, represented as the salt **3**, would react with *N,N*-dimethylaniline, giving 4-*N,N*-dimethylaminobenzaldehyde (**4**)(Eq. 2). No



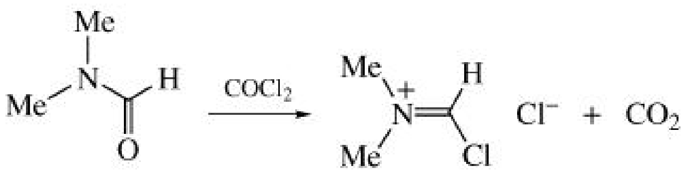
(1)



(2)

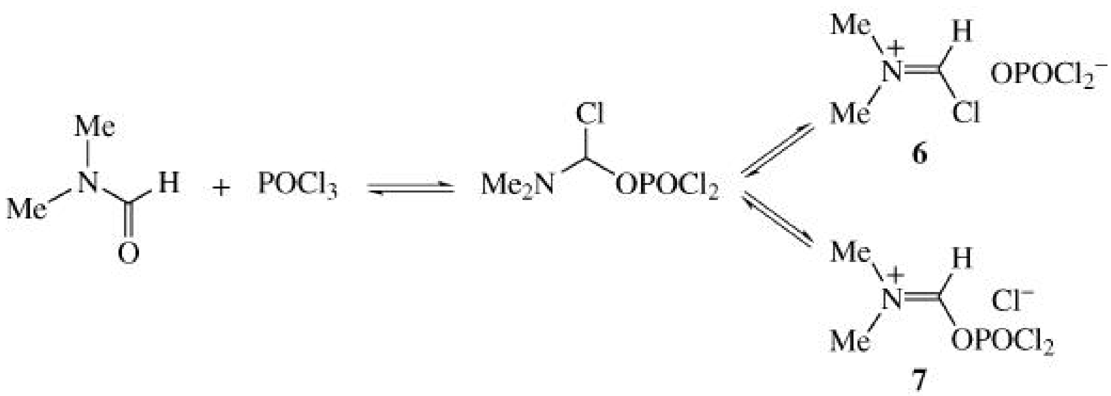
2-substituted products were observed in this reaction. Other *N,N*-dialkylaniline derivatives, including 3,*N,N*-trimethylaniline and 1-*N,N*-dimethylaminonaphthalene were also successfully used as substrates to prepare aromatic aldehyde derivatives.

The gradual development of the reagent for synthesis was accompanied by interest in the nature of the reagent. It was discovered that other acid chlorides (e.g., thionyl chloride, carbonyl chloride, and oxalyl chloride) could be used in the reaction and that substituted amides other than formamides gave ketones, although in generally poorer yields. Thionyl chloride frequently gives sulfur-containing products. The most commonly used amide is dimethylformamide (DMF) and there is now a consensus that the reagent formed from DMF and most acid chlorides, other than phosphoryl chloride, can be represented by the structure **5**, and this is illustrated for the reaction between DMF and carbonyl chloride (Eq. 3). Salt **5** is a stable compound and is often isolated before being reacted



(3)

with a substrate. It seems likely that the most commonly used reagent, that made from DMF and phosphoryl chloride, is an equilibrium mixture of the iminium salts **6** and **7** (Eq. 4). Recent unpublished spectroscopic studies (3) have indicated that in DMF solution there is an equilibrium mixture of iminium compounds, including the dipolar structure **8** (Eq. 5).



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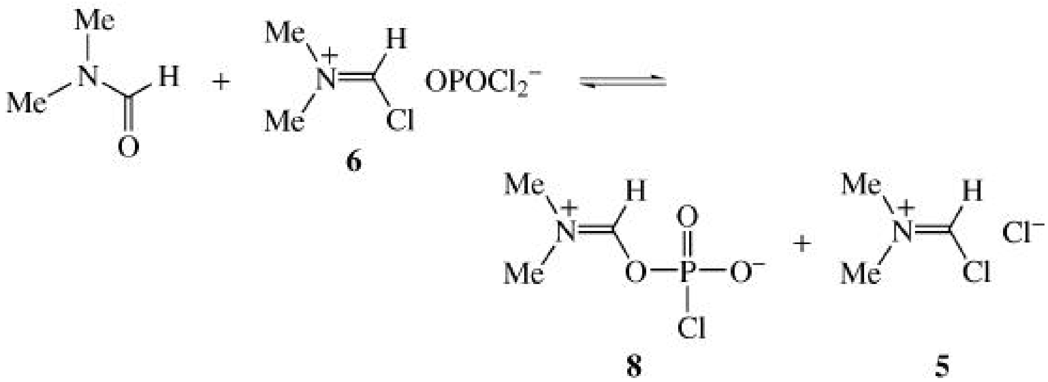
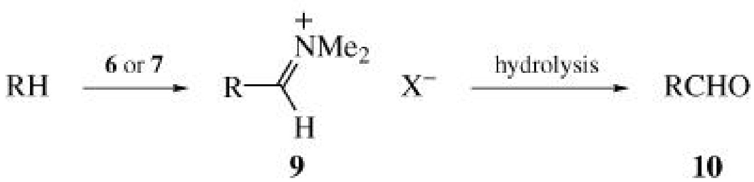


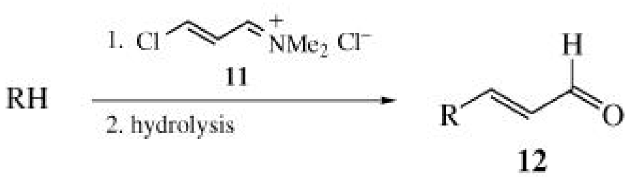
(5)

The electrophilic chloroiminium salt **6** or salt **7** then reacts with a substrate in an electrophilic substitution process yielding an iminium salt **9**, which is usually hydrolyzed to the aromatic aldehyde **10** (Eq. 6). Vinylogous chloroiminium salts



(6)

such as **11** can be prepared from the corresponding vinylogous formamide derivatives and these yield, after hydrolysis, α , β -unsaturated products **12** (Eq. 7). This particular reaction is generally limited to more reactive substrates.



(7)

The formation of carbon— carbon bonds to fully conjugated carbocycles and heterocycles is the subject of this chapter; a subsequent chapter considers carbon— carbon bond-formation reactions in alkenes (including heterosubstituted alkenes such as enamines and enol ethers), alkynes, and activated methyl and methylene compounds (aldehydes, ketones, carboxylic acid derivatives, and nitriles).

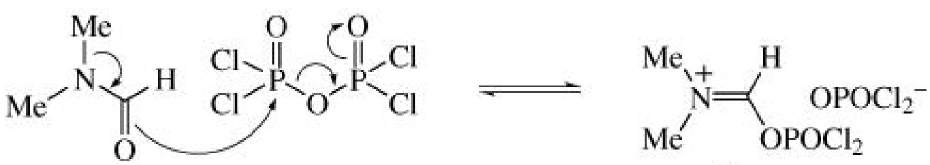
It is not surprising that the Vilsmeier reaction has been the subject of many review articles of varying scope and length. The author(s) and dates are, in chronological order: Vilsmeier (1951), (4) Bayer (1954), (5) Bredereck et. al. (1959), (6) Eilingsfeld, Seefelder, and Weidinger (1960), (7) Minkin and Dorofeenko (1960), (8) Oda and Yamamoto (1960), (9) de Maheas (1962), (10) Hafner et al. (1963), (11) Gore (1964), (12) Hazebroucq (1966), (13) Jutz (1968), (14) Ulrich (1968), (15) Kuehne (1969), (16) Seshadri (1973), (17) Jutz (1976), (18) Meth-Cohn and Tarnowski (1982), (19) Simchen (1983), (20) Marson (1992), (21) Meth-Cohn and Stanforth (1991), (22) and Meth-Cohn (1993). (23)

Kantlehner (1976) (24) has reviewed adducts from acid amides and acylation reagents and also the preparation and reaction of chloromethyliminium salts with nucleophiles. Liebscher and Hartmann (1979) (25) have published an article relating to vinylogous chloroiminium salts. With so many excellent reviews dealing with the Vilsmeier reaction, its mechanism, and the structure of the various electrophilic reagents, we have restricted our coverage to important concepts rather than reiterate all the literature material.

2. Mechanism and Regiochemistry

A brief description of the mechanism and regiochemistry of the Vilsmeier reaction is now presented and this is elaborated with appropriate cases in the following sections which deal with specific compound types.

From the early stages it was obvious that the Vilsmeier reagent is a relatively weak electrophile, generally requiring an activated aromatic nucleus. For this reason, it has been particularly successful with π -excessive heterocycles, such as furan, thiophene, and pyrrole. A recent discussion of the mechanism (26) has indicated that in the equilibrium leading to the formation of the reactive species, the use of an electrophilic anhydride (e.g., trifluoromethanesulfonic anhydride) should lead to a cationic species that cannot react with a nucleophile to give a lower energy and less reactive species, and the action of pyrophosphoryl chloride on DMF indeed produces an intermediate **13** (Eq. 8) for which the pathway to the



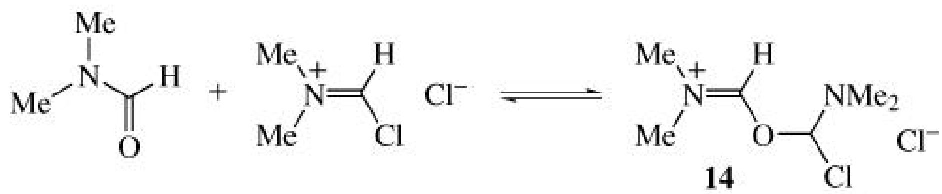
13

(8)

iminium chloride of the type **5** is precluded. Indeed, the reagent **13** thus produced is associated with a high reactivity and increased steric demand, which can increase regioselectivity.

Early reports of the Vilsmeier reaction, particularly on benzenoid aromatics, suggested regiospecificity, but careful examination has indicated that regioisomers are frequently formed, although quantities of minor isomers were small. Thus, the most recent study of the Vilsmeier formylation of anisole (26) reports a mixture of 2-methoxybenzaldehyde (4.5%) and 4-methoxybenzaldehyde (70.5%).

Commonly used solvents are chlorinated hydrocarbons, excess dimethylformamide, or excess phosphoryl chloride. When DMF is used as the solvent, a further equilibrium involving the chloroiminium salt **5** and DMF can produce a less reactive electrophilic species **14** (Eq. 9). (27-29) The choice of solvent and reaction temperature is an important consideration in many Vilsmeier reactions.

 (9)

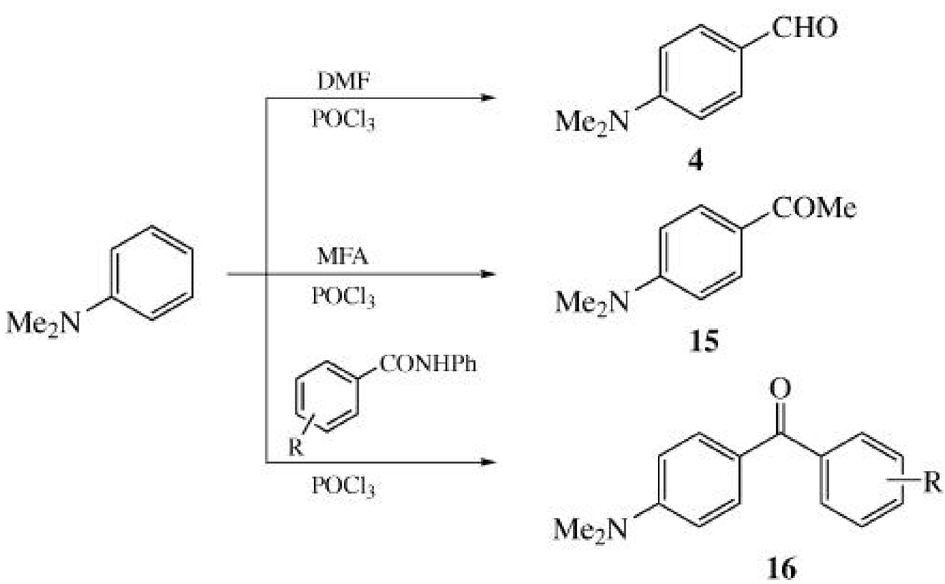
In all cases, the initial product of the Vilsmeier reaction is an iminium salt **9** (Eq. 6), which is often isolated as its chloride, perchlorate, or tetrafluoroborate, but is more commonly hydrolyzed to the aldehyde **10**. Iminium salt **9** can also be converted into groups other than aldehydes (e.g., thioaldehydes) by treatment with hydrogen sulfide, nitriles by treatment with hydoxylamine, and amines by reduction. In some cases, iminium salts can react intramolecularly with appositely located functional groups to generate fused-ring systems.

3. Scope and Limitations

In this section we consider first carbocyclic substrates and then heterocyclic substrates.

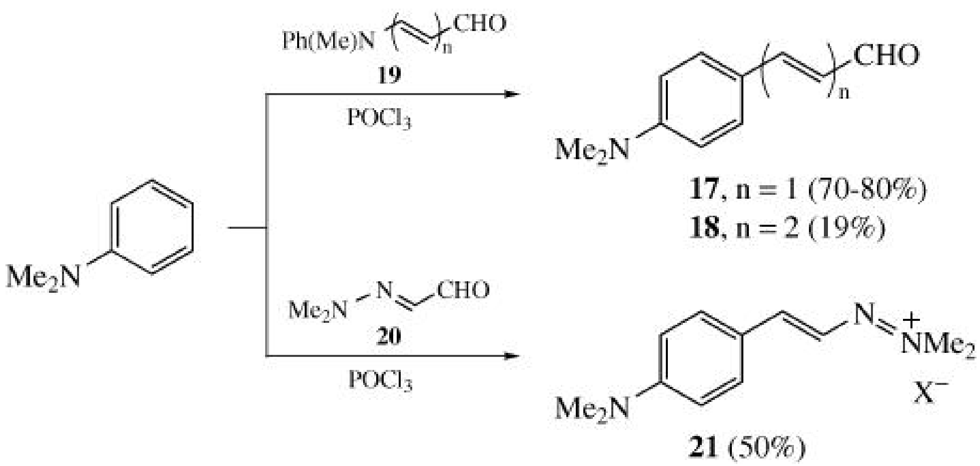
3.1. Monosubstituted Benzenes

A powerful activating group is normally required to achieve a successful Vilsmeier reaction on monosubstituted benzene derivatives. Most reactions have been performed on *O*-alkylated phenols and *N,N*-dialkylated aniline derivatives. Thioanisole has been reported to give 4-formylthioanisole in low yield. (30) *N,N*-Dimethylaniline offers representative examples of most of the reagents used for simple formylation and acylation reactions (Eq. 10). The reagents range from the



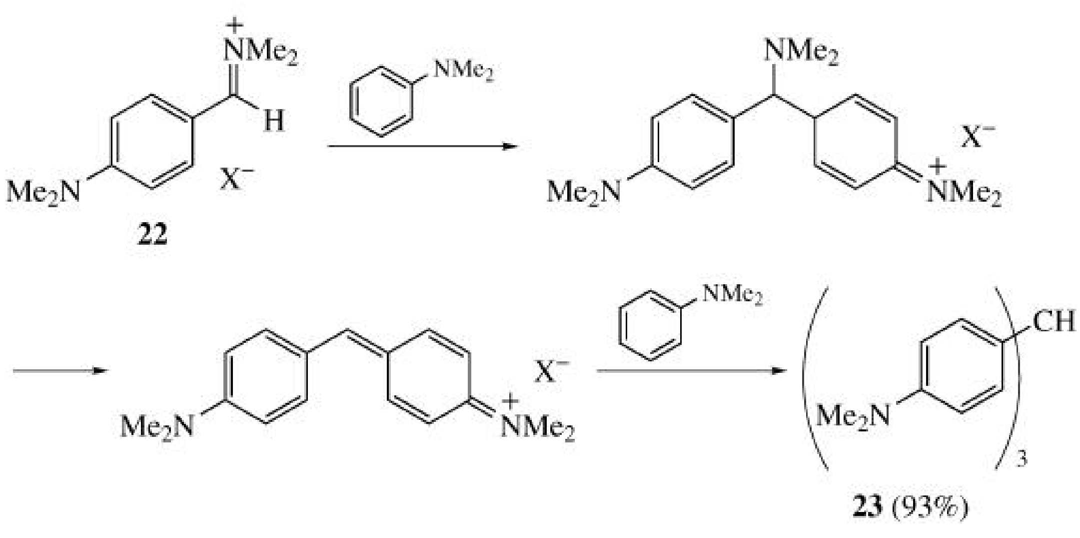
(10)

most commonly used mixture of DMF and phosphoryl chloride (maximum reported yield 85%); (31, 32) to the recent pyrophosphoryl chloride and DMF mixture reported to give 4-formyl-*N,N*-dimethylaniline **(4)** in 99% yield. (26) Diformylation of *N,N*-dimethylaniline has been reported with an excess of DMF and phosphoryl chloride to give a low yield of 2,4-diformyl-*N,N*-dimethylaniline together with the monoformylated product **4**. (33) Other acid chlorides which have been used in this formylation reaction include carbonyl chloride, (31) thionyl chloride (with (34) or more commonly without (31) aluminum trichloride), triphenylphosphine dibromide, (35) and the acid chloride equivalent, 2,4,6-trichloro-1,3,5-triazine. (36) Reaction with dimethylacetamide (DMA) (33) gives 4-acetyl-*N,N*-dimethylaniline **(15)** in poor yield, but moderate to good yields of benzophenone derivatives **16** have been obtained with benzamides (Eq. 10). (37) The synthesis of cinnamaldehyde derivative **17** (38) and dienal derivative **18** (39) from aldehyde **19** (cf. Eq. 7) and phosphoryl chloride illustrates an extension of the Vilsmeier reaction to the synthesis of α , β -unsaturated aldehydes and their homologues (Eq. 11). The aza-analogue **20** of aldehyde **19** yields iminium salt **21** (Eq. 11). (40)



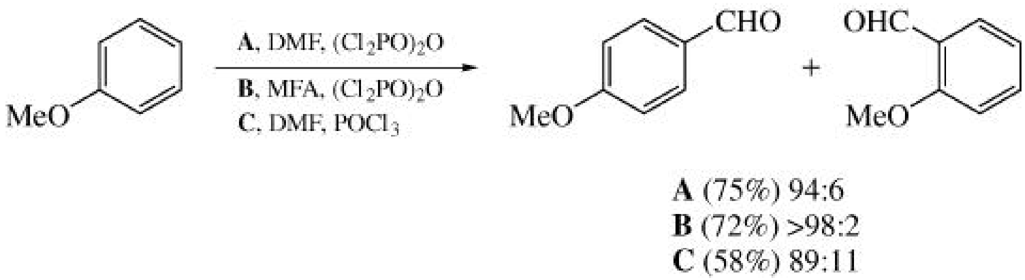
(11)

The iminium salt **22** formed by the action of DMF and phosphoryl chloride on *N,N*-dimethylaniline has been reacted with *N,N*-dimethylaniline to give the substituted triphenylmethane derivative **23** (Eq. 12). (41)



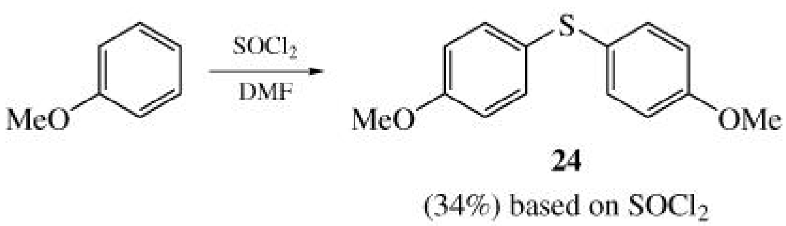
(12)

No authors quote any lack of regioselectivity in the reactions of *N,N*-dimethylaniline. Recent studies of the reaction of anisole (Eq. 13) have shown



(13)

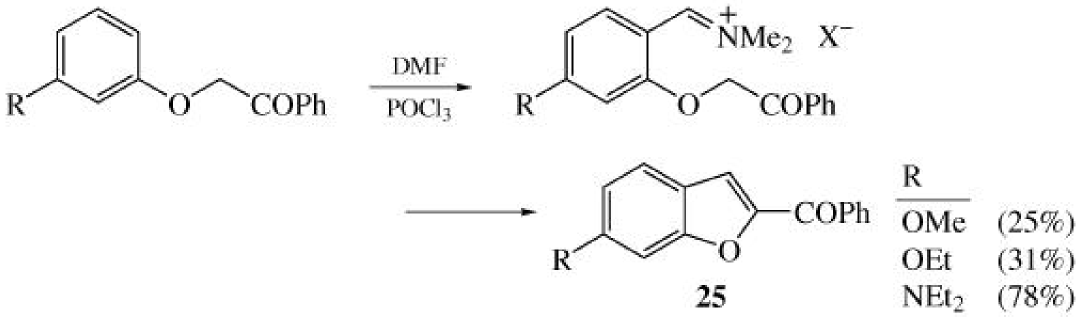
that in this less-hindered substrate, perceptible amounts of the 2-formyl isomer can be formed. Not surprisingly, the steric demands of the reagent influence the ratio of 4- and 2-substituted products (26) so that pyrophosphoryl chloride and DMF give a 94:6 ratio, whereas *N*-methylformanilide (MFA) gives a ratio greater than 98:2. (26) The conventional DMF and phosphoryl chloride gave, in the hands of these authors, a ratio of 89:11, but with a much poorer yield. Thionyl chloride and DMF give the sulfur-containing product **24** with anisole, and other ethers react similarly (Eq. 14). (42)



(14)

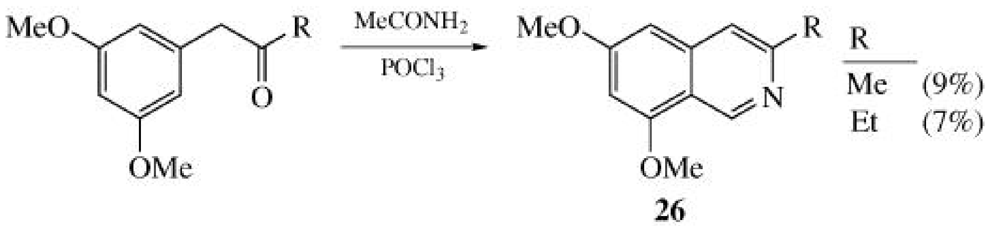
3.2. Di- and Polysubstituted Benzenes

Regioselectivity becomes more important with di- or polysubstitution. A second factor which can give rise to abnormal products is the presence of an appositely located group which can react intramolecularly with the primary product to give a new ring system, as illustrated for the production of benzo[*b*]furans **25** (Eq. 15). (43) Benzo[*b*]thiophenes can be formed in a similar process. (44) Other products

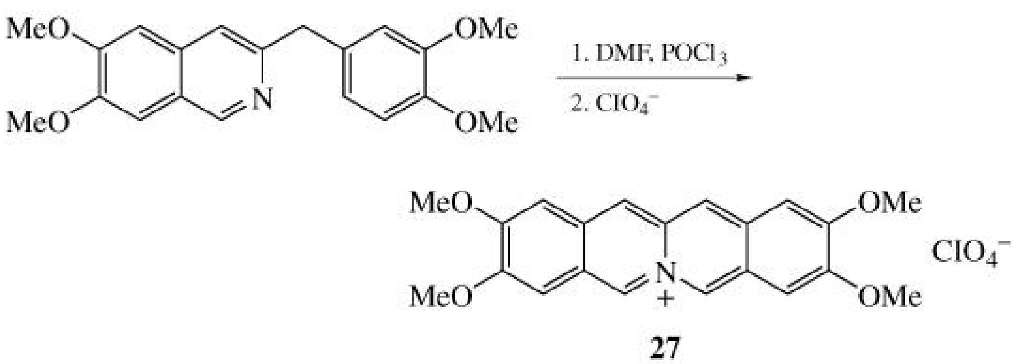


(15)

formed by intramolecular cyclizations include isoquinolines **26** (Eq. 16) (45) and salt **27** (Eq. 17). (46) The formation of isoquinolines **26** provides an interesting



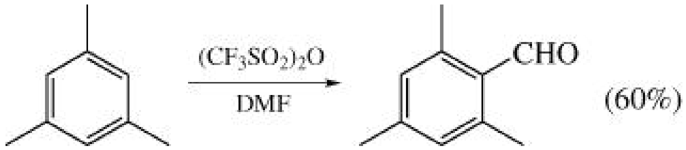
(16)



(17)

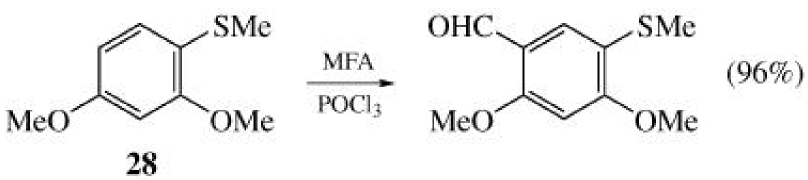
application of a cyclization reaction because the nitrogen of the Vilsmeier reagent is retained in the product. However, the yield in these cyclizations is often quite low.

The lowest degree of activation reported to give successful formylation is shown by 1,3,5-trimethylbenzene (Eq. 18), which is formylated by a mixture of



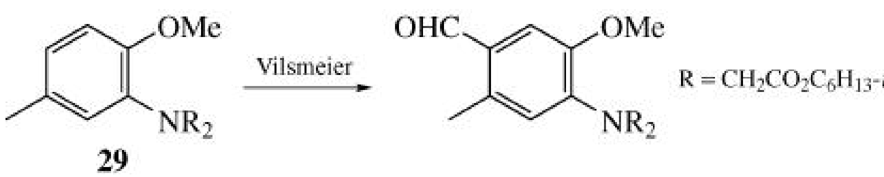
(18)

DMF and trifluoromethanesulfonic anhydride. (47) The position of substitution is normally predictable by considering the relative directing power of the substituents, as illustrated for the trisubstituted benzene derivatives **28** (48) (Eq. 19) and



(19)

29 (49) (Eq. 20), but can be modified by steric factors, as shown by the formation of the 6-formyl derivative **30** from 3-*tert*-butylanisole (Eq. 21). (50) In a number of



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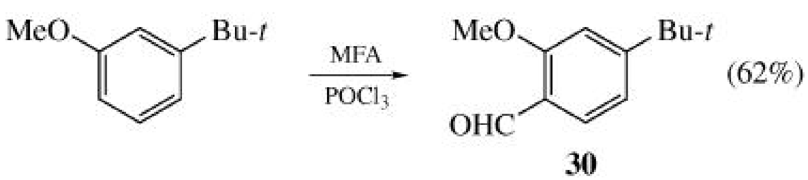
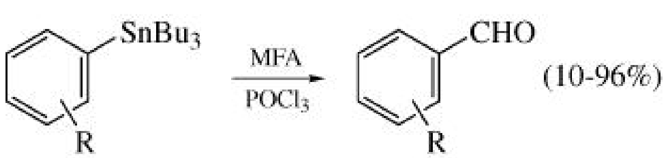


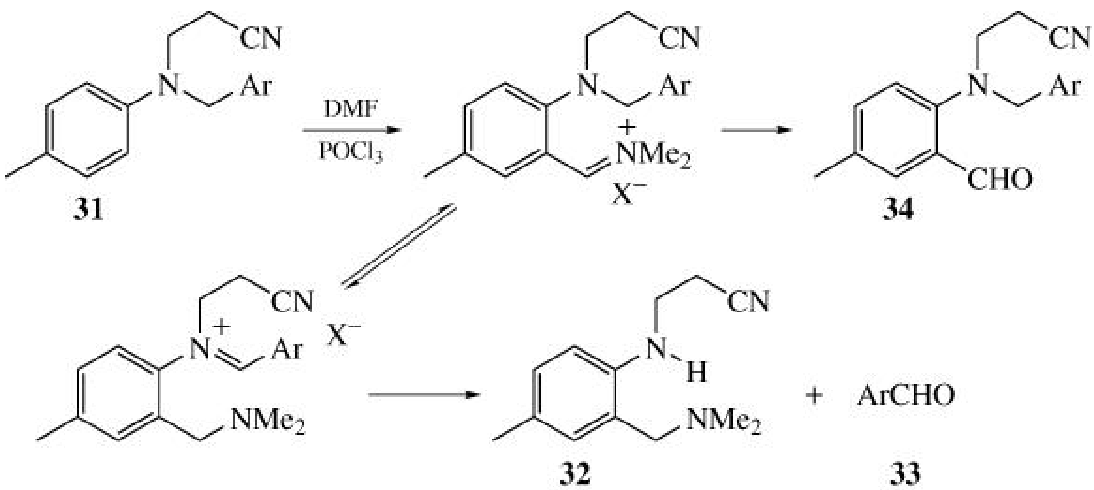
(21)

cases, a free phenolic hydroxy group has been reported to exercise direction over a methyl ether, but yields were low and other products may have been formed. (51, 52) High regioselectivity can be achieved when the Vilsmeier reagent replaces the tributylstannyl group (Eq. 22). (53)



(22)

An interesting reaction of substituted *N*-benzyl-4-methylaniline derivatives **31** has been reported (Eq. 23). (54, 55) If the benzyl substituent is relatively electron

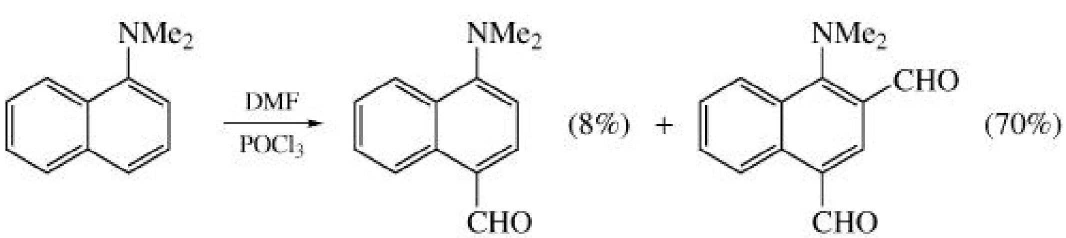


(23)

rich, hydride transfer is the major reaction, yielding amine **32** and aldehyde **33**. When the benzyl group is relatively electron deficient, aldehydes **34** are the major products.

3.3. Naphthalenes and Polycyclic Benzenoid Hydrocarbons

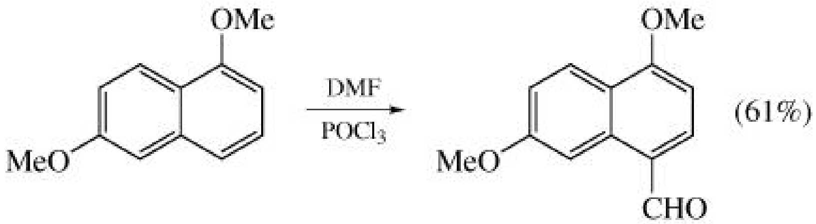
Naphthalene has not been reported to undergo formylation with the usual DMF and phosphoryl chloride mixture, but with the more potent combination of DMF and trifluoromethanesulfonic anhydride, naphthalene-1-carbaldehyde is produced in 50% yield. (47) The presence of a single activating substituent, as in *N,N*-dimethylaminonaphthalene, has been reported to give up to 70% of diformylated product as well as the monoformylated product (Eq. 24). (56)



(24)

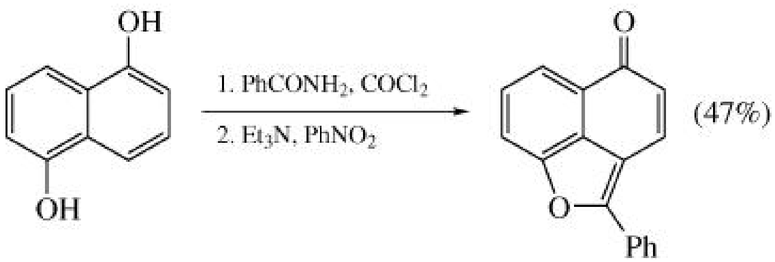
The pattern of entry of the reagent is that normally found in naphthalenes possessing electron-rich substituents (i.e., 1-substituents direct to the 4-position and 2-substituents direct to the 1-position). It has been reported that

1,6-dimethoxynaphthalene gives 4-formylation with DMF and phosphoryl chloride; (57) previous work had indicated 5-formylation with MFA and phosphoryl chloride (Eq. 25). (58)



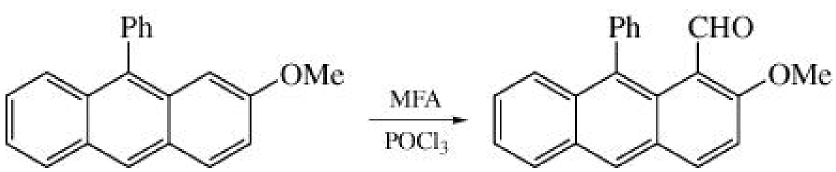
(25)

Pericyclization has also been reported (Eq. 26). (59)



(26)

Anthracene gives anthracene-9-carbaldehyde in the Vilsmeier reaction (60) with MFA and phosphoryl chloride, and many other formylating mixtures also yield this product. A methoxy group provides sufficient activation to allow substitution to occur at other positions (Eq. 27). (50) Phenanthrene gives a poor yield of phenanthrene-3-carbaldehyde with the potent trifluoromethanesulfonic anhydride

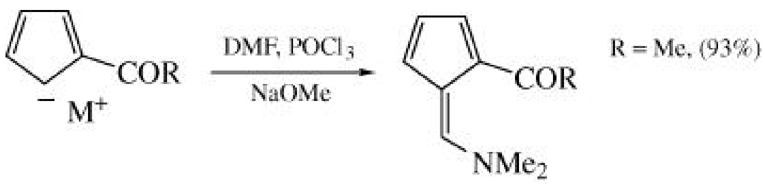


(27)

and DMF mixture, (47) and 3-methoxyphenanthrene gives a moderate yield of 3-methoxyphenanthrene-9-carbaldehyde. (61)

3.4. Nonbenzenoid Aromatic Hydrocarbons

Derivatives of the cyclopentadienyl anion and its benzologues react with the simple Vilsmeier reagent (Eq. 28) (62) or with various vinylogous equivalents such as the polymethyleniminium salt **35** (Eq. 29) (63) to give fulvene derivatives. By



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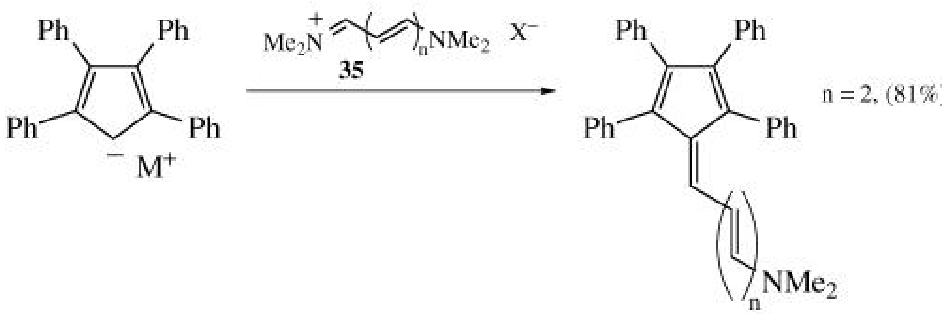
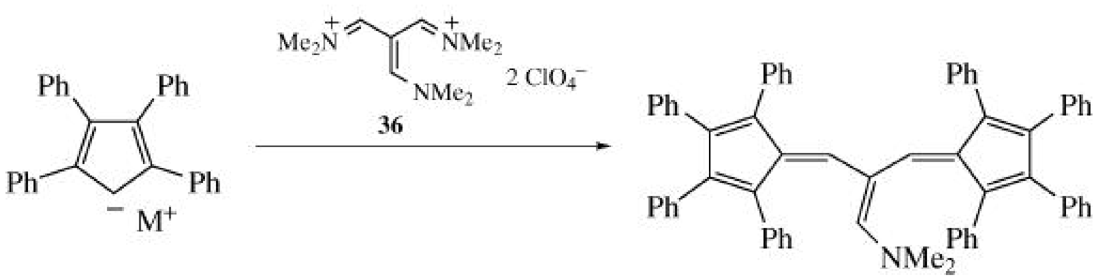


(29)

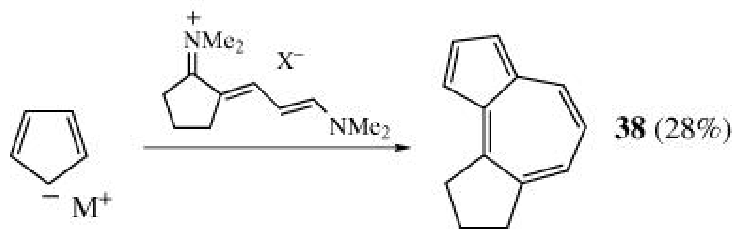
using the cross-conjugated reagent **36**, it is possible to prepare a variety of linked products such as compound **37** (Eq. 30). (63) The presence of a second potential



37 (89%)

(30)

electrophile in the reagent allows cyclization to occur, resulting in the formation of a new ring, as exemplified by the production of the azulene derivative **38** (Eq. 31) (64) and pyrene (Eq. 32). (65)



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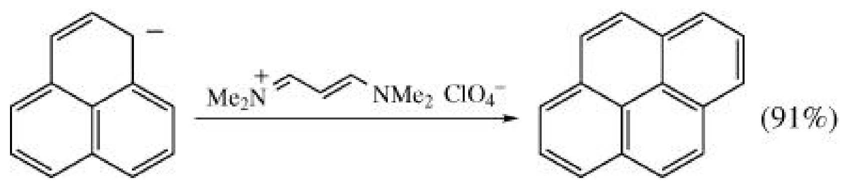
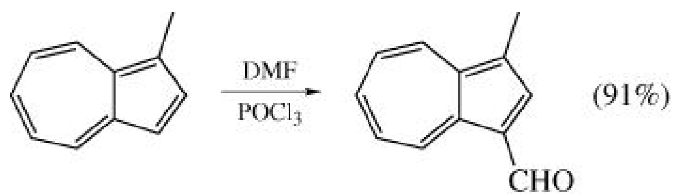


(32)

Azulenes are the most comprehensively studied bicyclic nonbenzenoid aromatic hydrocarbons and yield 1-substituted products, often in excellent yields (Eq. 33). (66) The reactivity of the azulene ring is sufficient to allow the preparation of ketone derivatives (Eq. 34), (67) acraldehydes, or pentadienaldehydes (Eq. 35). (68)



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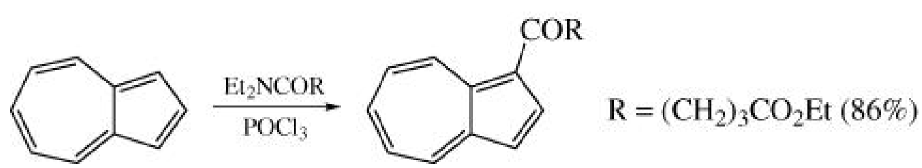
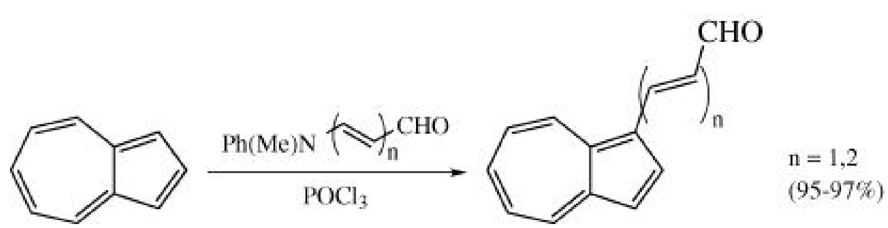
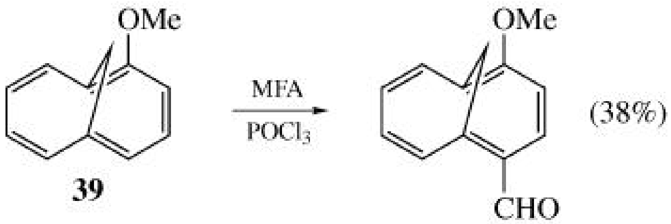


(34)



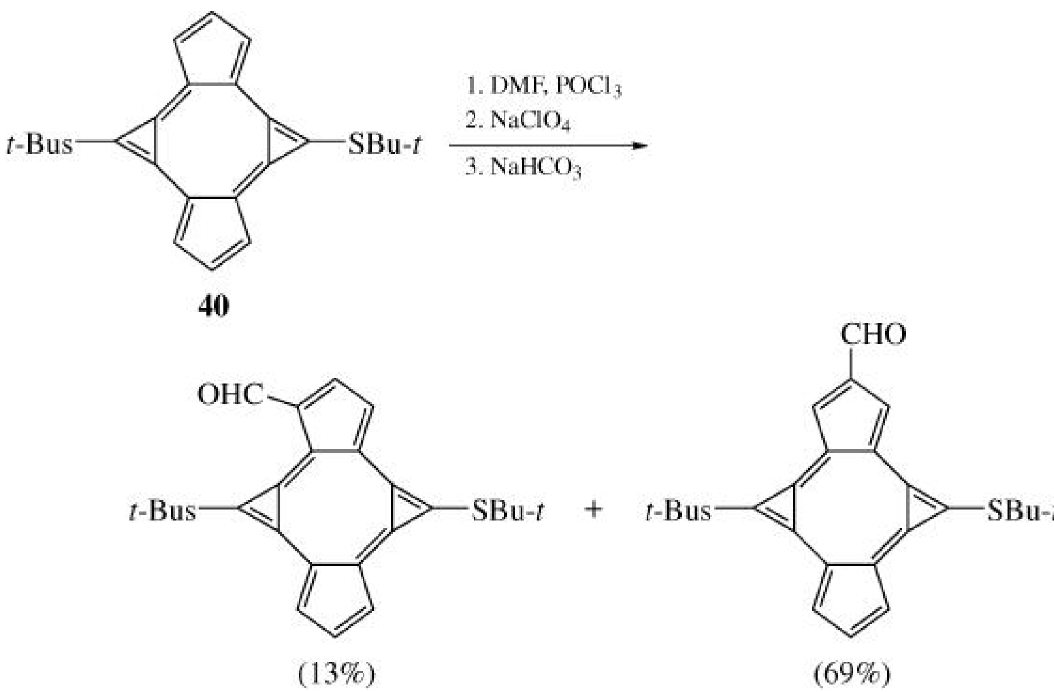
(35)

The bridged 10 π -annulene derivative **39** gave a modest yield of the 4-formyl derivative (Eq. 36) (69) and the polycyclic compound **40** afforded a mixture of formylated products (Eq. 37). (70)



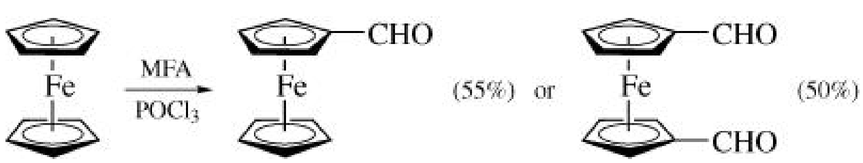
39

(36)



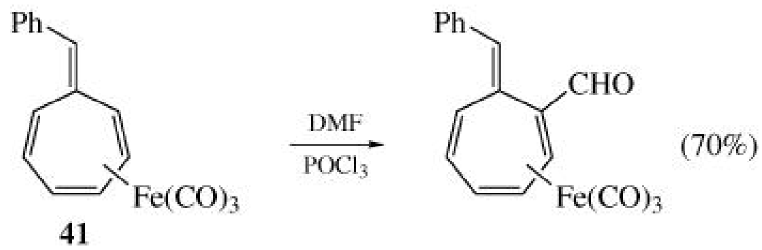
(37)

Organometallic compounds react normally, and examples include mono- and diformylation of ferrocene (Eq. 38), (71) monoformylation of the cycloheptatrienyl



(38)

iron tricarbonyl compound **41** (Eq. 39), (72) diformylation of the biscyclobutadiene iron tricarbonyl compound **42** (Eq. 40), and monoformylation of the cobalt derivative **43** (Eq. 41). (73)



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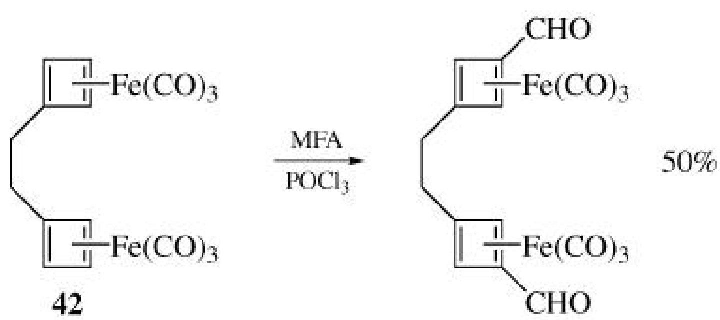

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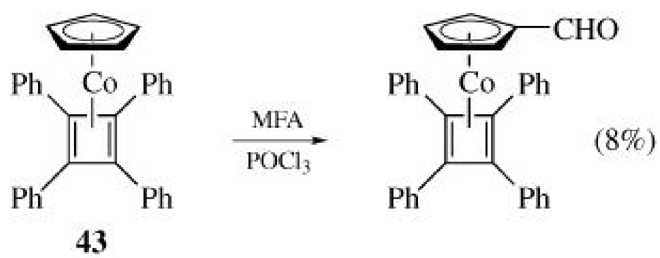
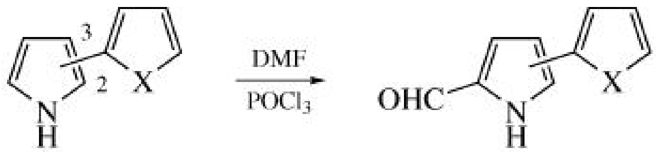


(41)

3.5. Furans, Thiophenes, Selenophenes, and Pyrroles

The extension of the Vilsmeier reaction from activated benzene derivatives to the electron-rich heterocycles furan, thiophene, selenophene, and pyrrole is well documented and the main interest is associated with the relative reactivities of these heterocycles and the regioselectivity within these systems, which is generally good.

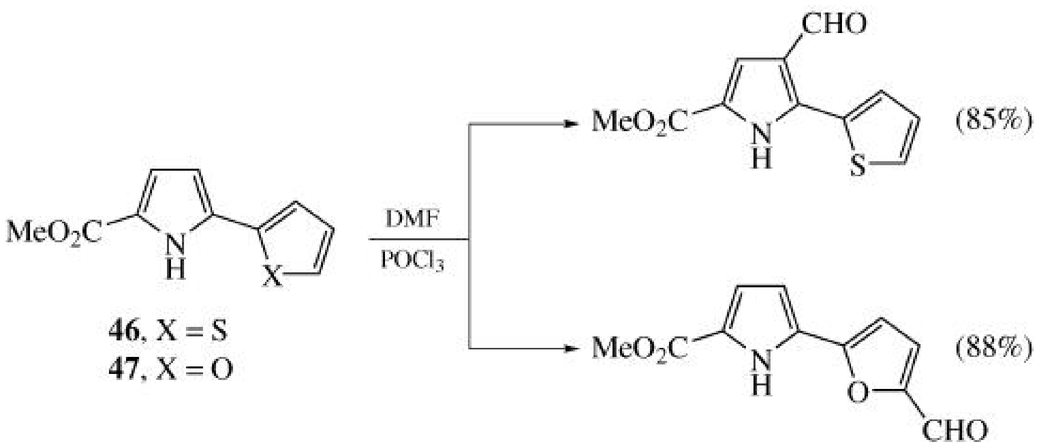
The relative reactivity of these electron-rich heterocycles is well established as pyrrole > furan > thiophene, and this has been confirmed (Eq. 42) by the



(42)

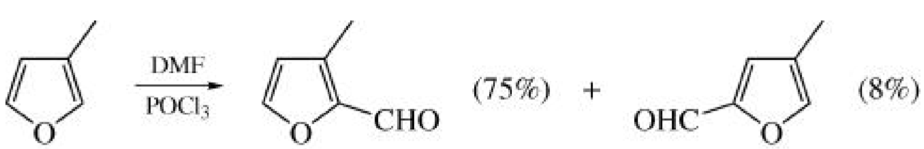
44, X = O, 2- or 3-substituted   X = O, 2-substituted (62%)
45, X = S, 2- or 3-substituted   X = O, 3-substituted (56%)

formylation of the pyrrolylfurans **44** (74) and pyrrolylthiophenes **45**. (74, 75) The pyrrolylfurans **44** also give a small quantity of diformylated products where formylation has occurred in both rings. (74) The presence of a deactivating ester group in the pyrroles **46** and **47** provides a more precise picture of relative reactivity where the deactivated pyrrole ring competes successfully against a thiophene ring but not a furan ring (Eq. 43). (74)



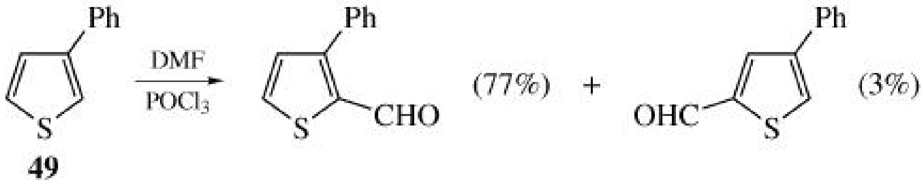
(43)

Regioselectivity within each group of heterocycles can be influenced by electronic or steric effects. Furans that possess a single substituent at the 2-position give uniformly 5-formyl derivatives, whereas substituents at the 3-position, such



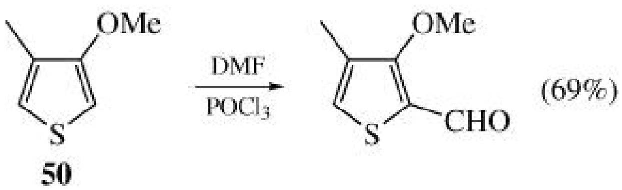
(44)

as compound **48**, produce, rather surprisingly, 2-formyl derivatives (Eq. 44). (76) Thiophene shows a similar pattern of substitution; 3-substituted compounds such as **49** give mainly products of formylation at the 2-position (Eq. 45). (77) In the

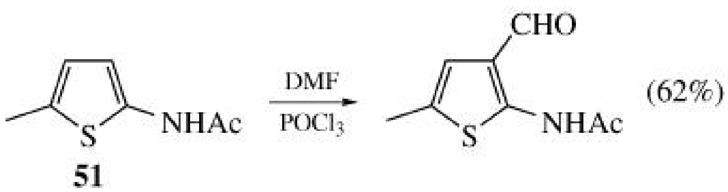


(45)

cases of 3,4- or 2,5-disubstituted thiophenes, the most strongly electron-releasing substituent determines the point of attack, as illustrated for compounds **50** (Eq. 46) (76) and **51** (Eq. 47). (78) The replacement of a 2-bromo substituent in compound

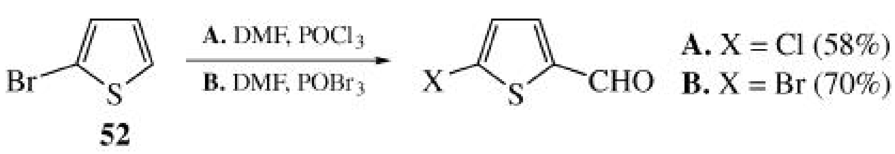


(46)



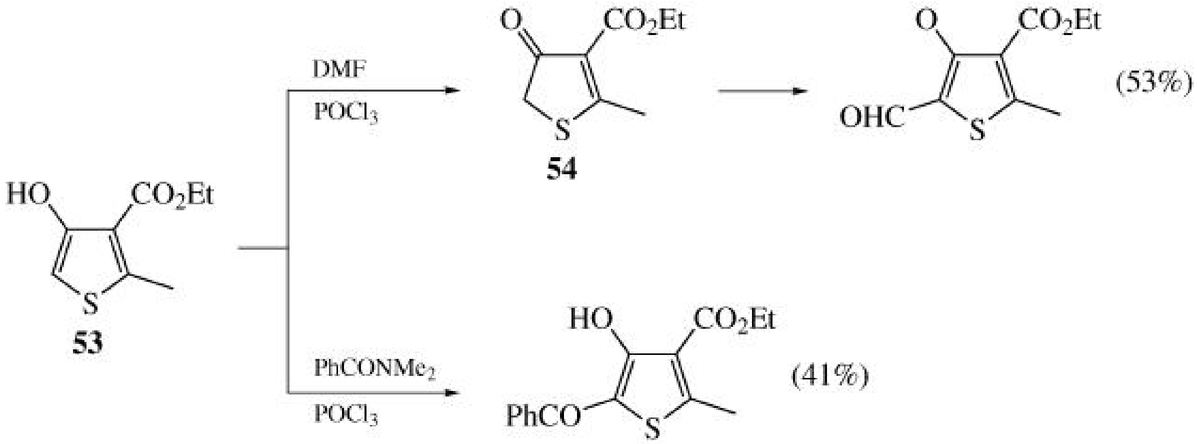
(47)

52 by chlorine has been reported (79) when DMF/phosphorus oxychloride was the formylating reagent, but this problem can be overcome (80) by using phosphorus oxybromide (Eq. 48); 3-bromothiophene appears stable to DMF and phosphorus oxychloride. (76)



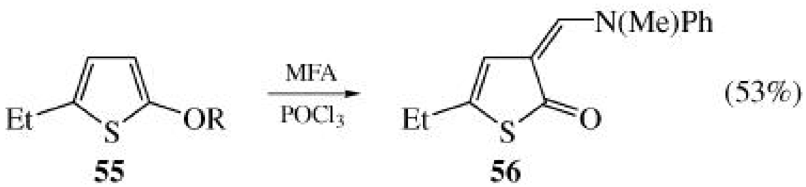
(48)

A hydroxy group has also been reported to be replaced by chlorine in the formylation of compound **53** (Eq. 49), (81) although not during benzoylation. (82) This is analogous to the reactions of acyclic and alicyclic keytones, and hence may indicate



(49)

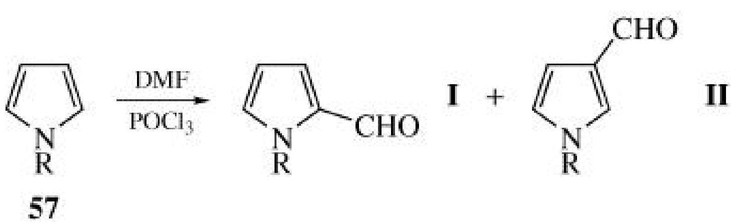
the intermediacy of the tautomeric dihydrothiophene-3-one **54**, which is behaving as an activated methylene compound. Dealkylation of 2-alkoxythiophenes **55** has been observed to give products **56** (Eq. 50). (83)



(50)

Selenophene reacts similarly to thiophene, with the same regioselectivity. (84)

Pyrroles have provided numerous substrates for Vilsmeier formylations or acylations with appropriate amide derivatives, and lactams have also been extensively used because of the importance of the products in the synthesis of pyrrole pigments. Included in a very large range of *N*-substituted pyrroles **57**, the isopropyl and *tert*-butyl derivatives provide good examples of steric hindrance forcing formylation to the normally unfavored 3-position (Eq. 51). (85)

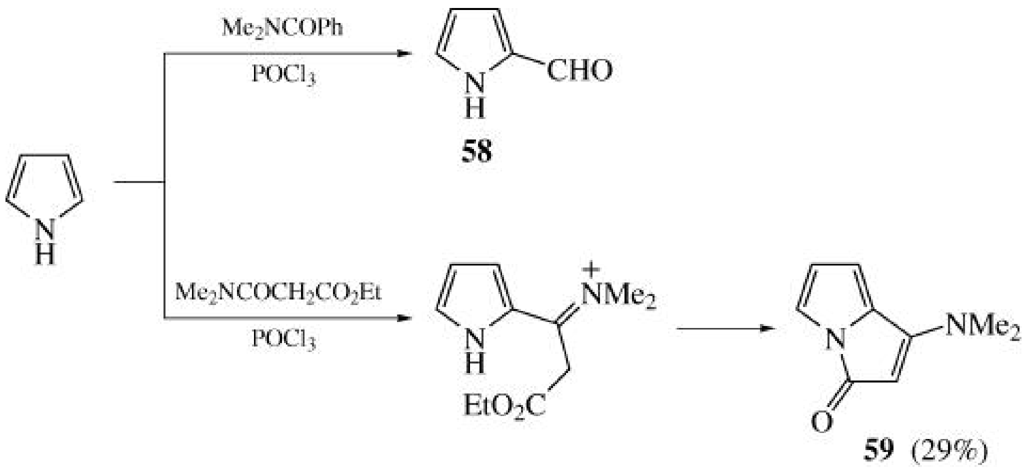


R	I	II
Me	(95%)	(0%)
i-Pr	(8%)	(71%)
i-Bu	(5%)	(64%)

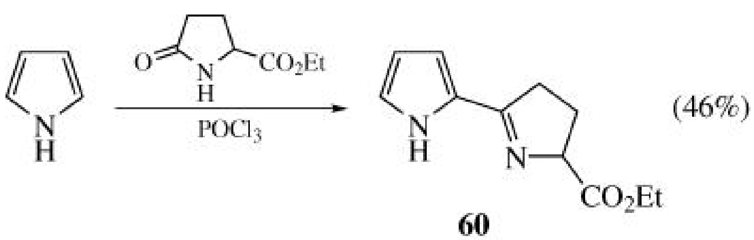
(51)

The greater reactivity of pyrrole has allowed the production of a wide range of product types, including ketones such as compounds **58** (86) and products such as compound **59** (87) (Eq. 52) (the latter example illustrating the production of bicyclic heterocycles), imines such as compound **60** (Eq. 53), (88) the bipyrrolyl derivative **61** (Eq. 54), (89) and the acraldehyde **62** (Eq. 55). (38)

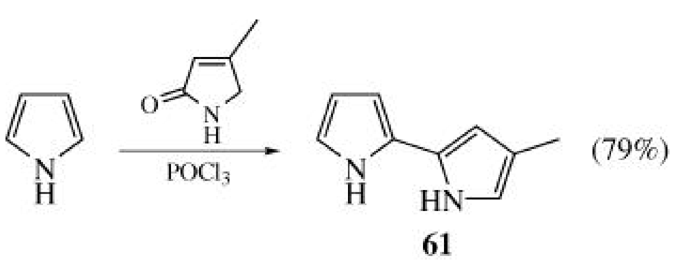
Pyrroles that are not substituted on nitrogen can be formylated, and the resulting iminium salts can then be deprotonated, giving azafulvene derivatives **63** (Eq. 56). (90) Azafulvene derivative **64** has been reacted with a variety of alkyllithium reagents to give pyrroles **65** (Eq. 57). (91) Some illustrative examples of the



(52)



(53)



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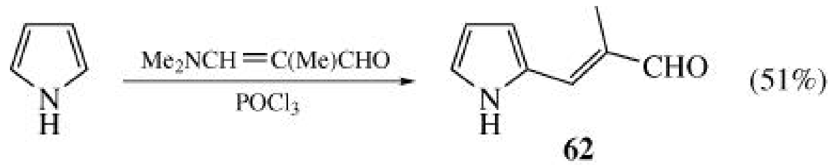
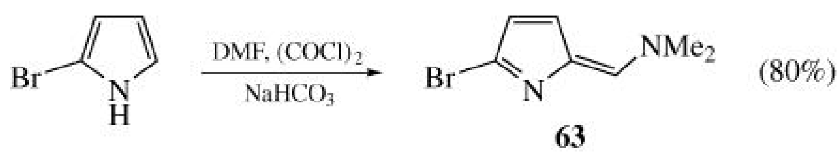
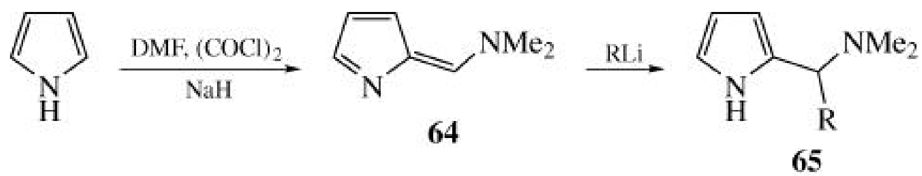


(55)

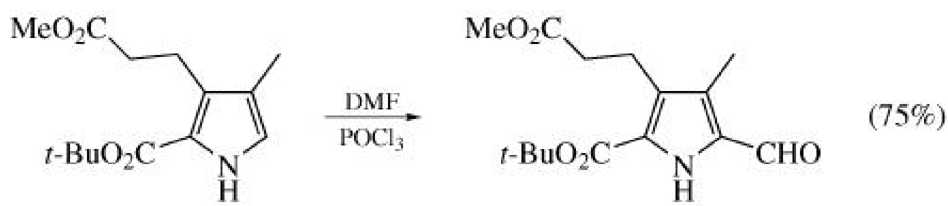


(56)

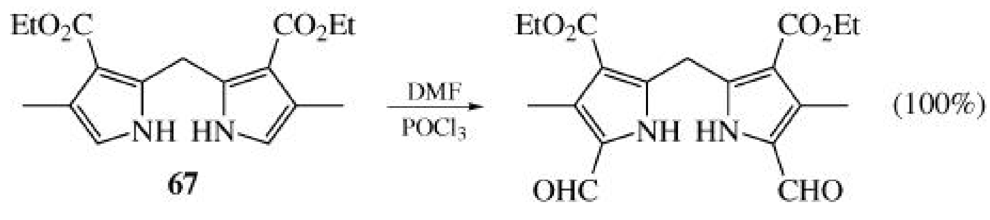


(57)

application of the Vilsmeier reaction to give intermediates for pyrrole pigments are provided by compounds **66** (Eq. 58) (92) and **67** (Eq. 59). (93)

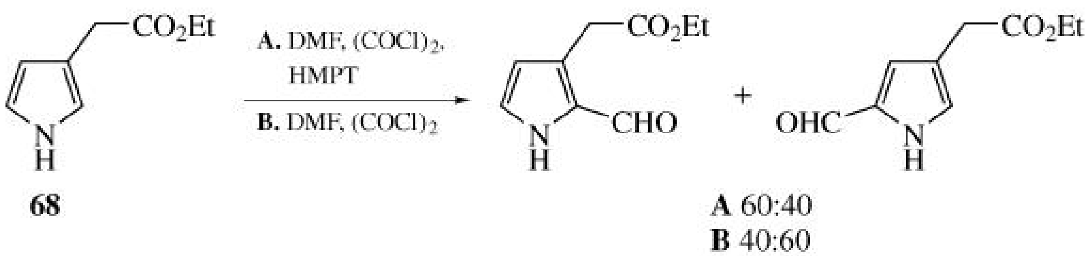


(58)



(59)

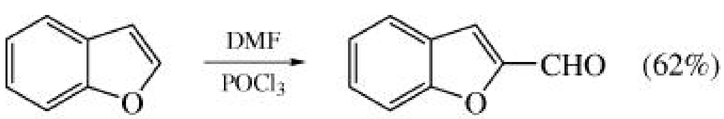
The presence of a 3-substituent in pyrrole gives less selectivity toward formylation at the 2-position than is observed with furan and thiophene. An interesting observation reported for the pyrrole derivative **68** is that the presence of 1 equivalent of hexamethylphosphoric triamide (HMPT) changes the ratio of 2- and 5-substitution (Eq. 60), and the reaction can be conducted at lower temperature. (94)



(60)

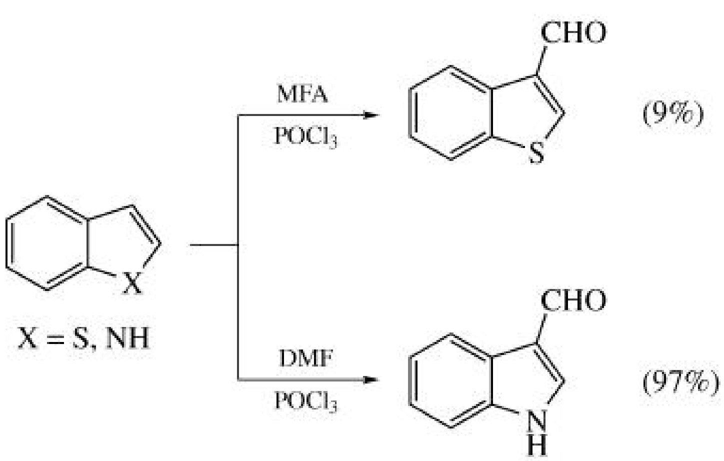
3.5.1. Annulated Furans, Thiophenes, and Pyrroles

Benzo[*b*]furan participates in the Vilsmeier reaction giving benzo[*b*]furan-2-carbaldehyde (95) (Eq. 61),

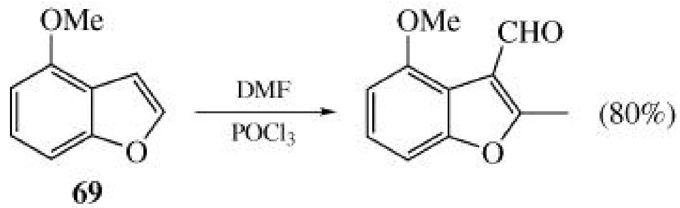


(61)

whereas benzo[*b*]thiophene (96) and indole (97) undergo substitution at the 3-position (Eq. 62). The presence of appropriate substituents can allow changes in regioselectivity and provides an approximate guide to relative reactivities. Thus, in benzo[*b*]furan, a methoxy substituent in the benzene ring of compound **69** is not

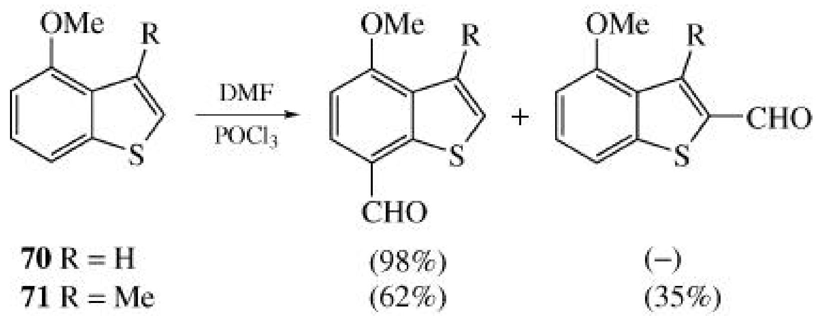


(62)



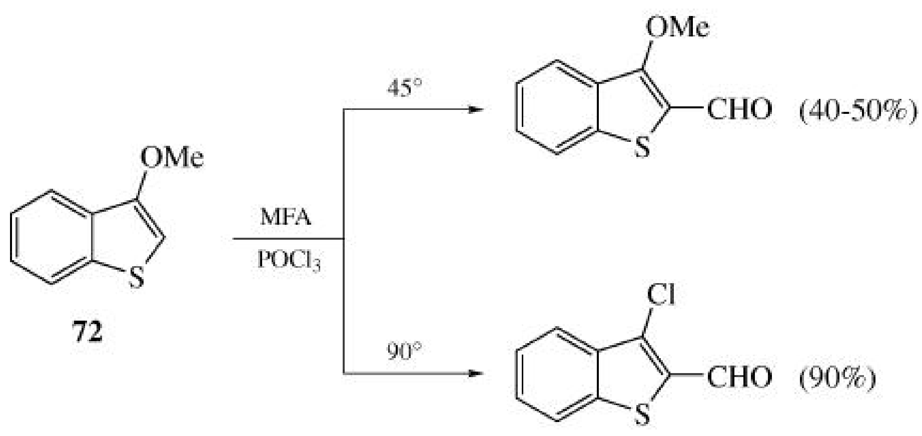
(63)

sufficiently activating to direct formylation away from the furan ring (Eq. 63), (98) whereas in the related benzo[*b*]thiophene derivatives **70** and **71**, formylation does occur in the benzene-ring fragment of the molecule (Eq. 64). (99) For



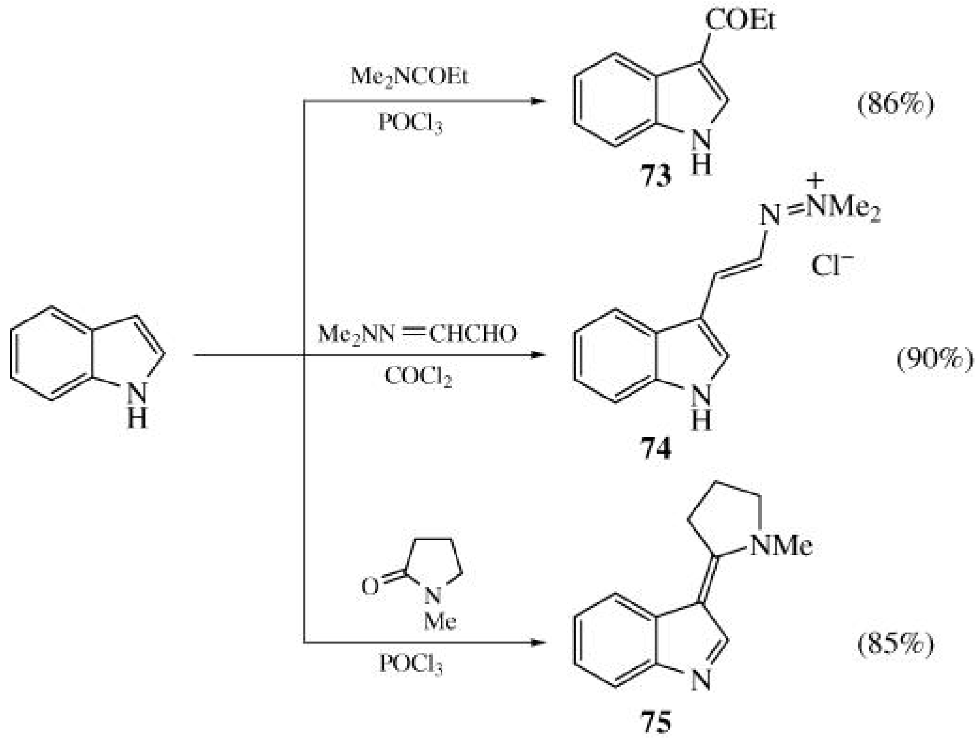
(64)

3-methoxybenzo[*b*]thiophene (**72**), a normal formylation is observed at 45° and an abnormal formylation in which the methoxy substituent is replaced by chlorine at 90° (Eq. 65). (100)



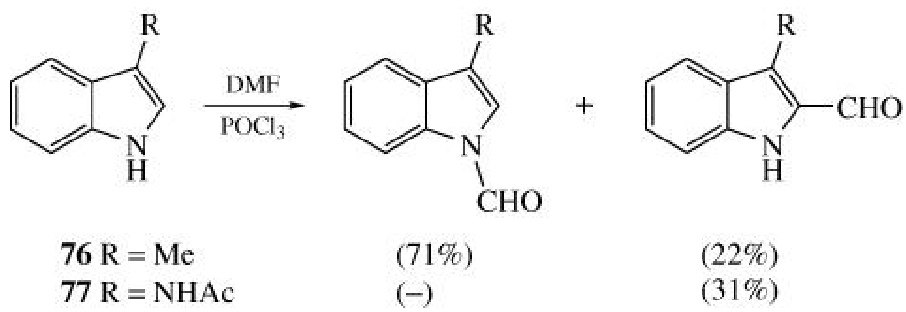
(65)

Indole has the highest reactivity, and a large number of substituents have been introduced into the 3-position, as exemplified by the preparation of compounds **73**, (101) **74**, (40) and **75**; (102) the last example illustrates that indolenines can be isolated (Eq. 66). There is a report (103) that a trace of 1-acetylindole is formed when indole



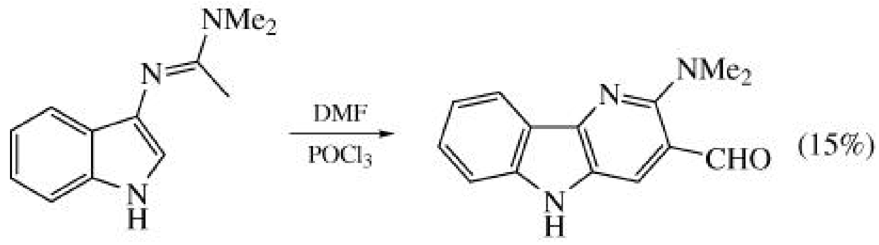
(66)

is treated with DMA and carbonyl chloride, but only in the ratio 2:98 against the expected 3-acetylindole. Substituents at the 2-position do not affect the normal 3-substitution, but a substituent in the 3-position generally produces predominantly *N*-formylation (or acylation), as illustrated for skatole **76** (Eq. 67), (104) unless the substituent has a strong activating effect, as shown for 3-acetylaminoindole



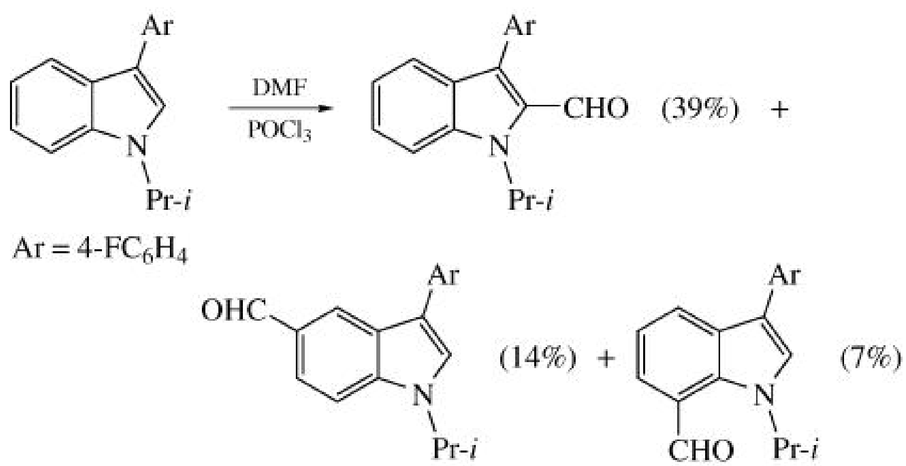
(67)

(**77**), in which case substitution at the 2-position occurs (Eq. 67). (104, 105) Compound **78** gave heterocycle **79** (Eq. 68). (106)



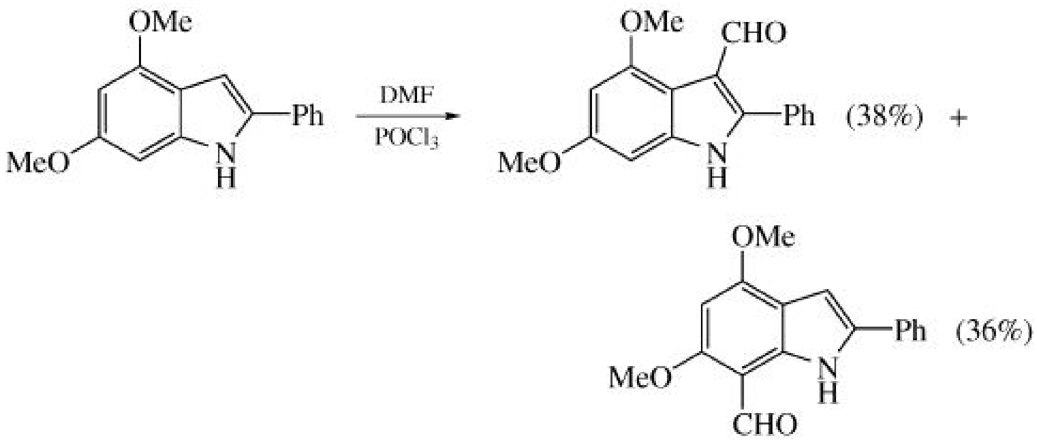
78 79 (68)

There are no reports of single substituents in the benzene ring that can override the normal 3-substitution in indole. High yields of 2-formyl indole derivatives are obtained from 1,3-disubstituted indoles, (107, 108) but if the two substituents produce a large degree of steric obstruction, a mixture of formylated products results (Eq. 69). (108) With two reinforcing methoxy substituents in the benzene ring



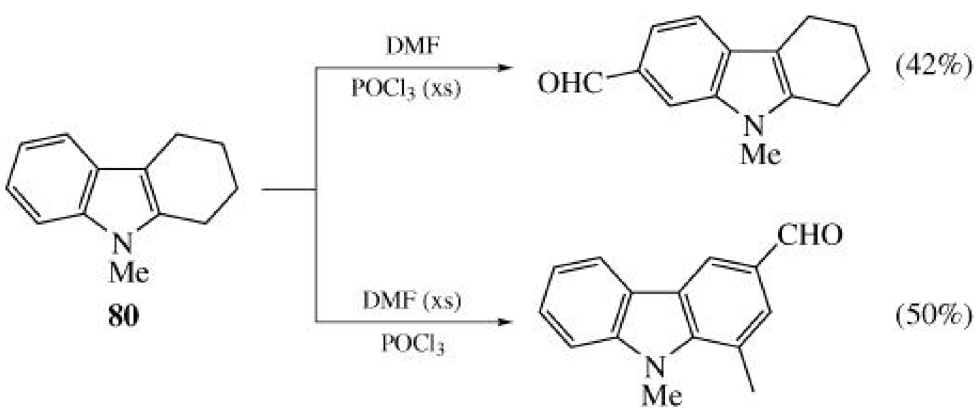
(69)

and a degree of steric obstruction at the 2 position, a mixture of products derived from substitution in both the benzene and pyrrole rings is observed (Eq. 70). (109)



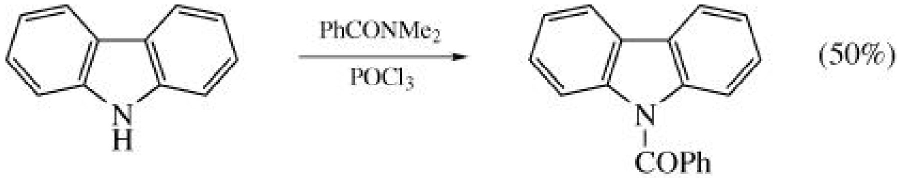
(70)

Tetrahydrocarbazole derivatives undergo a wealth of unusual transformations in which the product distribution is very sensitive to the reaction conditions, and this is illustrated for 1-methyltetrahydrocarbazole (**80**) (Eq. 71). (110)



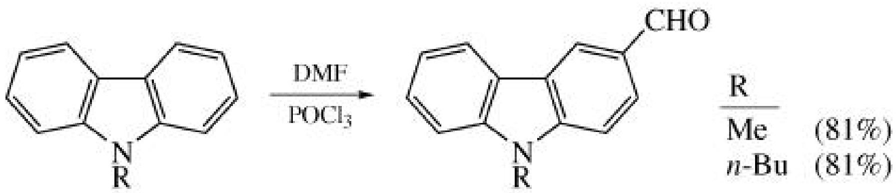
(71)

Of the dibenzo derivatives, carbazole has attracted some interest. Benzoylation is reported to give the product of *N*-substitution **81** (Eq. 72), (111) but the normal substitution position is 3 or 6 (Eq. 73), (112, 113) unless an activating substituent directs to other sites, as illustrated for hydroxy derivatives **82** (Eq. 74). (114)

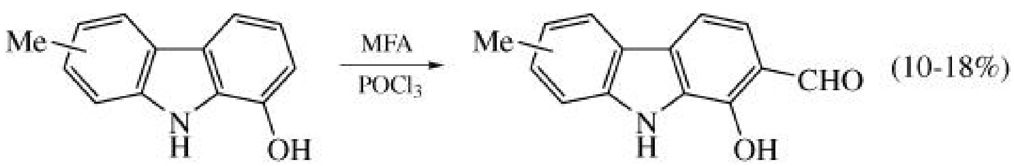


81

(72)



(73)

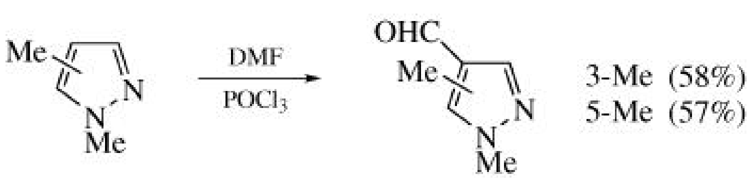


82

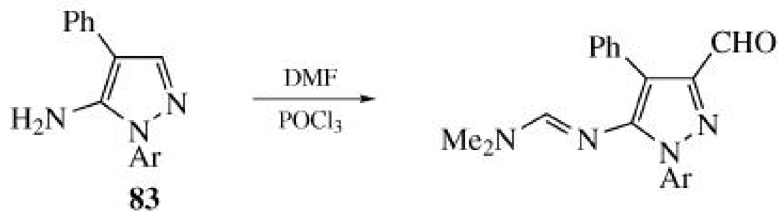
(74)

3.6. Other Heterocycles with One Fully Conjugated Ring

There are few examples of Vilsmeier formylation of common five-membered heterocycles with two heteroatoms. A range of 1-substituted pyrazoles has, however, been formylated, the simplest examples giving 4-formyl derivatives (Eq. 75). (115) A series of 1-aryl-4-phenyl-5-aminopyrazoles **83** gave products of ring formylation and amino substitution (Eq. 76). (116) Pyrazolone derivative **84** reacts normally, giving the expected aldehyde (Eq. 77). (117)
Pyrazol-5-ones

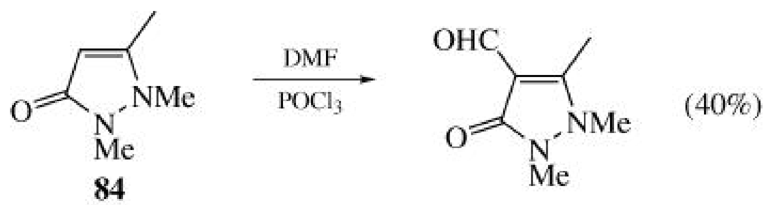


(75)



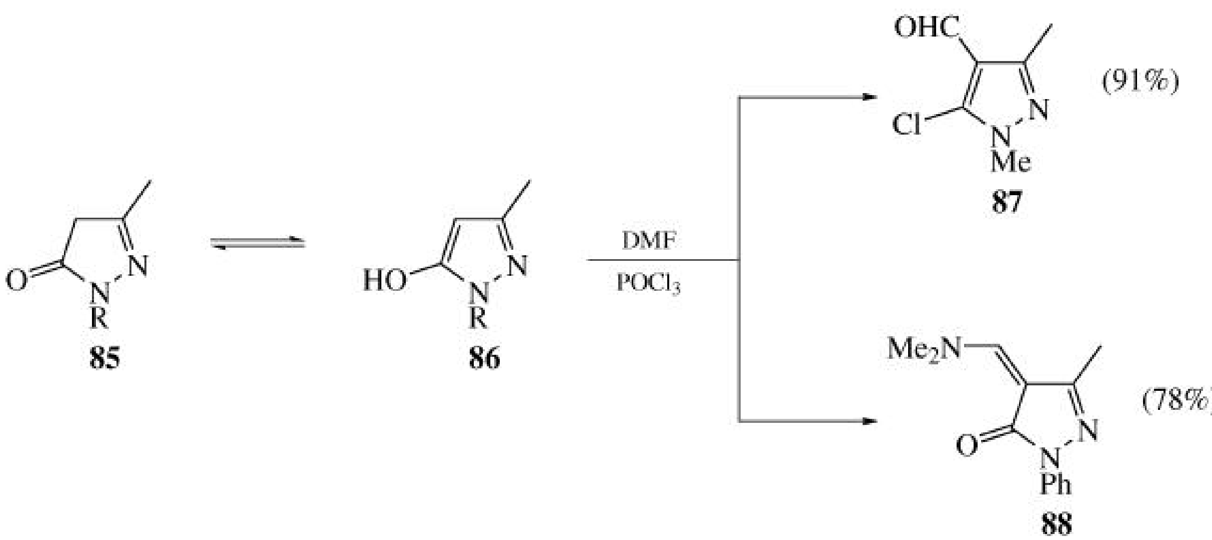
Ar	
Ph	(83%)
4-ClC_6H_4	(94%)
4-$O_2NC_6H_4$	(99%)
4-MeC_6H_4	(91%)
4-$MeOC_6H_4$	(74%)

(76)



(77)

85 can give 5-chloro-4-formyl derivatives such as compound **86**, (118) or 4-dimethylaminomethylene derivatives such as compound **87** (119) (Eq. 78). Although



(78)

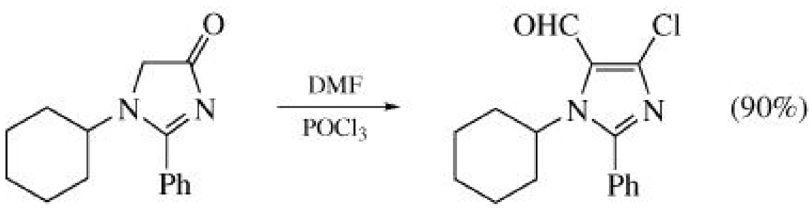
compound **85** is not fully conjugated, and its reactivity is similar to that of cyclic ketones and lactams, this system is conveniently dealt with in this chapter because its fully conjugated tautomer **88** may well be a reaction intermediate. Other potentially tautomeric systems are similarly considered in this chapter.

The reaction of imidazole derivative **89** (120) indicates that formylation of this ring system is possible (Eq. 79), and the imidazol-4-one derivative **90** gives a chlorocarbaldehyde product **91** (Eq. 80). (121)

89

Ar = 2,4-$Cl_2C_6H_3$

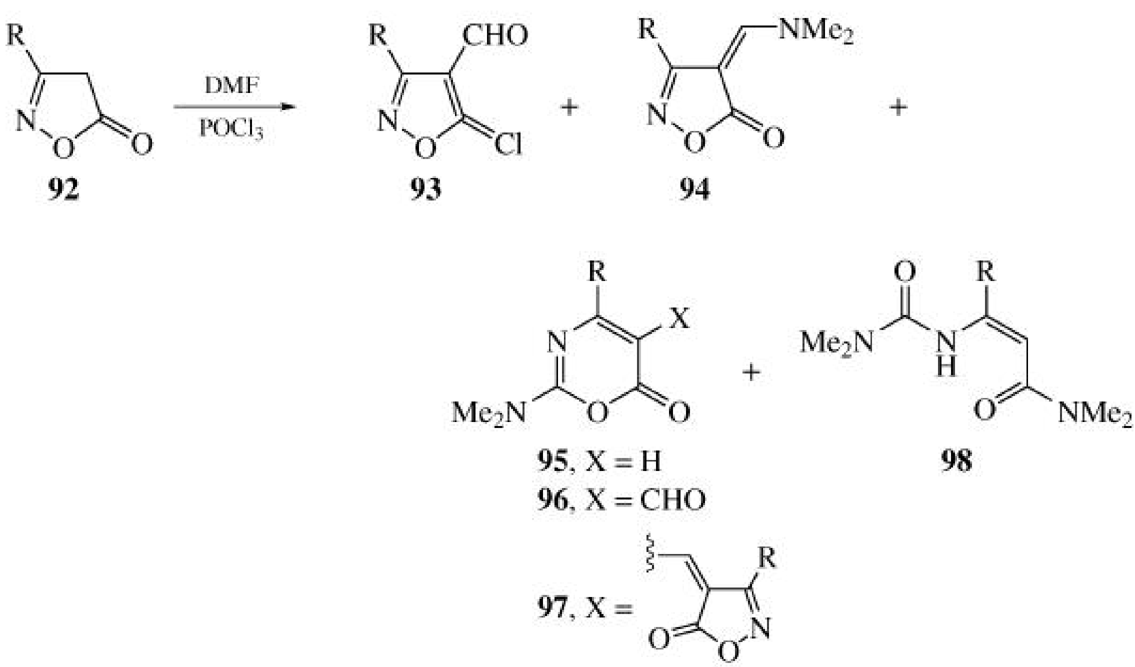
(79)



90 **91**

(80)

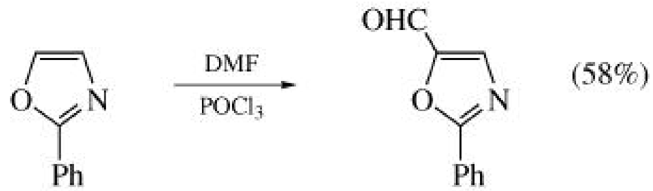
Isoxazol-5-ones **92** can give many types of products in the Vilsmeier reaction depending upon the reaction conditions (Eq. 81)). (122) Besides the expected products



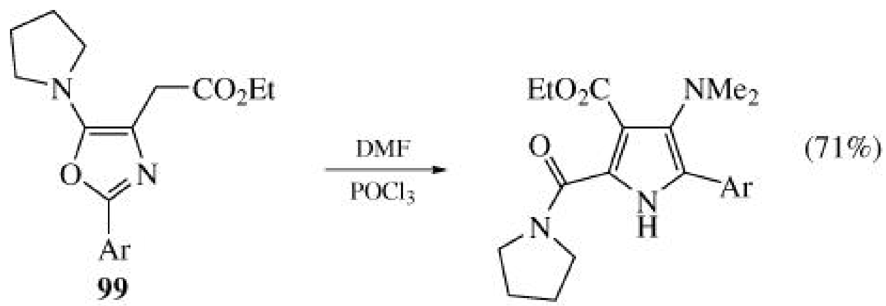
(81)

93 and **94** of the Vilsmeier reaction, ring-expansion products **95–97** and fragmentation products **98** can also be isolated. Normal formylation is observed for 2-phenyloxazole (Eq. 82), (123) and oxazole derivative **99**

underwent an interesting conversion giving pyrrole derivative **100** in the Vilsmeier reaction (Eq. 83). (124)



(82)



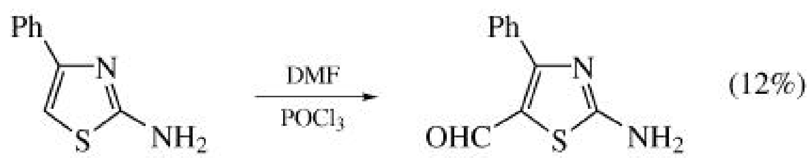
(83)

99

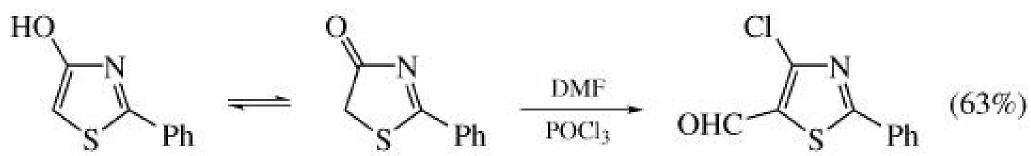
Ar = 4-ClC$_6$H$_4$

100

A low-yield formylation is reported for 2-amino-4-phenylthiazole (Eq. 84), (125) and thiazol-4-one derivative **101** gave the chloroaldehyde derivative **102** (Eq. 85). (121) Tetrazoles fragment with elimination of nitrogen (Eq. 86), (126) whereas sydnones give variable yields of formylated products (Eq. 87). (127)



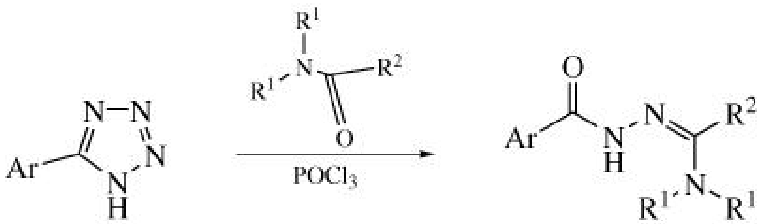
(84)



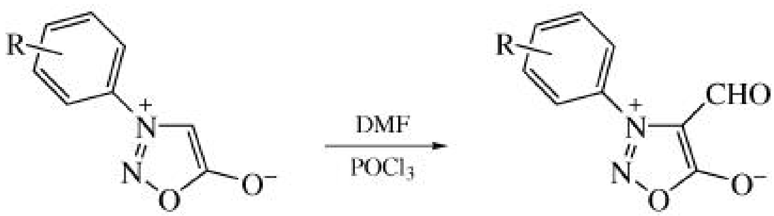
(85)

101

102



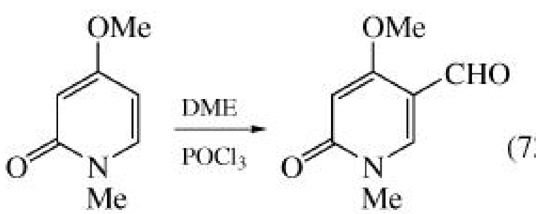
(58-83%) (86)



R	
4-MeO	(76%)
2-Me	(30%)
4-Me	(61%)
4-Cl	(34%)
4-Br	(40%)

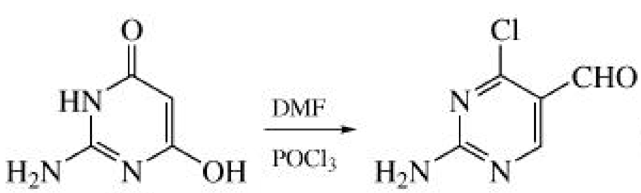
(87)

Six-membered heterocycles such as pyridine and pyrimidine require strongly electron-donating groups to be present for successful formylation. Most of the reported reactions involve pyridinones and pyrimidinones, and in substrates that have an electron-donating hydroxy group, conversion of this group to a chloro substituent is frequently observed. Examples are provided by the pyridinone **103** (Eq. 88) (128) and the pyrimidinone **104** (Eq. 89). (129) Cyclization is possible to a suitably placed phenyl ring, as illustrated for compound **105** (Eq. 90). (130)



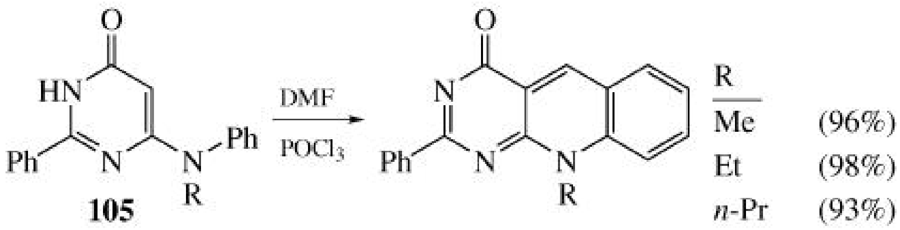
103

(73%) (88)



104

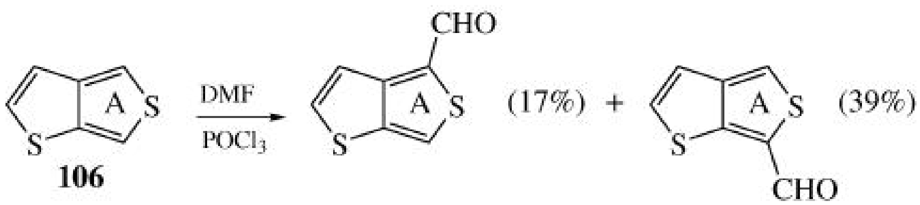
(80%) (89)



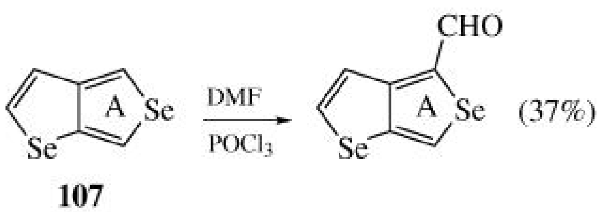
(90)

3.7. Other Heterocycles with Two Fully Conjugated Rings

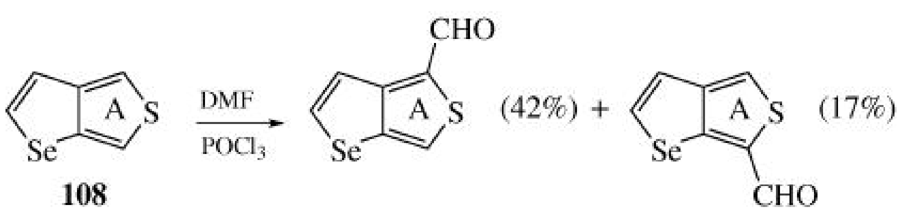
A wide variety of bicyclic heterocycles react with Vilsmeier reagents, particularly those with one or two five-membered rings. The simplest examples have two fused five-membered heterocyclic rings, and in these compounds substitution occurs predominantly as predicted by the parent monocyclic systems. Thus, thieno[2,3-*c*]thiophene (**106**) (Eq. 91), (131) its selenium analogue **107** (Eq. 92), (132)



(91)



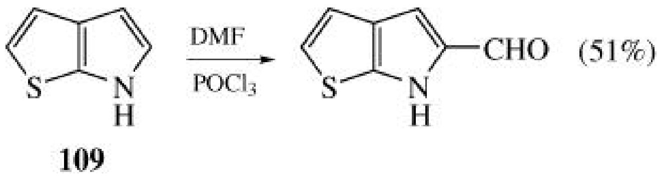
(92)



(93)

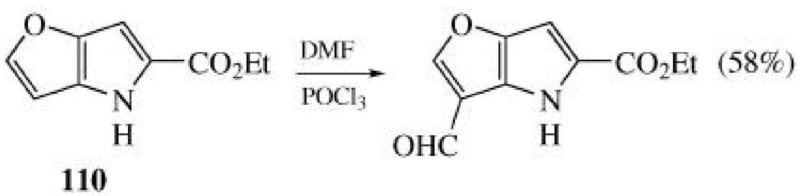
and thieno[3,4-*b*]selenophene (**108**) (Eq. 93) (133) all react to give mixtures of aldehyde products where substitution has occurred in ring A. Some ring-opening and degradation products are also reported with compound **107**.

Thieno[2,3-*b*]pyrrole (**109**) undergoes formylation mainly in the pyrrole ring as expected (Eq. 94), (134)



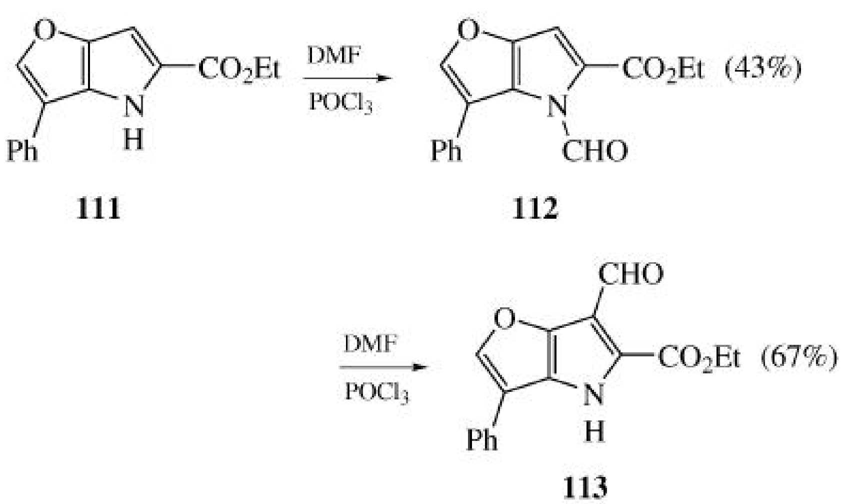
(94)

and traces of other formylated isomers are also obtained. The furo[3,2-*b*]pyrrole derivative **110** is formylated in the furan ring (Eq. 95), (135) and with the phenyl derivative



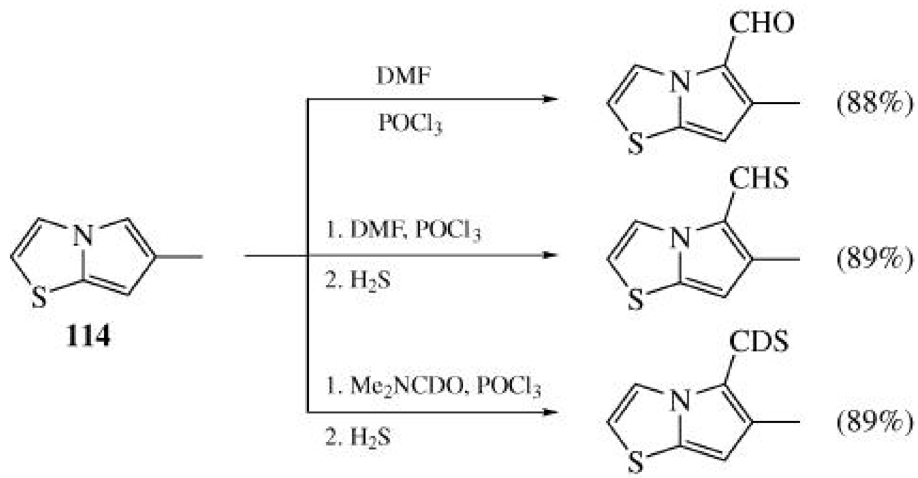
(95)

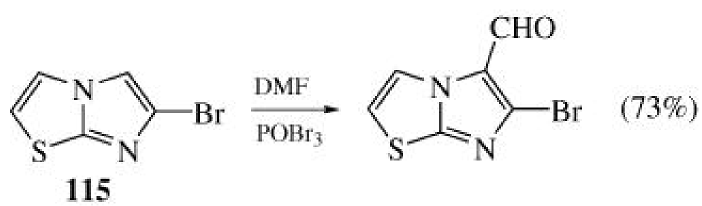
111 of compound **110** where the furan ring is blocked, formylation occurs first on the pyrrole nitrogen giving compound **112**, but eventually the thermodynamically more stable product **113** is obtained after a protracted reaction time (Eq. 96). (135)



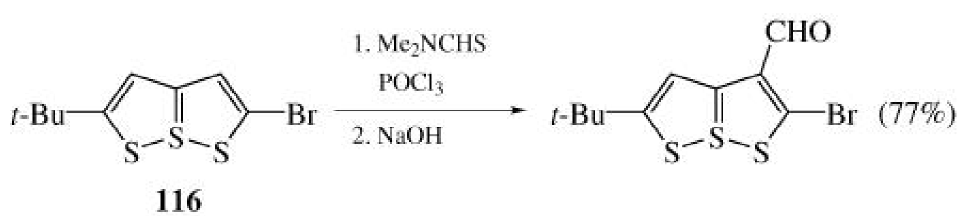
(96)

Bicycles with bridgehead nitrogen react well, as illustrated for compounds **114** (Eq. 97) (136) and **115** (Eq. 98). (137) Compound **114** also provides an example of the

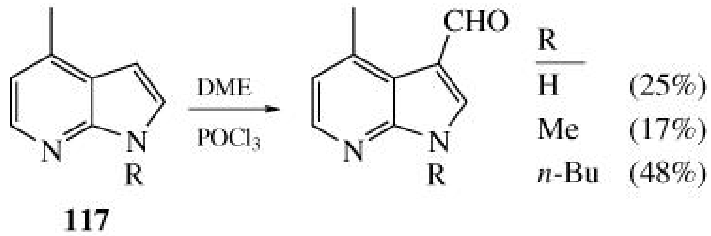
 (97)

 (98)

synthesis of a thioaldehyde and a deuterated thioaldehyde. Phosphoryl bromide was used in the reaction of compound **115** because of the potentially replaceable bromine substituent. Compounds with a bridgehead sulfur atom such as heterocycle **116** can also be formylated, although yields are commonly lower than that shown (Eq. 99). (138)

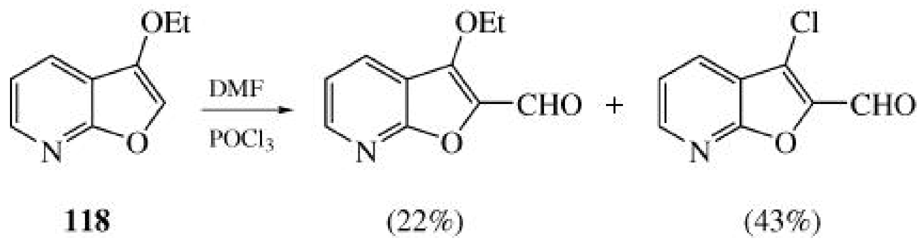
 (99)

Fusion of a six-membered ring to a five-membered ring (excluding those systems with a bridgehead nitrogen) leads predictably to substitution in the five-membered ring. Yields are usually lower than those for indole; the pyrrolo[2,3-*b*]pyridines **117** illustrate the range of yields achieved (Eq. 100). (139)

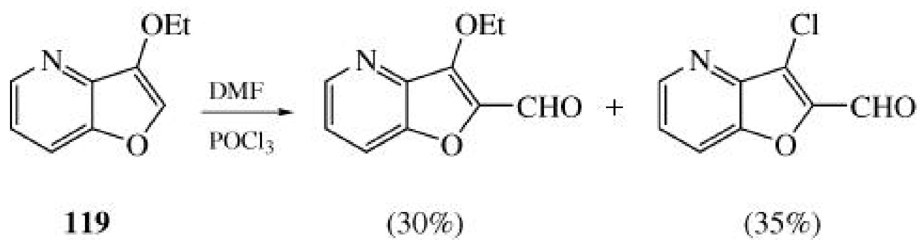


(100)

The furo[2,3-*b*]pyridine derivative **118** (Eq. 101) and the furo[3,2-**b**]pyridine derivative **119** (Eq. 102) can undergo dealkylation and subsequently behave as hydroxyfurans, and chloroformylation as well as normal substitution is observed. (140)

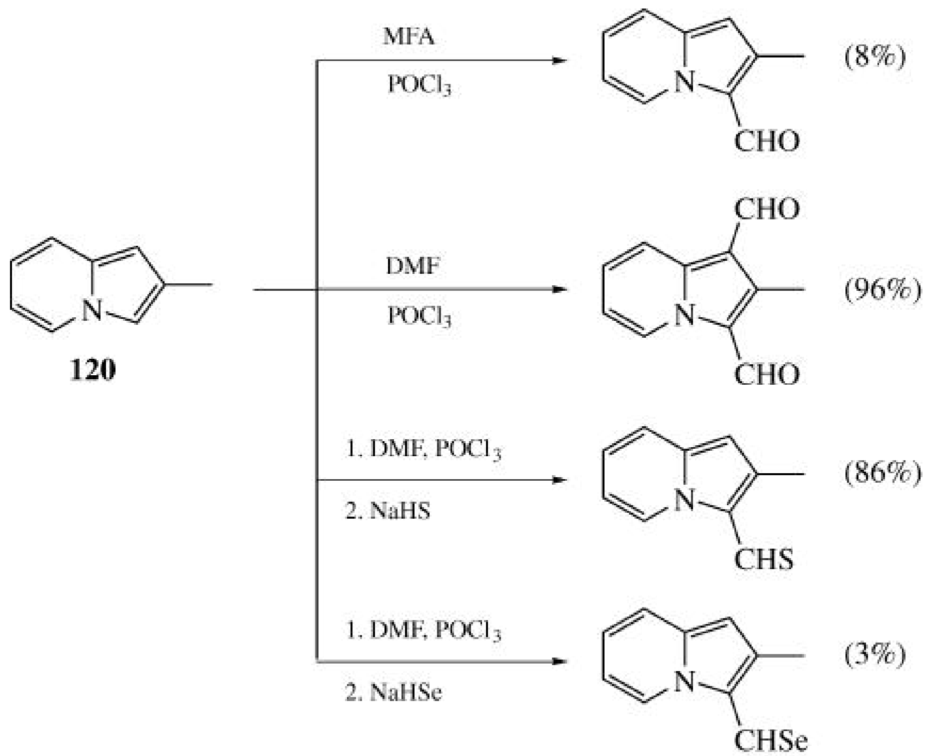


(101)



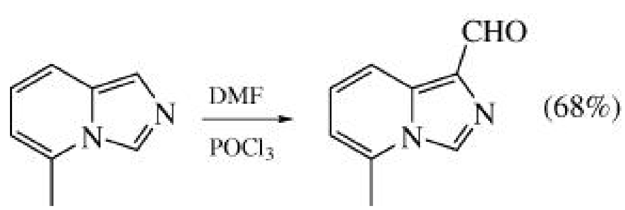
(102)

Bicycles with bridgehead nitrogen are readily formylated. Indolizines such as compound **120** (Eq. 103) are substituted in high yield in the 3-position, or if this

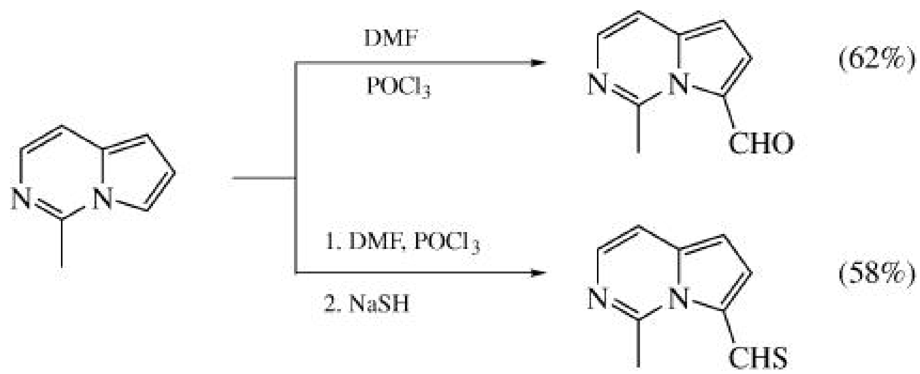


(103)

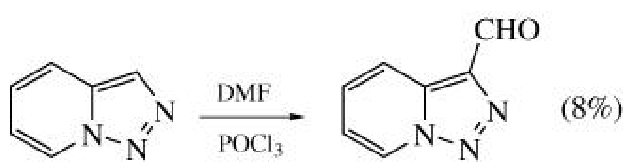
is blocked, in the 1-position. Compound **120** also illustrates the production of a thioaldehyde, (141, 142) a selenoaldehyde, (143) and a dialdehyde under forcing conditions. (141, 142) Azaindolizines also undergo Vilsmeier formylation whether the second nitrogen is located in the five-membered ring (Eq. 104) (144) or in the six-membered ring (Eq. 105). (145) The poor yield of formyl derivative from triazolopyridine **121** probably reflects the ease of ring opening with loss of nitrogen (Eq. 106). (146)



(104)



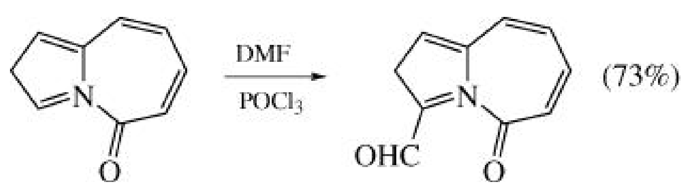
(105)



121

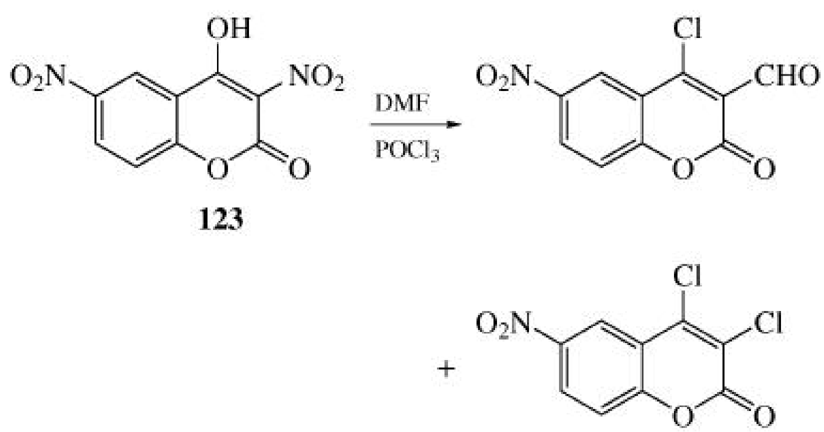
(106)

The pyrroloazepinone **122** has been formylated in good yield (Eq. 107). (147) Coumarins can give various products if the benzenoid ring is deactivated as shown for the formylation of compound **123** (Eq. 108). (148) Activation in the



122

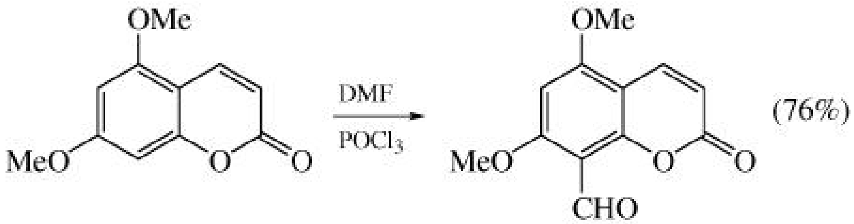
(107)



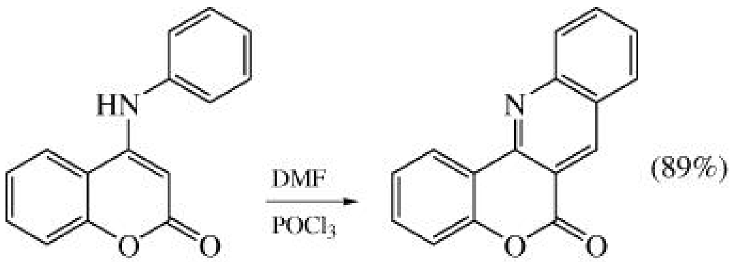
123

(108)

benzenoid ring gives formylation in the predicted position (Eq. 109) (149) and activation in the heterocyclic ring gives formylation which can be followed by cyclization (Eq. 110). (150)

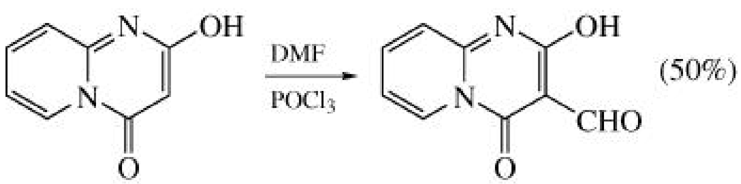


(109)

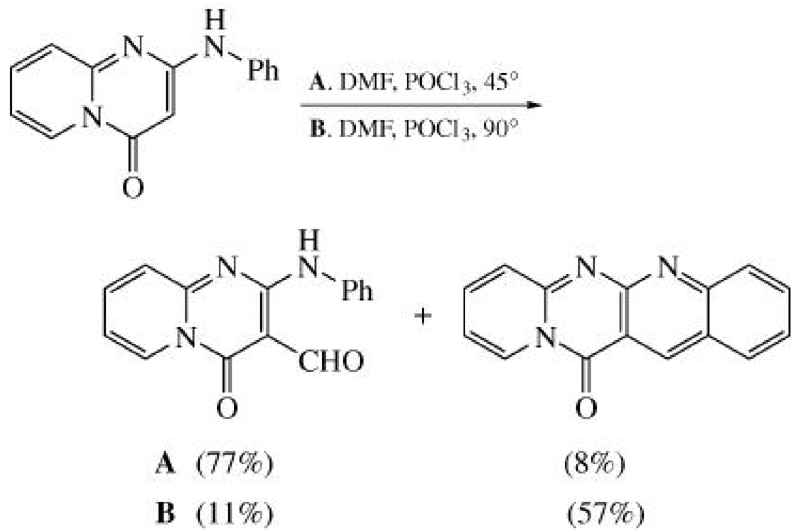


(110)

Pyrimidopyridines need electron-donating substituents for successful formylation (Eq. 111), (151) and when the activation is provided by an *N*-arylamino group, polycyclic products can be formed (Eq. 112). (152)



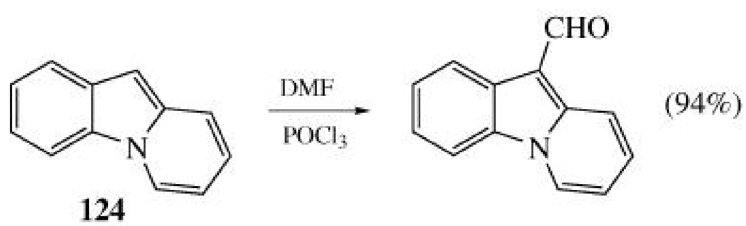
(111)



(112)

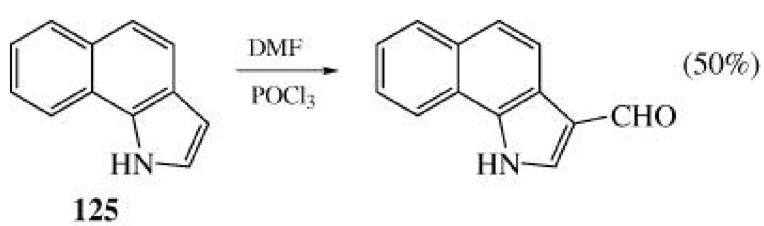
3.8. Other Heterocycles with Three or More Fully Conjugated Rings

The simplest examples of the many systems with three or more fully conjugated rings are the benzindolizine **124** (Eq. 113) (153) and the benzindoles **125**

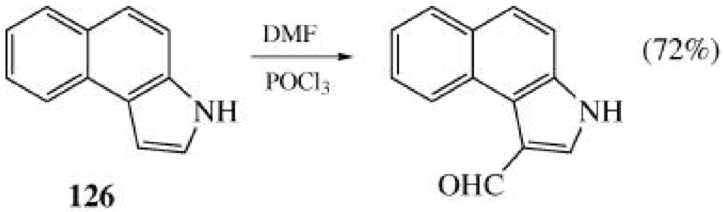


(113)

(Eq. 114) (154, 155) and **126** (Eq. 115). (154) The benzo[*e*]indoles **127** (Eq. 116) and **128** (Eq. 117) may illustrate some similarities with phenanthrene since formylation can be achieved in the central ring. (154, 155)

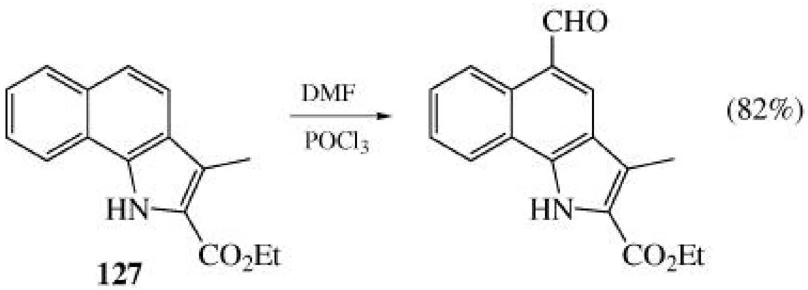


(114)



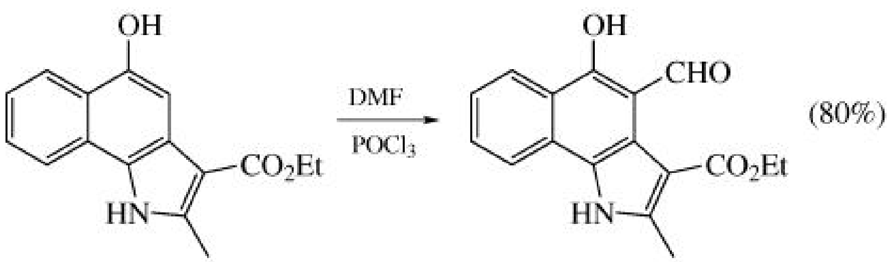
126

(115)



127

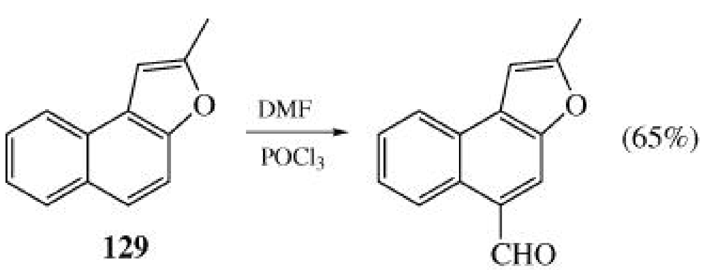
(116)



128

(117)

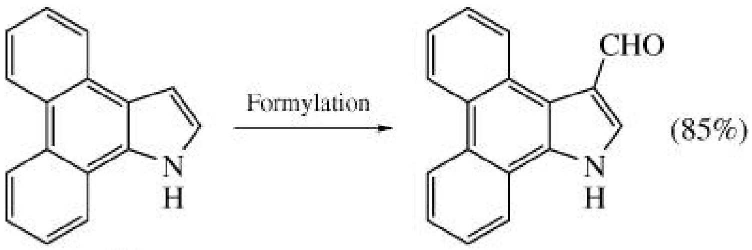
The tricyclic furan derivative **129** was originally reported to undergo formylation in the furan ring, (156) but a reinvestigation of this reaction concluded that substitution had occurred in the naphthalene ring (Eq. 118). (157)



129

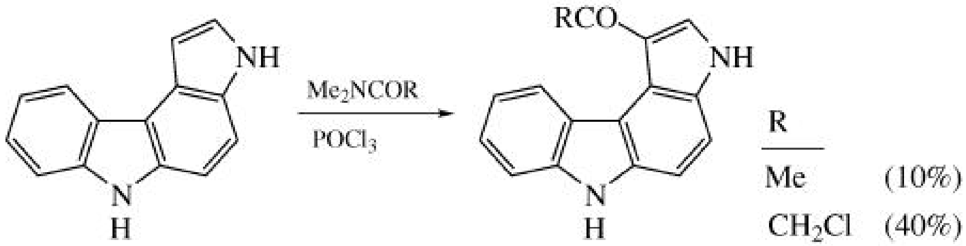
(118)

In larger polycycles based on indole, the phenanthrenopyrrole **130** (Eq. 119) (158) and the pyrrolocarbazole **131** (Eq. 120) (159) give the expected products in formylation and acylation reactions, but benzo[*e*]pyrrolo[3,2-*g*]indole **132** undergoes an unprecedented chlorination when excess phosphoryl chloride is used (Eq. 121). (160)



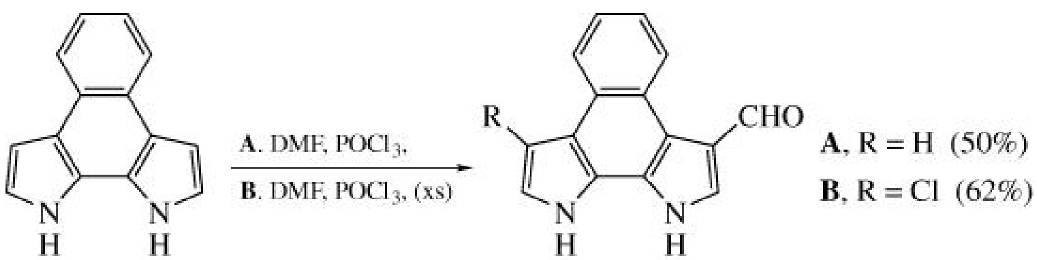
130

(119)



131

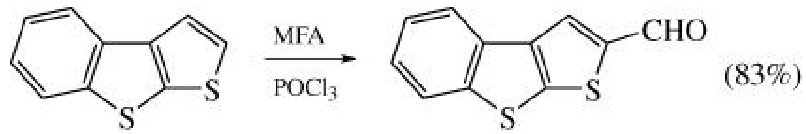
(120)



132

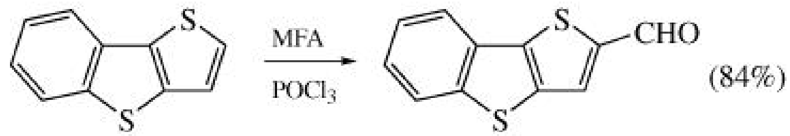
(121)

Examples of 5:5:6 tricycles which undergo the Vilsmeier reaction include the benzthienothiophenes **133** (Eq. 122) and **134** (Eq. 123) (161) and the furo[3,2-*b*]indoles **135** (Eq. 124). (162) Heterocycle **136** yielded a benzthienothiophene derivative (Eq. 125). (163)



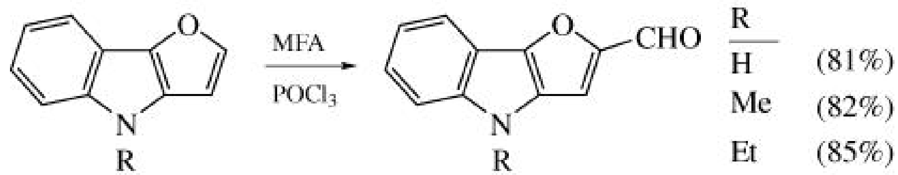
133

(122)



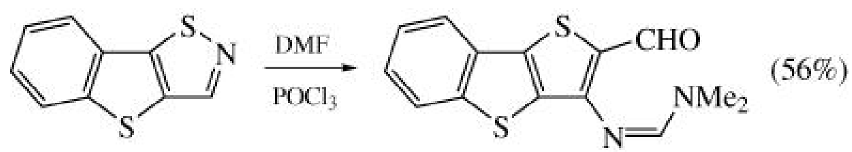
134

(123)



135

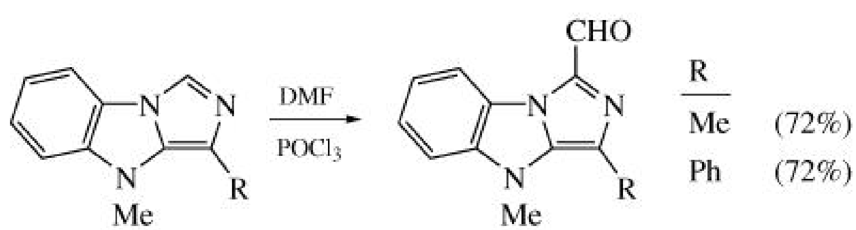
(124)



136

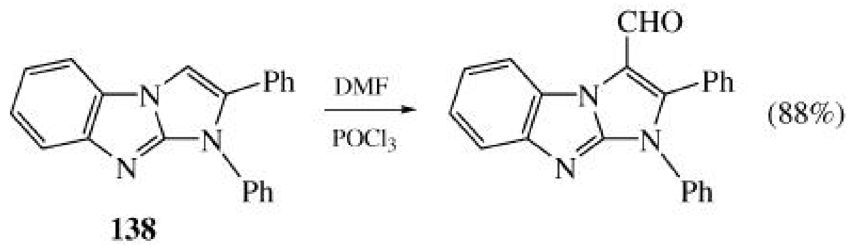
(125)

With three heteroatoms distributed between the two five-membered rings in 5:5:6 systems, the yields of aldehydes remain excellent, as illustrated for heterocycles **137** (Eq. 126), (164) **138** (Eq. 127), (165) and **139** (Eq. 128). (166)

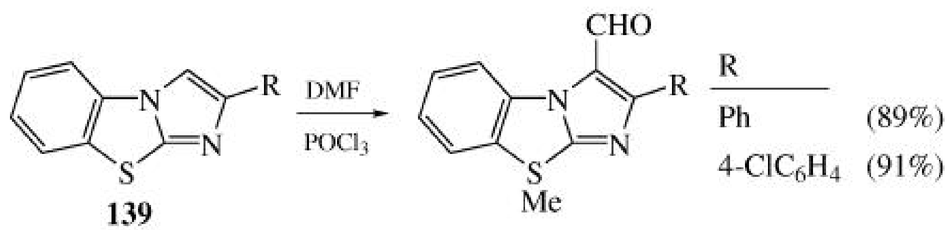


137

(126)

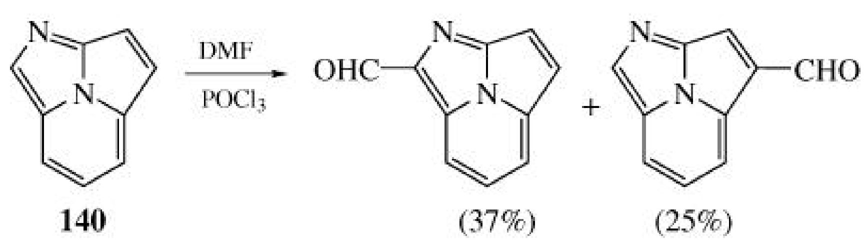


(127)

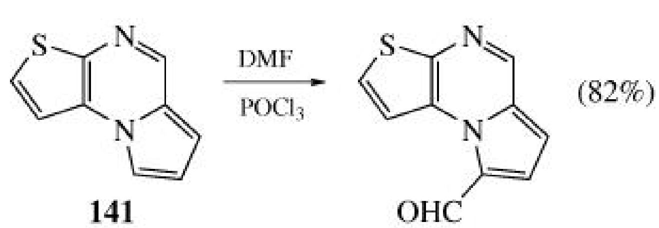


(128)

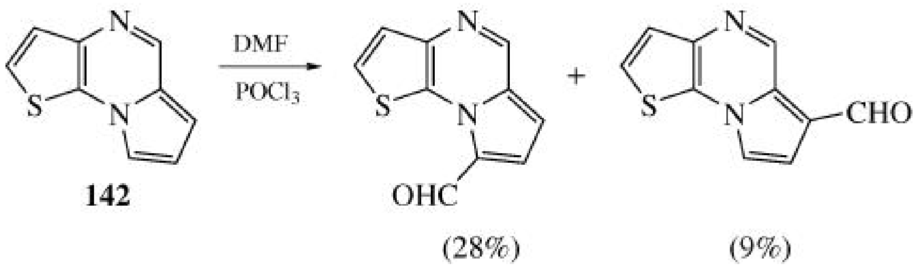
The azacyclazine **140** gives a mixture of two products (Eq. 129). (167) The isomers **141** (Eq. 130) (168) and **142** (Eq. 131) (169) give contrasting results, the former



(129)



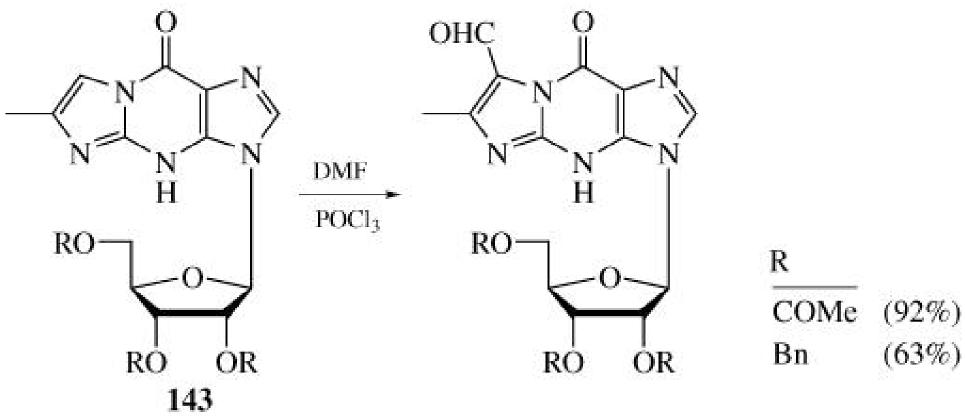
(130)



(131)

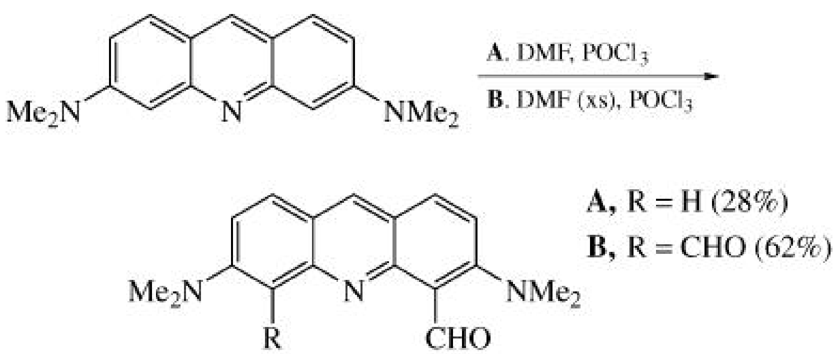
with a single high-yield site for formylation and the latter giving poor yields of two products.

Protected sugars are tolerant of the Vilsmeier reagent, as illustrated for heterocycle **143** (Eq. 132), (170, 171) although an unusually low temperature was used in one



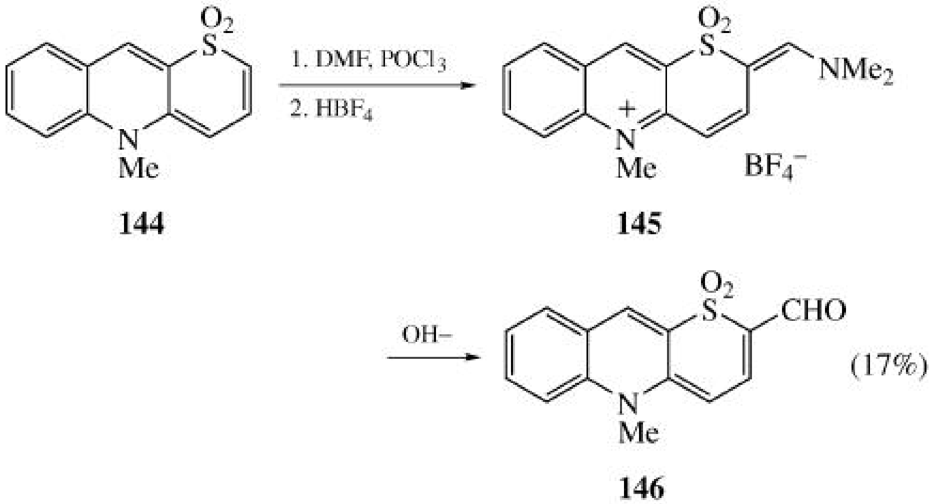
(132)

case. Acridine requires electron-donating substituents for successful formylation, and with two powerful groups diformylation is possible (Eq. 133). (172) The tricycle



(133)

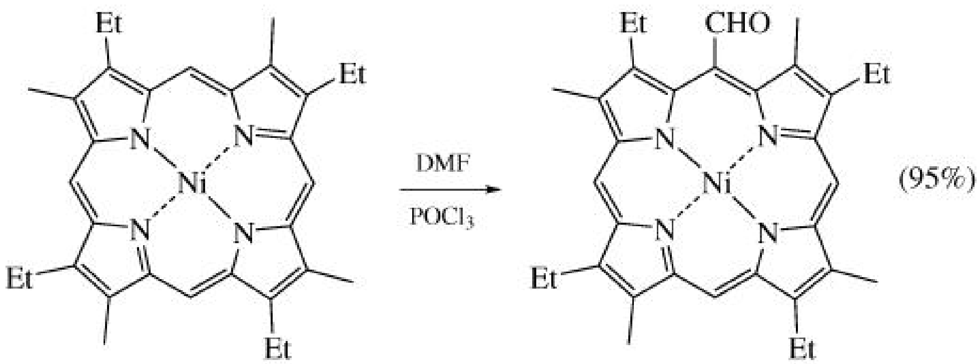
144 behaves as a vinylogous enamine in the Vilsmeier reaction and aldehyde **145** is obtained via salt **146** (Eq. 134). (173)



(134)

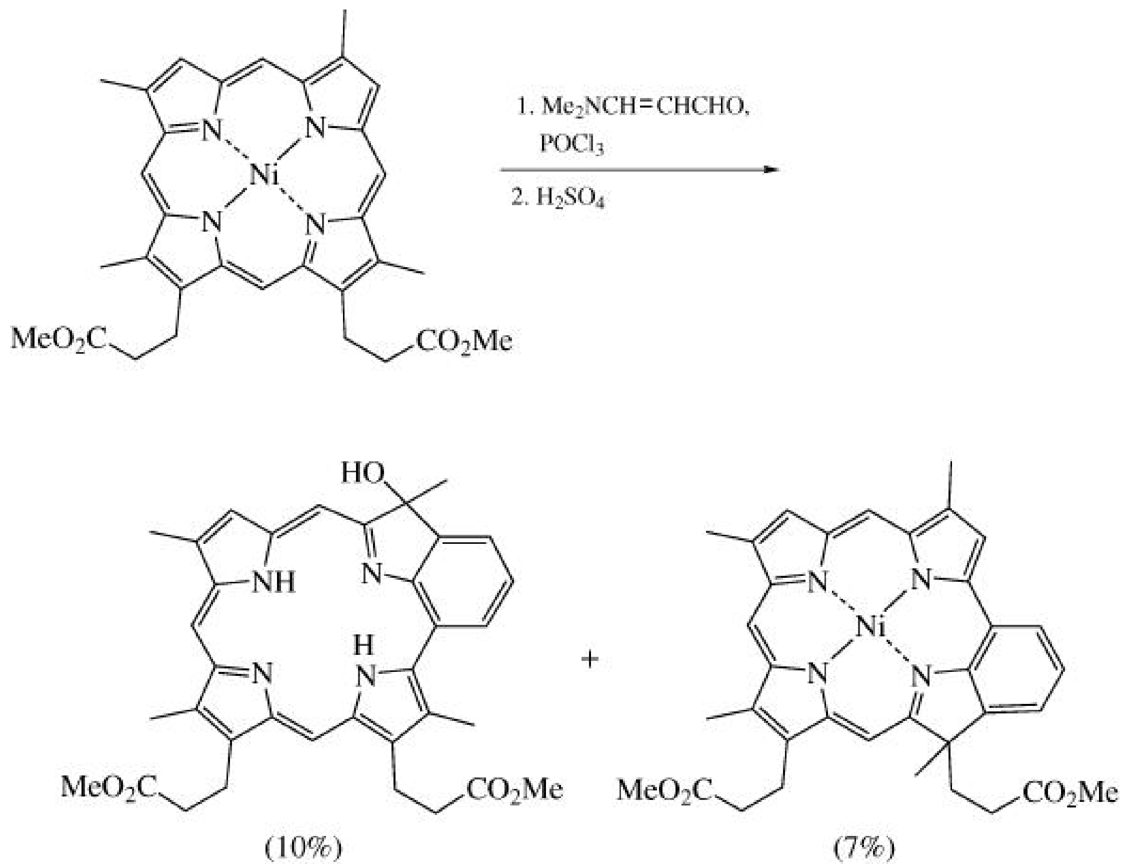
3.8.1. Porphyrins

There are many examples of porphyrins that participate in the Vilsmeier reaction. The general rule is that substitution occurs at one or more of the *meso* positions (Eq. 135) (174, 175) and mixtures result from unsymmetrical porphyrins.



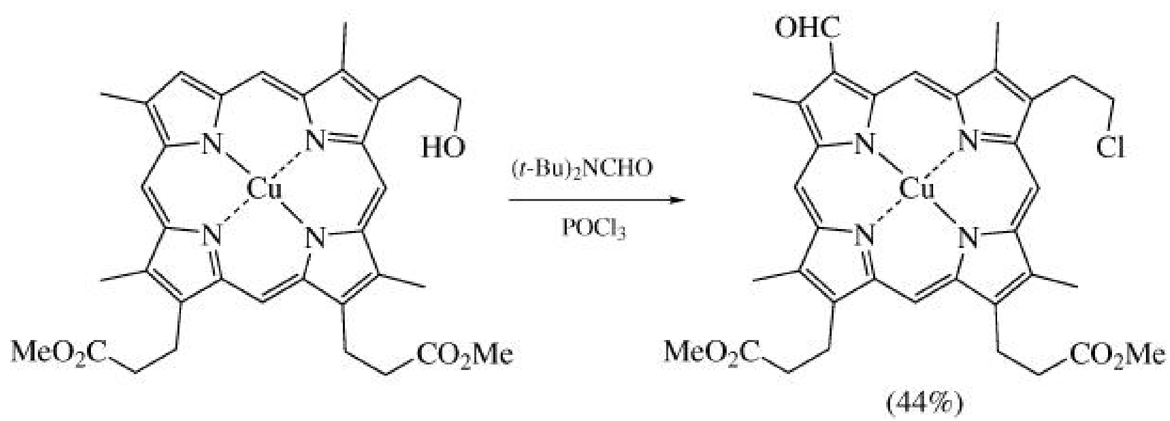
(135)

The use of a vinylogous amide can allow annulation to an adjacent pyrrole ring (Eq. 136), (176) although in other cases the *meso* acraldehyde is



(136)

obtained. (176) Substitution can occur at a pyrrole ring if a hindered amide is used (Eq. 137). (177)



(137)

4. Comparison with Other Methods

There are several methods for converting an aromatic derivative ArH into its corresponding aldehyde derivative ArCHO using an electrophilic substitution reaction and the scope and limitations of these reactions have been summarized. (20, 178) The Gattermann–Koch reaction uses carbon monoxide in the presence of hydrogen chloride and a Lewis-acid catalyst as the formylating reagent and is applicable to simple alkyl- and haloaromatics and polycyclic aromatic hydrocarbons, but fails for phenols. In contrast, the Gattermann reaction, which uses hydrogen cyanide, hydrogen chloride, and a Lewis-acid catalyst, will formylate phenols. Related to the Gattermann–Koch reaction is the direct formylation of aromatic hydrocarbons with formyl fluoride in the presence of boron trifluoride. Dichloromethyl alkyl ethers also formylate aromatic hydrocarbons in the presence of a Lewis-acid catalyst to give α -alkoxybenzyl chlorides from which aldehydes can be obtained by heating or hydrolysis. Electron-rich aromatics such as phenols and aromatic amines can be formylated with substantial *ortho* selectivity using hexamethylenetetramine in acetic acid (the Duff reaction). With trifluoroacetic acid, simple aromatics such as toluene can be formylated but the reaction is *para* selective in these cases. The Reimer–Tiemann reaction of phenols uses chloroform and alkali and gives a high proportion of *ortho* products. (178)

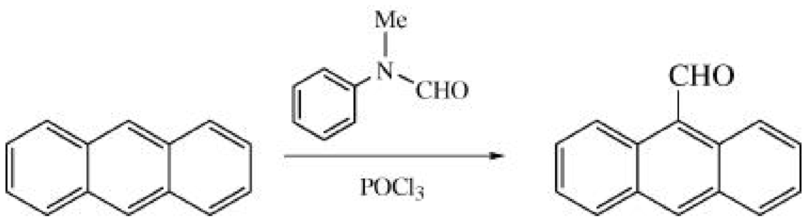
5. Experimental Procedures

5.1.1. 4-N,N-Dimethylaminobenzaldehyde (Formylation of an Activated Benzene Derivative with Pyrophosphoryl Chloride and DMF) (26)

Pyrophosphoryl chloride (2.27 g, 9.0 mmol) was added dropwise to stirred, cold (ice bath) DMF (1.10 g, 15.0 mmol) and *N,N*-dimethylaniline (0.91 g, 7.5 mmol) to give a thick green syrup. The mixture was heated at 65° for 15 hours and allowed to cool, and the resulting green solid was dissolved in water and basified with 2 M sodium hydroxide solution giving a yellow solid. The solid was sublimed at 140–150° (0.6 mm) to give 1.11 g (99%) of 4-*N,N*-dimethylaminobenzaldehyde, mp 73–75°; IR 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.06 (s, 6 H), 6.67 (d, *J*=9 Hz, 2 H), 7.71 (d, *J*=9 Hz, 2 H), 9.72 (s, 1 H).

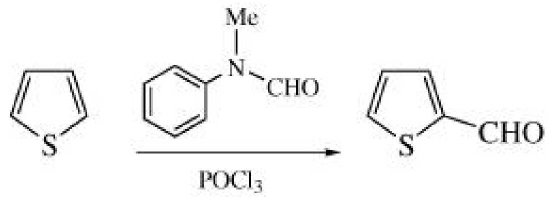
5.1.2. 4-N,N-Dimethylaminobenzaldehyde (Formylation of an Activated Benzene Derivative with Phosphoryl Chloride and DMF)

A detailed procedure for this reaction is described in *Organic Syntheses*. (32) The yield of 4-*N,N*-dimethylaminobenzaldehyde was 84%.



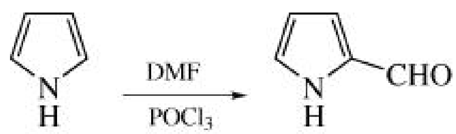
5.1.3. Anthracene-9-carbaldehyde (Formylation of a Polycyclic Hydrocarbon with Phosphoryl Chloride and N-Methylformanilide)

A detailed procedure for this reaction is described in *Organic Syntheses*. (179) The yield of anthracene-9-carbaldehyde was 84%.



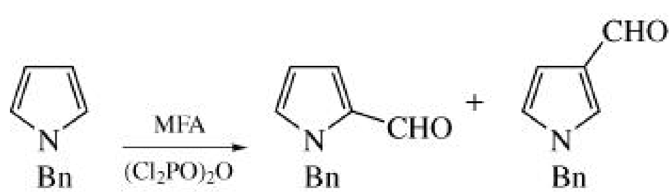
5.1.4. Thiophene-2-carbaldehyde (Formylation of Thiophene with Phosphoryl Chloride and N-Methylformanilide)

A detailed procedure for this reaction is described in *Organic Syntheses*. (180) The yield of thiophene-2-carbaldehyde was 74%.



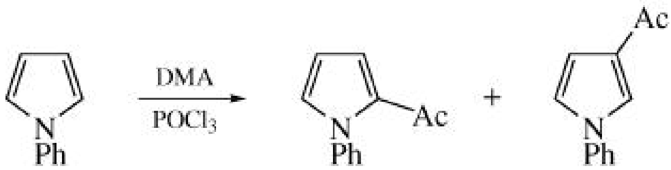
5.1.5. Pyrrole-2-carbaldehyde (Formylation of Pyrrole with Phosphoryl Chloride and DMF)

A detailed procedure for this reaction is described in *Organic Syntheses*. (181) The yield of pyrrole-2-carbaldehyde was 95%.



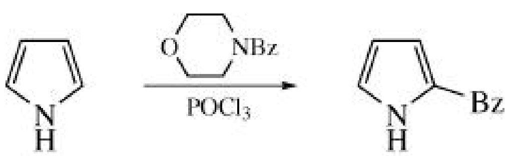
5.1.6. 1-Benzylpyrrole-2-carbaldehyde and 1-Benzylpyrrole-3-carbaldehyde (Formylation of a Pyrrole Derivative with Pyrophosphoryl Chloride and MFA) (26)

Pyrophosphoryl chloride (2.14 g, 8.5 mmol) was added dropwise to a stirred mixture of cold (ice bath) MFA (2.03 g, 15 mmol) and 1-benzylpyrrole (1.18 g, 7.5 mmol) and the resulting syrup was stirred at 20° for 19 hours. The mixture was basified with 2 M sodium hydroxide solution, and extracted with dichloromethane, and the combined organic extracts were washed with dilute hydrochloric acid, dried ($MgSO_4$), and evaporated. The unreacted MFA was removed by distillation (Kugelrohr) at 70° (1 mm) and the residue was fractionated by column chromatography on silica gel (eluting with petroleum ether–ether 5:1) to give 1.03 g (75%) of 1-benzylpyrrole-2-carbaldehyde; IR 1658 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.54 (s, 2 H), 6.24 (m, 1 H), 6.94 (m, 2 H), 7.14–7.10 (m, 2 H), 7.31–7.18 (m, 3 H), 9.54 (s, 1 H), and 0.303 g (22%) of 1-benzylpyrrole-3-carbaldehyde; IR 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.08 (s, 2 H), 6.65 (dd, *J*=2.8 and 1.8 Hz, 1 H), 6.70 (t, *J*=2.8 Hz, 1 H), 7.18–7.13 (m, 2 H), 7.37–7.29 (m, 4 H), 9.73 (s, 1 H).



5.1.7. 2-Acetyl-phenylpyrrole and 3-Acetyl-1-phenylpyrrole (Acylation of a Pyrrole Derivative with Phosphoryl Chloride and DMA) (182)

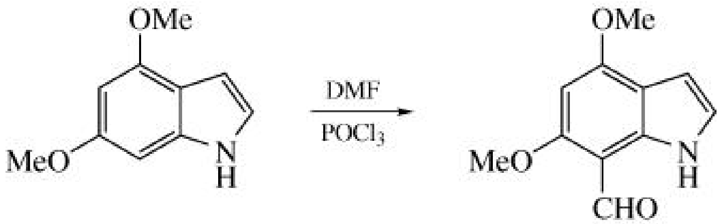
DMA (2.87 g, 33 mmol) was added to phosphoryl chloride (6.0 g, 39 mmol) cooled to 5° and the mixture was then stirred at room temperature for 6 hours. A solution of 1-phenylpyrrole (4.0 g, 27 mmol) in dichloroethane (25 mL) was added and the mixture was stirred at 60° for 24 hours under a nitrogen atmosphere, poured into 30% aqueous sodium carbonate solution (100 mL), extracted with dichloromethane, and evaporated. The residue was fractionated by column chromatography on silica gel (eluting with toluene— ethyl acetate 9:1) to give 3.0 g (60%) of 2-acetyl-1-phenylpyrrole, mp 56–57°, and 0.8 g (15%) of 3-acetyl-1-phenylpyrrole, bp 165° (1 mm). 2-Acetyl-1-phenylpyrrole: ^{1}H NMR ($CDCl_3$) δ 2.3 (s, 3 H), 6.65 (d, *J*=3 Hz, 1 H), 7.0 (d, *J*=3 Hz, 1 H), 7.3 (s, 5 H), 7.55 (s, 1 H).



5.1.8. 2-Benzoylpyrrole (Benzoylation of Pyrrole with Phosphoryl Chloride and N-Benzoylmorpholine) (183)

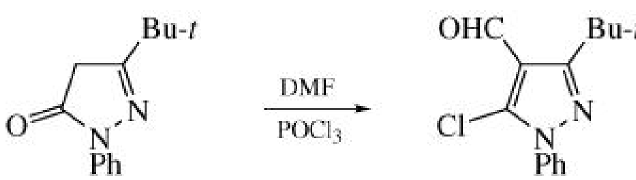
A mixture of *N*-benzoylmorpholine (2.96 g, 20 mmol) and phosphoryl chloride (4.0 mL, 20 mmol) was kept at 25° for 6 hours. A solution of pyrrole (1.38 g, 20 mmol) in anhydrous 1,2-dichloroethane (100 mL) was added and, after swirling, the reaction mixture was left at 25° for 14 hours. After hydrolysis with 10% aqueous sodium carbonate solution (100 mL), the organic layer was separated and the aqueous layer washed with 1,2-dichloroethane (2 × 20 mL).

The combined organic layers were dried (Na_2CO_3), the solvent removed, and the residue recrystallized (charcoal) from petroleum ether giving 2-benzoylpyrrole, 2.95 g (86%) as colorless needles, mp 77.5–78°.



5.1.9. 4,6-Dimethoxyindole-7-carbaldehyde (Formylation of an Indole Derivative in the Benzene Ring with Phosphoryl Chloride and DMF) (109)

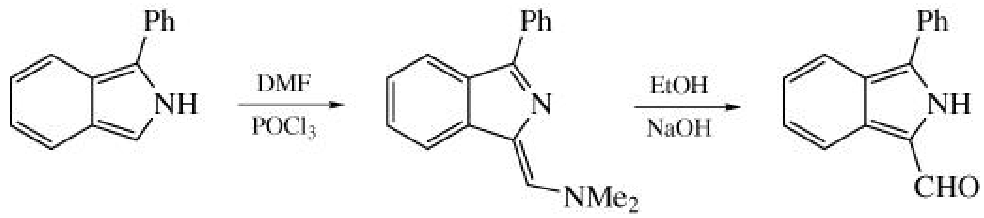
To a stirred solution of 4,6-dimethoxyindole (0.18 g, 4 mmol) in DMF (1 mL) at 0° was added dropwise an ice-cold solution of phosphoryl chloride (0.37 mL, 4.05 mmol) in DMF (1 mL). The mixture was kept at 0° for 1 hour and then allowed to warm to room temperature, added to ice water (10 mL), and made strongly alkaline with 10% sodium hydroxide solution. The resulting solid was collected, washed with water, dried, and recrystallized from chloroform—petroleum ether to give 0.11 g (56%) of 4,6-dimethoxyindole-7-carbaldehyde, mp 201–202°; IR 1639 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.92 (s, 3 H), 3.98 (s, 3 H), 6.4 (m, 2 H), 7.05 (t, J=2.5 Hz, 1 H), 10.26 (s, 1 H), 11.20 (broad s, 1 H); mass spectrum, *m/z* (rel. intensity) 205 (100).



5.1.10. 5-Chloro-3-tert-butyl-1-phenylpyrazole-4-carbaldehyde (Chloroformylation of a Pyrazolone Derivative with Phosphoryl Chloride and DMF) (184)

Phosphoryl chloride (14.85 mL, 0.162 mol) was slowly added with stirring to ice-cold DMF (5.37 mL, 0.069 mol) over 0.75 hour. 3-*tert*-Butyl-1-phenyl-5(1*H*)-pyrazolone (5.0 g, 0.023 mol) was added and the mixture was heated at reflux for 0.25 hour. The cooled mixture was poured into water (100 mL, 0°) and extracted continuously with ether. The organic extact was dried (Na_2SO_4), evaporated, and distilled under reduced pressure at 86° (2 mm) to give 4.8 g (79%) of

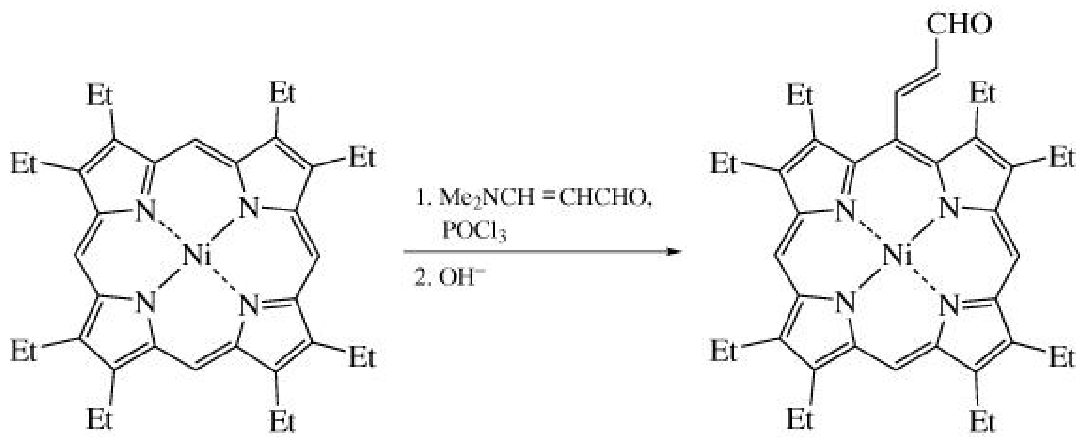
5-chloro-3-*tert*-butyl-1-phenylpyrazole-4-carbaldehyde; IR (neat) 1689 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9 H), 7.30–7.90 (m, 5 H); mass spectrum, *m/z* (rel. intensity) 262 (52), 77 (100).



5.1.11. 1-(N,N-Dimethylaminomethylidene)-3-phenyl-1H-isoindole and 1-Phenylisoindole-3-carbaldehyde (Dimethylaminomethylenation of an Isoindole Derivative with Phosphoryl Chloride and DMF and its Conversion to the Corresponding Aldehyde) (185)

Phosphoryl chloride (2.5 g, 0.016 mol) was added to DMF (20 mL, 0.26 mol) with stirring at –5 to –10° under an argon atmosphere. 1-Phenylisoindole (1.5 g, 7.77 mmol) in DMF (20 mL) was added dropwise and the mixture was stirred at –5° for 1 hour, then at room temperature for 5 hours. The mixture was poured into saturated sodium hydrogen carbonate solution (500 mL) with stirring, and the resulting brownish yellow solid (1.84 g) was washed with water and dried. The solid was purified by column chromatography on silica gel (eluting with petroleum ether–acetone 2:1) and the product was recrystallized from ethyl acetate–petroleum ether to give 1.31 g (68%) of 1-(*N,N*-dimethylaminomethylidene)-3-phenyl-1*H*-isoindole as brilliant yellow-green needles, mp 152–153°; ^{1}H NMR ($CDCl_3$) δ 3.57 (broad s, 6 H) and 7.0–8.2 (m, 10 H); mass spectrum, *m/z* (rel. intensity) 248 (100).

The above compound (0.218 g, 0.93 mmol), ethanol (20 mL), and 4% sodium hydroxide solution (1.3 mL) were heated under reflux under an argon atmosphere for 3.25 hours. The mixture was evaporated and the residue was dissolved in dichloromethane. The organic layer was washed with water and the aqueous washings were back-extracted with dichloromethane. The combined organic extracts were dried (Na_2SO_4) and evaporated to give a residue which was triturated with ether (2 mL). The resulting solid was recrystallized from ethyl acetate to give 93 mg (48%) of 1-phenylisoindole-3-carbaldehyde as bright-yellow needles, mp 183–184°; IR (Nujol) 3210, 1630, 1615, 1290, 1275, 1230, 745 cm^{-1}; ^{1}H NMR (CD_3SOCD_3) δ 7.17–8.25 (m, 9 H), 9.96 (s, 1 H), 13.34 (broad s, 1 H); mass spectrum, *m/z* (rel. intensity) 221 (100).



5.1.12. Nickel(II) meso-(2-Formylvinyl)octaethylporphyrin [Vinylogous Formylation of a Porphyrin Derivative with Phosphoryl Chloride and 3-(Dimethylamino)acrolein] (176)

Phosphoryl chloride (1.0 mL, 10 mmol) was added dropwise to a solution of 3-(dimethylamino)acrolein (1.0 mL, 10 mmol) in dichloromethane (4.0 mL) and the mixture was kept at 0° for 0.25 hour. The mixture was added to nickel(II) octaethylporphyrin (200 mg, 0.338 mmol) at 0° and then stirred at room temperature for 8 hours. After basic hydrolysis, the final neutralized residue was purified by column chromatography over silica gel (eluting with dichloromethane) and was further purified by preparative TLC on silica plates (eluting with dichloromethane–petroleum ether 8:2). The less polar compound was collected and crystallized from dichloromethane–methanol to give 186 mg (85%) of nickel(II) *meso*-(2-formylvinyl)octaethylporphyrin, mp 245–246°; ^{1}H NMR ($CDCl_3$) δ 1.66–1.79 (overlapping t, 24 H), 3.65–3.86 (overlapping q, 16 H), 5.53 (dd, *J*=7.7 and 15.2 Hz, 1 H), 9.36 (s, 3 H), 9.69 (d, *J*=15.2 Hz, 1 H), 9.84 (d, *J*=7.7 Hz, 1 H).

6. Tabular Survey

We have attempted to cover thoroughly the literature until the end of 1991, but some additional references after this date have also been included. The principal exclusions from this chapter are intramolecular cyclization reactions of the Bischler–Napieralski type. Only carbon–carbon bond formation reactions are included in the tables. Where a reaction has been performed by different workers, the yield in the table corresponds to the first reference.

To assist the reader who might be searching for specific substitution patterns, Tables I, II, V, and VIII–XV have been subdivided according to substitution pattern with the unsubstituted parent compounds being considered before monosubstituted compounds. Within subdivisions which are associated with multiple substitution, for example, disubstituted compounds, the 1,2-substitution pattern is considered before the 1,3-disubstituted pattern.

Tables III, IV, and VII have been subdivided according to the number of component rings, with monocyclic systems having precedence over bicyclic systems. Rings containing the least number of carbon atoms are considered first within this subdivision. Similarly, in Tables XVI–XVIII, rings containing the least number of carbon atoms have precedence. To give additional structure to Tables XVI–XVIII, the parent heterocyclic ring system (e.g., pyrimidine) is considered before derivatives possessing a conjugated exocyclic substituent (e.g., pyrimidinediones) which have precedence over derivatives possessing two conjugated exocyclic substituents (e.g., pyrimidiones). Heterocycles which can become fully conjugated through tautomerism are considered in these tables.

Table XIX is not subdivided, and entries are ordered by increasing number of carbon atoms.

The following abbreviations are used in the tables:

DMF Dimethylformamide
MFA *N*-Methylformanilide
DMA *N,N*-Dimethylacetamide

Table I. Benzenes

View PDF

Table II. Naphthalenes

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Table III. Other Polycyclic Benzenoid Hydrocarbons

View PDF

Table IV. Carbocyclic Anions

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Table V. Azulenes

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Table VI. Other Polycyclic Nonbenzenoid Hydrocarbons

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Table VII. Carbocyclic Organometallics

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Table VIII. Furans

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Table IX. Thiophenes

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Table X. Selenophenes

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Table XI. Pyrroles

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Table XII. Benzo[*b*]furans

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Table XIII. Benzo[*b*]thiophenes

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Table XIV. Indoles

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Table XV. Carbazoles

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Table XVI. Other Heterocycles with One Fully Conjugated Ring

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Table XVII. Other Heterocycles with Two Fully Conjugated Rings

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Table XVIII. Other Heterocycles with Three or More Fully Conjugated Rings

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Table XIX. Porphyrins

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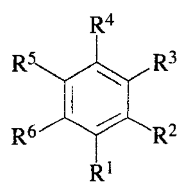
TABLE I. BENZENES



R^1 - R^6 = H except as indicated

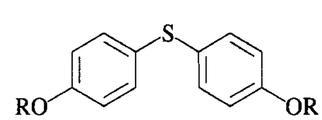
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Monosubstituted Benzenes		
C_6			
R^1 = OH	DMF, $POCl_3$	R^4 = CHO (5)	186
	DMF, $SOCl_2$, $AlCl_3$	R^4 = CHO (60)	34
C_7			
R^1 = OMe	DMF, $POCl_3$	R^4 = CHO (~70)	186
	DMF, $POCl_3$	R^2 = CHO (4) + R^4 = CHO (34)	26
	$Me_2N^{13}CHO$, $POCl_3$	R^4 = ^{13}CHO (—)	187
	DMF, $SOCl_2$, $AlCl_3$	R^2 = CHO (4) + R^4 = CHO (69)	34
	DMF, $(Cl_2PO)_2O$	R^2 = CHO (5) + R^4 = CHO (70)	26, 188
	MFA, $(Cl_2PO)_2O$	R^2 = CHO (<1) + R^4 = CHO (72)	26, 188
	MFA, $POCl_3$	R^4 = CHO (—)	189
	—	R^4 = CHO (70)	190
	DMF, $(CF_3SO_2)_2O$	R^2 = CHO (22) + R^4 = CHO (78)	47
	$[Me_2N{=}CHCl]^+ Cl^-$	R^4 = CHO (<4)	26
R^1 = SMe	DMF, $POCl_3$	R^4 = CHO (14)	30, 186
C_{7-11}			
R^1 = OR	DMF, $SOCl_2$		42
R			
Me		(34)	
Et		(30)	
n-Pr		(29)	

TABLE I. BENZENES (*Continued*)

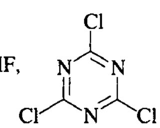
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R			
n-Bu		(30)	
i-Bu		(29)	
C_5H_{11}		(33)	
C_8			
$R^1 = OEt$	DMF, $POCl_3$	$R^4 = CHO$ (—)	186
$R^1 = NMe_2$	DMF, $POCl_3$	$R^4 = CHO$ (85)	31, 32, 191, 192
	DMF, $POCl_3$ (2-3 eq)	$R^4 = CHO$ (—) + $R^2 = R^4 = CHO$ (15-20)	33
	DMF, $COCl_2$	$R^4 = CHO$ (50)	31
	DMF, $SOCl_2$	$R^4 = CHO$ (60)	31
	DMF, 	$R^4 = CHO$ (41)	36
	$(CD_3)_2NCXO$, $COCl_2$ or $POCl_3$	$R^4 = CXO$ (—), X = H, D	29
	DMF, $SOCl_2$, $AlCl_3$	$R^4 = CHO$ (70)	34
	DMF, SO_2Cl_2	$R^4 = CHO$ (—)	193
	DMF, $(Cl_2PO)_2O$	$R^4 = CHO$ (99)	188, 26
	DMF, Ph_3PBr_2	$R^4 = CHO$ (72)	35
	DMF, $P(NCl_2)_3$	$R^4 = CHO$ (21)	194
	DMF, $P(NCl_2)_3$, $AlCl_3$	$R^4 = CHO$ (51)	194
	1. DMF, $POCl_3$ 2. $Me_2NC_6H_5$	$(Me_2NC_6H_4)_3CH$ (93)	41
	MeNHCOMe, $POCl_3$	$R^4 = COMe$ (25)	31
	DMA, $POCl_3$	$R^4 = COMe$ (15)	31
	MeNHCOPh, $POCl_3$	$R^4 = COPh$ (65)	31
	PhNHCOPh, $POCl_3$	$R^4 = COPh$ (85)	31
	Me_2NCOPh, $POCl_3$	$R^4 = COPh$ (80)	31, 111

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	PhNHCOAr	$R^4 = COAr$	37
	Ar		
	Ph	(65)	
	$4\text{-}BrC_6H_4$	(75)	
	$3\text{-}HOC_6H_4$	(50)	
	$4\text{-}HOC_6H_4$	(60)	
	$2\text{-}O_2NC_6H_4$	(—)	
	$3\text{-}O_2NC_6H_4$	(40)	
	$4\text{-}O_2NC_6H_4$	(45)	
	$2\text{-}MeOC_6H_4$	(55)	
	$3\text{-}MeOC_6H_4$	(40)	
	$4\text{-}MeOC_6H_4$	(50)	
	$1\text{-}C_{10}H_7$	(35)	
	$2\text{-}C_{10}H_7$	(35)	
	PhN(Me)CH=CHCHO, $POCl_3$	$R^4 = CH{=}CHCHO$ (70-80)	39
	PhN(Me)CH=CHCHO, MeCOBr or PhCOBr	$R^4 = CH{=}CHCHO$ (—)	195
	$Me_2NCH{=}C(R)CHO$, $POCl_3$	$R^4 = CH{=}C(R)CHO$	38
	R		
	H	(42)	
	Me	(61)	
	Et	(37)	
	n-Pr	(32)	
	n-C_5H_{11}	(21)	39
	$PhN(Me)(CH{=}CH)_2CHO$, $POCl_3$	$R^4 = (CH{=}CH)_2CHO$ (19)	40
	$Me_2NN{=}CHCHO$, $POCl_3$	$R^4 = CH{=}CHN{=}NMe_2^+\ Cl^-$ (—)	

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{10}			
$R^1 = NEt_2$	H_2NCHO, $POCl_3$, Py	$R^4 = CHO$ (94)	196
	DMF, $POCl_3$	$R^4 = CHO$ (—)	191
	MFA, $POCl_3$	$R^4 = CHO$ (—)	2
	1. MFA, $POCl_3$ 2. H_2NOH 3. Dehydration	$R^4 = CN$ (30)	197
	PhNHCOAr, $POCl_3$	$R^4 = COAr$	137
	Ar		
	Ph	(70)	
	2-ClC_6H_4	(50)	
	3-$O_2NC_6H_4$	(20)	
	4-$O_2NC_6H_4$	(60)	
	4-$MeOC_6H_4$	(40)	
$C_{10\text{-}16}$ $R^1 = N(CH_2CH_2)_2X$	PhN(Me)CH=CHCHO, $POCl_3$	$R^4 = CH{=}CHCHO$ (84)	39
X			
O	DMF, $POCl_3$	$R^4 = CHO$ (97)	198, 191
$NCOCF_3$	DMF, $POCl_3$	$R^4 = CHO$ (—)	199
NPh	DMF, $POCl_3$	$R^4 = R^{4'} = CHO$ (—)	191, 200
$C_{12\text{-}25}$ $R^1 = N(Me)R$			
R			
$(CH_2)_4CO_2H$	DMF, $POCl_3$	$R^4 = CHO$ (~60)	201
Ph	DMF, $POCl_3$	$R^4 = R^{4'} = CHO$ (—)	191, 202
$(CH_2)_4CO_2Me$	DMF, $POCl_3$	$R^4 = CHO$ (~60)	201
$(CH_2)_2NEt_2$	MFA, $POCl_3$	$R^4 = CHO$ (—)	203
Bn	DMF, $POCl_3$	$R^4 = CHO$ (80)	204
	MFA, $POCl_3$	$R^4 = CHO$ (82)	2

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R			
$(CH_2)_2$(*N*-piperidyl)	—	$R^4 = CHO$ (—)	203
$(CH_2)_2N(Me)Ph$	DMF, $POCl_3$	$R^4 = R^{4'} = CHO$ (—)	191
n-C_9H_{19}	DMF, $POCl_3$	$R^4 = CHO$ (~60)	201
$(CH_2)_3N(Me)Ph$	DMF, $POCl_3$	$R^4 = R^{4'} = CHO$ (50)	205
n-$C_{18}H_{37}$	DMF, $POCl_3$	$R^4 = CHO$ (~60)	201
C_{14}			
$R^1 = NBu_2$	DMF, $POCl_3$	$R^4 = CHO$ (58)	206
$C_{14\text{-}16}$			
$R^1 = N(R)(CH_2)_2CN$			
R			
$CH_2C_6H_4Cl$-4	DMF, $POCl_3$	$R^4 = CHO$ (91)	55
Bn	DMF, $POCl_3$	$R^4 = CHO$ (100)	55
$(CH_2)_2OCO_2Et$	—	$R^4 = CHO$ (—)	207
$C_{14\text{-}18}$			
$R^1 = N(Et)R$			
R			
$(CH_2)_2NEt_2$	—	$R^4 = CHO$ (—)	203
$CH_2C_6H_4(SO_2NMe_2$-3)	—	$R^4 = CHO$ (—)	208
$(CH_2)_2N(Et)Ph$	DMF, $POCl_3$	$R^4 = R^{4'} = CHO$ (—)	191
C_{16}			
$R^1 = CH{=}CHC_6H_4(NMe_2$-4)	DMF, $POCl_3$ (1 eq)	$R^4 = CHO$ (33)	209
	DMF, $POCl_3$ (4 eq)	$R^4 = R^{2'} = CHO$ (60)	209
$C_{16\text{-}18}$			

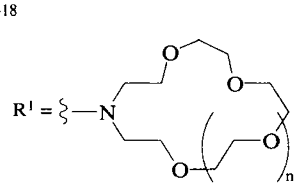


TABLE I. BENZENES (*Continued*)

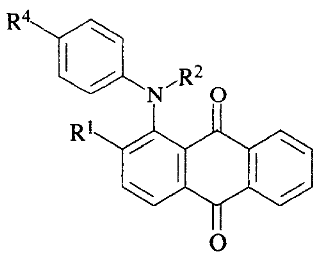
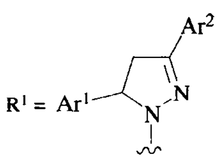
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
n = 1	DMF, $POCl_3$	R^4 = CHO (75)	210
n = 2	DMF, $POCl_3$	R^4 = CHO (65)	210
C_{18}			
$R^1 = NPh_2$	DMF, $POCl_3$	$R^4 = R^{4'} = R^{4''}$ = CHO (—)	191
$R^1 = SnBu_3$	MFA, $POCl_3$	R^1 = CHO (56)	53
C_{20}			
$R^1 = N(Bn)_2$	MFA, $POCl_3$	R^4 = CHO (100)	2
C_{21} 	DMF, $POCl_3$	R^4 = CHO	211
R^1 = H, R^2 = Me, R^4 = H		(100)	
R^1 = Me, R^2 = H, R^4 = H		(100)	
$C_{21\text{-}36}$ 			

TABLE I. BENZENES (*Continued*)

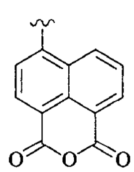
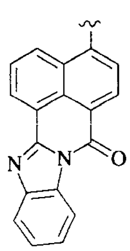
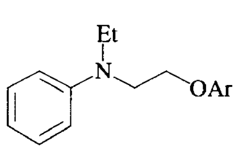
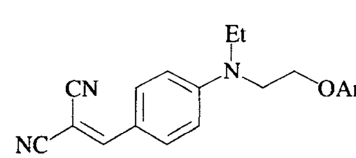
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
Ar^1 = Ph, Ar^2 = 4-$O_2NC_6H_4$	DMF, $POCl_3$	R^4 = CHO (60)	212
Ar^1 = Ph, Ar^2 = 	DMF, $POCl_3$	R^4 = CHO (50)	212
Ar^1 = 4-$MeOC_6H_4$, Ar^2 = 	DMF, $POCl_3$	R^4 = CHO (83)	212
C_{22}  Ar = 4-$(C_6H_{11})C_6H_4$	1. — 2. $CH_2(CN)_2$	 (—)	213
$R^1 = N(C_8H_{17})_2$	1. — 2. $CH_2(CN)_2$	R^4 = CH=C(CN)$_2$ (—)	214

TABLE I. BENZENES (*Continued*)

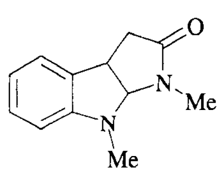
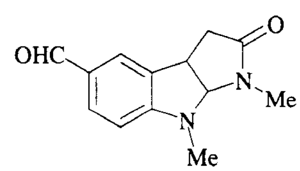
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	B. Disubstituted Benzenes **B1. R^1, R^2 Substituents**		
C_7			
$R^1 + R^2$ = $-OCH_2O-$	DMF, $POCl_3$	R^4 = CHO (70)	215
C_8 $R^1 + R^2$ = $-NH(CH_2)_2-$	—	R^4 = CHO (36)	216
R^1 = OMe, R^2 = Me	DMF, $POCl_3$	R^4 = CHO (70)	217, 186
R^1 = R^2 = OMe	DMF, $POCl_3$	R^4 = CHO (30-40)	186
	DMF, $(Cl_2PO)_2O$	R^4 = CHO (54)	26
	MFA, $(Cl_2PO)_2O$	R^4 = CHO (83)	26
	MFA, $POCl_3$	R^4 = CHO (38)	218, 219
C_9 $R^1 + R^2$ = $-N(Me)CONMe-$	DMF, $POCl_3$	R^4 = CHO (47)	220
C_{10} $R^1 + R^2$ = $-N(Me)(CH_2)_3-$	DMF, $POCl_3$	R^4 = CHO (90) + R^4 = R^6 = CHO (4)	221
R^1 = OH, R^2 = *t*-Bu	MFA, $POCl_3$	R^4 = CHO (18)	222
C_{11} $R^1 + R^2$ = $-OC(Me)_2(CH_2)_2-$	DMF, $POCl_3$	R^4 = CHO (71)	223
R^1 = NEt_2, R^2 = Me	DMF, $POCl_3$	R^4 = CHO (—)	191
C_{12} 	DMF, $POCl_3$	 (80)	224
C_{13} R^1 = Ph, R^2 = OMe	DMF, $POCl_3$	R^5 = CHO (—)	186

TABLE I. BENZENES (*Continued*)

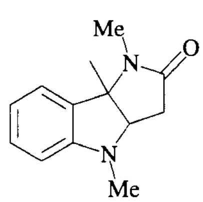
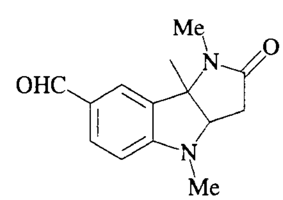
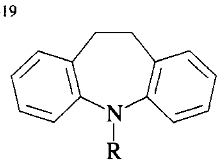
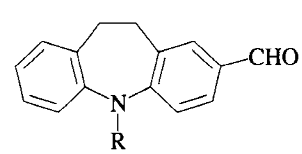
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (80)	224
C_{15}			
$R^1 + R^2$ = $N(Bn)(CH_2)_2$	DMF, $POCl_3$	R^4 = CHO (88)	225
C_{15-19} 	DMF, $POCl_3$		
R: Me		(—)	226
R: $(CH_2)_3NMe_2$		(—)	227
C_{16} R^1 = NEt_2, R^2 = Ph	DMF, $POCl_3$	R^4 = CHO (—)	191
C_{19} R^1 = OMe, R^2 = $SnBu_3$	MFA, $POCl_3$	R^2 = CHO (79)	53

TABLE I. BENZENES (*Continued*)

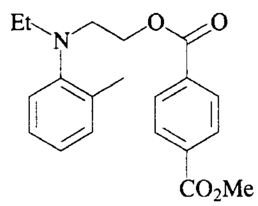
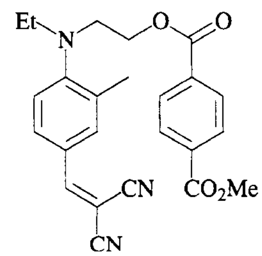
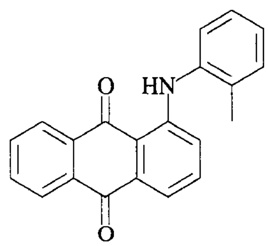
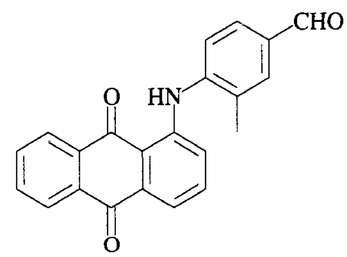
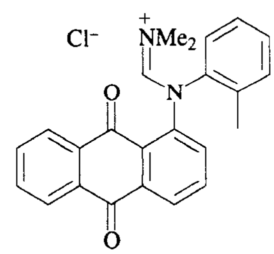
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{20} 	1. DMF, $POCl_3$ 2. $CH_2(CN)_2$	 (85)	228
C_{21} 	DMF, $POCl_3$	 (6) +  (17)	211

TABLE I. BENZENES (*Continued*)

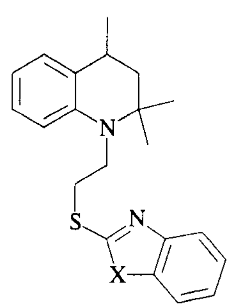
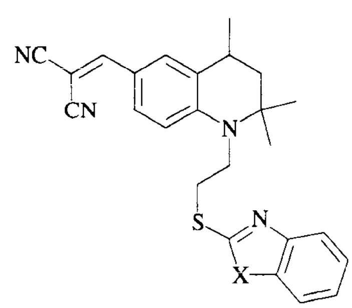
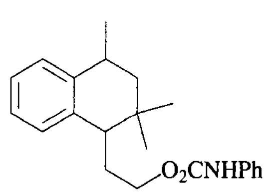
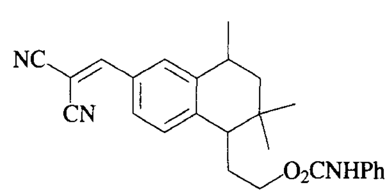
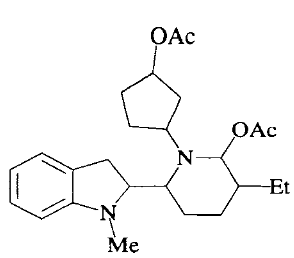
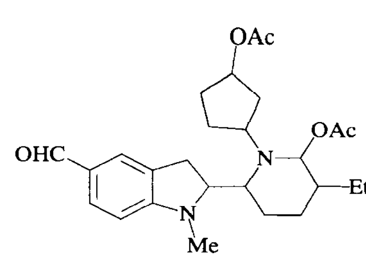
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
 X S O	1. DMF, $POCl_3$ 2. $CH_2(CN)_2$	 (—) (—)	229
	1. DMF, $POCl_3$ 2. $CH_2(CN)_2$	 (83)	230
C_{25} 	—	 (—)	231

TABLE I. BENZENES (*Continued*)

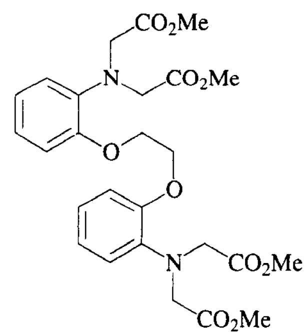
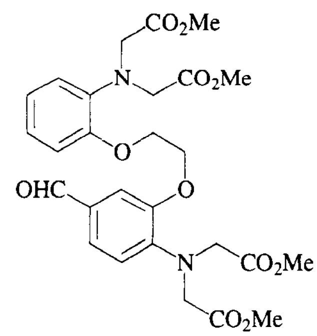
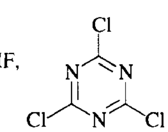
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{26} 	—	 (—)	232
B 2. R^1, R^3 Substituents			
C_6			
$R^1 = R^3 = OH$	DMF, $POCl_3$	$R^4 = CHO$ (68)	52
	H_2NCHO, $POCl_3$	$R^4 = CHO$ (75)	233
	DMF, $(Cl_2PO)_2O$	$R^4 = CHO$ (88)	26
C_7			
$R^1 = OH$, $R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (—)	186
$R^1 = OH$, $R^3 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (25)	51, 52
C_8			
$R^1 = OMe$, $R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (72)	217
$R^1 = R^3 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (8998)	234, 52
	MFA, $POCl_3$	$R^4 = CHO$ (85)	218, 50
	DMF, 	$R^4 = CHO$ (36)	36

TABLE I. BENZENES (*Continued*)

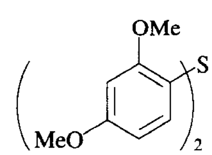
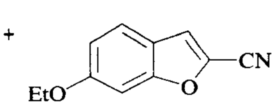
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. NH_2OH 3. Dehydrate	$R^4 = CN$ (43)	197, 235
	PhN(Me)CH=CHCHO, $POCl_3$	$R^4 = CH{=}CHCHO$ (90)	39
	DMF, $SOCl_2$	 (18) + $R^4 = CHO$ (59)	42
$C_{8\text{-}12}$			
$R^1 = OR$, $R^3 = Me$	DMF, $SOCl_2$	$R^4 = CHO$	42
R			
Me		(42)	
Et		(52)	
n-Pr		(44)	
n-Bu		(46)	
n-C_5H_{11}		(37)	
C_9			
$R^1 = NMe_2$, $R^3 = Me$	MFA, $POCl_3$	$R^4 = CHO$ (—)	2
C_{10}			
$R^1 = OCH_2CN$, $R^3 = OEt$	DMF, $POCl_3$	$R^4 = CHO$ (11) +  (7)	236

TABLE I. BENZENES (*Continued*)

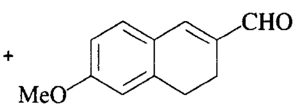
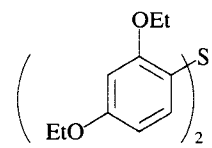
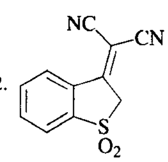
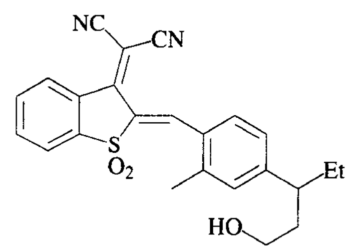
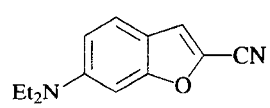
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^1 = OMe, R^3 = CH_2CH=CH_2	MFA, $POCl_3$	R^4 = CHO (40) +  (11)	237
R^1 = R^3 = OEt	DMF, $SOCl_2$	 (33) + R^4 = CHO (20)	42
C_{11}			
R^1 = OMe, R^3 = *t*-Bu	MFA, $POCl_3$	R^6 = CHO (62)	50
R^1 = NEt_2, R^3 = Me	DMF, $POCl_3$	R^4 = CHO (—)	191
R^1 = $N(Et)(CH_2)_2OH$, R^3 = Me	1. DMF, $POCl_3$ 2. 	 (—)	238
C_{12}			
R^1 = NEt_2, R^3 = OCH_2CN	DMF, $POCl_3$	 (4)	236

TABLE I. BENZENES (*Continued*)

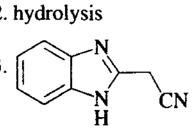
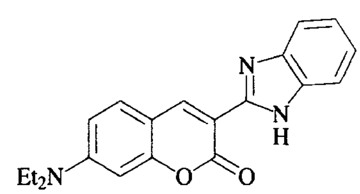
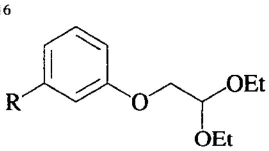
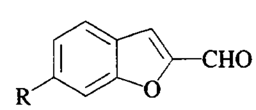
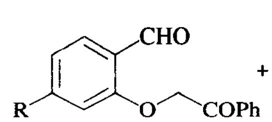
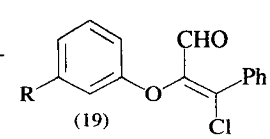
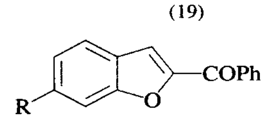
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{13}			
R^1 = NEt_2, R^3 = OTMS	1. DMF, $POCl_3$ 2. hydrolysis 3. 	 (—)	239
$C_{13\text{-}16}$			
	DMF, $POCl_3$		240
R = OMe		(27)	
R = OEt		(29)	
R = NEt_2		(33)	
C_{14}			
R^1 = R^3 = NEt_2	DMF, $POCl_3$	An aldehyde (—)	191
R^1 = $N(Me)(CH_2)_2NEt_2$, R^3 = Me	—	R^4 = CHO (—)	203
$C_{15\text{-}18}$			
R^1 = R, R^3 = OCH_2COPh R = OMe	DMF, $POCl_3$	 (8) +  (19) +  (25) I	43

TABLE I. BENZENES (*Continued*)

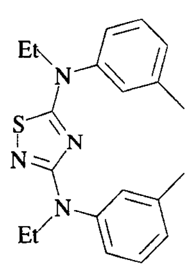
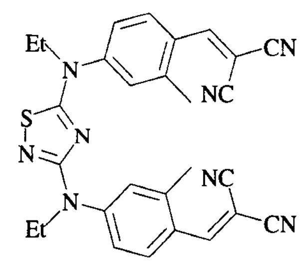
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R = OEt		I (31)	
R = NEt_2		I (78)	
C_{18}			
$R^1 = N(Et)(CH_2)_2O_2CPh$, $R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (—)	241
C_{18-21}			
$R^1 = N(Et)(CH_2)_2R$, $R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$	242
C_{18} R			
$SCH_2C_6H_3Cl_2$-2,5		(—)	
$SCH(OAc)CH_2C_6H_3Cl_2$-2,5		(—)	
C_{19}			
$R^1 = Me$, $R^3 = SnBu_3$	MFA, $POCl_3$	$R^3 = CHO$ (55)	53
C_{20}			
	1. DMF, $POCl_3$ 2. $CH_2(CN)_2$	 (85)	243
C_{20-22}			
$R^1 = N(Bn)_2$, $R^3 = R$	DMF, $POCl_3$	$R^4 = CHO$	244
R			
F		(93)	
Cl		(83)	
Me		(81)	
Et		(80)	

TABLE I. BENZENES (*Continued*)

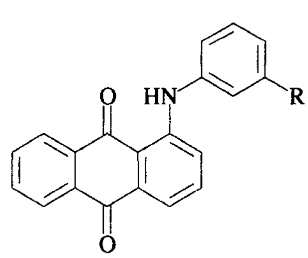
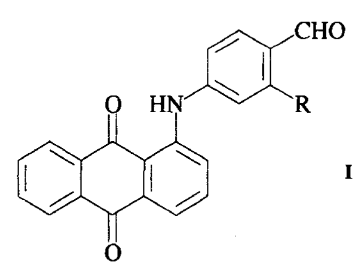
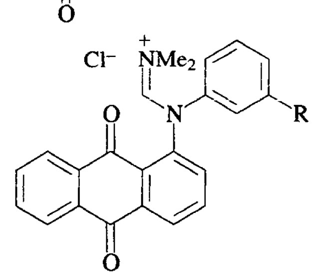
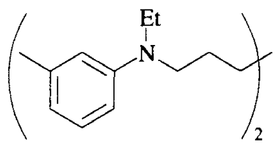
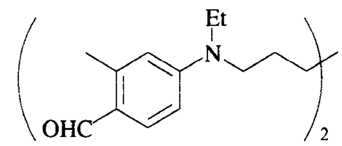
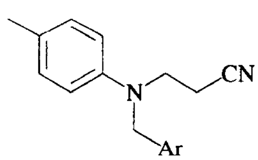
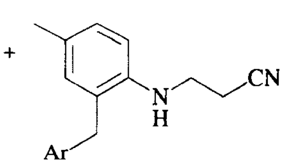
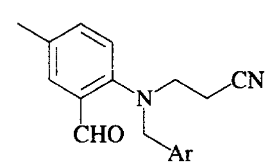
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{21} 	DMF, $POCl_3$	 I +  II	211
R			
Me		I (4) + II (84)	
OMe		I (13) + II (83)	
C_{24}			
$R^1 = N[(CH_2)_2SAr][(CH_2)_3SAr]$, $R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$	242
Ar			
2,5-$Cl_2C_6H_3$		(—)	
4-ClC_6H_4		(—)	

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	—	 (—)	245
B3. R¹, R⁴ Substituents			
C_7			
R^1 = OH, R^4 = Me	DMF, $POCl_3$	R^2 = CHO (—)	186
C_8			
R^1 = R^4 = OMe	MFA, $POCl_3$	R^2 = CHO (16)	218
	DMF, $(Cl_2PO)_2O$	R^2 = CHO (40)	26, 188
C_{10}			
R^1 = OMe, R^4 = $CH_2CH{=}CH_2$	MFA, $POCl_3$	R^2 = CHO (16)	237
R^1 = NMe_2, R^4 = COMe	$(Me_2N{=}CHCl)^+$ Cl^-	R^2 = CHO, R^4 = $C(Cl{=}C(CHO)_2$ (25) + R^4 = $CCl{=}C(CHO)_2$ (23)	246
C_{13}			
R^1 = $N[(CH_2)_2CN]_2$, R^4 = Me	DMF, $POCl_3$	R^2 = CHO (95)	55
C_{15}			
R^1 = NMe_2, R^4 = $C(NMe_2){=}CHCH{=}NMe_2^+$ ClO_4^-	1. DMF, $POCl_3$ 2. NaOH	R^2 = CHO, R^4 = $COC(CHO){=}CHOH$ (73)	246

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{15-19}			
		ArCHO (I) +  II +  III	

Ar	I	II	III	Refs.
2,3,4,5,6-F_5C_6	(0)	(0)	(67)	54
2,4-$F_2C_6H_3$	(30)	(39)	(43)	54
3,5-$F_2C_6H_3$	(32)	(39)	(35)	54
2-Thienyl	(47)	(59)	(0)	54
3-FC_6H_4	(40)	(49)	(13)	54
4-FC_6H_4	(71)	(82)	(0)	54
4-ClC_6H_4	(80)	(67)	(0)	55
3-BrC_6H_4	(71)	(58)	(0)	54
4-BrC_6H_4	(82)	(62)	(0)	54
4-$O_2NC_6H_4$	(30)	(0)	(0)	54
Ph	(94)	(71)	(0)	55
3-MeC_6H_4	(92)	(79)	(0)	54
4-MeC_6H_4	(88)	(76)	(0)	54
3-$MeOC_6H_4$	(89)	(80)	(0)	54
4-$MeOC_6H_4$	(76)	(74)	(0)	54
Cinnamyl	(40)	(24)	(0)	54

TABLE I. BENZENES (*Continued*)

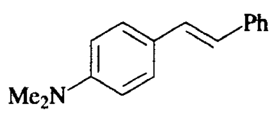
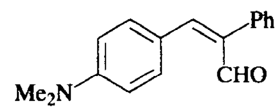
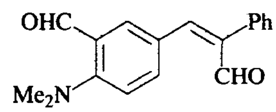
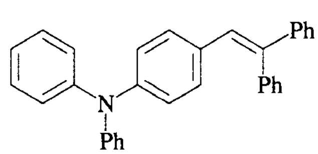
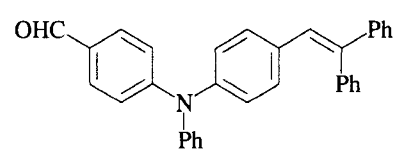
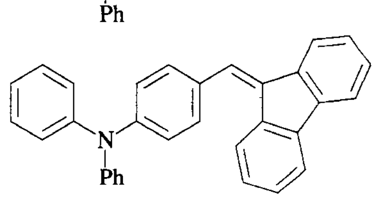
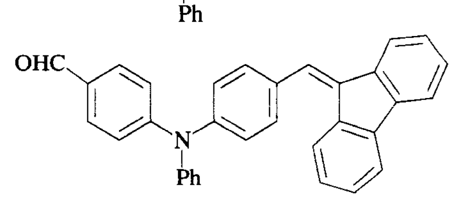
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMF, $POCl_3$	 (40) +	247
		 (35)	
C_{18}			
$R^1 = Cl$, $R^4 = SnBu_3$	MFA, $POCl_3$	$R^4 = CHO$ (10)	53
$R^1 = N[(CH_2)_2CN]CH_2Ar$, $R^4 = Me$	1. DMF, $POCl_3$ 2. $NaBH_4$		54
Ar			
$4\text{-}MeC_6H_4$		$R^2 = CH_2NMe_2$ (39)	
$4\text{-}MeOC_6H_4$		$R^2 = CH_2NMe_2$ (76)	
C_{19}			
$R^1 = Me$, $R^4 = SnBu_3$	MFA, $POCl_3$	$R^4 = CHO$ (70)	53
$R^1 = OMe$, $R^4 = SnBu_3$	MFA, $POCl_3$	$R^4 = CHO$ (96)	53
$C_{19\text{-}22}$			
$R^1 = N(Bn)CH_2Ar$, $R^4 = Me$	DMF, $POCl_3$	PhCHO (**I**) + ArCHO (**II**)	54
Ar		**I**:**II**	
2-Thienyl		1:1.7	
$2,3,4,5,6\text{-}F_5C_6$		1:0	
$4\text{-}FC_6H_4$		1.3:1	
$4\text{-}ClC_6H_4$		1.6:1	
$4\text{-}BrC_6H_4$		1.6:1	
$4\text{-}MeOC_6H_4$		1:8.5	

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{32}			
	DMF, $POCl_3$	 (67)	248
	—	 (75)	248

C. Trisubstituted Benzenes

C1. R^1, R^2, R^3 Substituents

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_8			
$R^1 = OMe$, $R^2 + R^3 = OCH_2O$	—	$R^6 = CHO$ (50)	250
	DMF, $POCl_3$, KI	$R^4 = CHO$ (21) + $R^6 = CHO$ (59)	251
	DMF, $POCl_3$	$R^4 = CHO$ (30) + $R^6 = CHO$ (53)	251
	DMF, $POCl_3$	$R^4 = CHO$ + $R^6 = CHO$ (—) 70:30	252
	MFA, $POCl_3$	$R^6 = CHO$ (63)	253, 254
	MFA, $POCl_3$	$R^4 = CHO$ (10) + $R^6 = CHO$ (34)	255
C_9			
$R^1 = i\text{-}Pr$, $R^2 = R^3 = OH$	DMF, $POCl_3$	$R^4 = CHO$ (50)	256
$R^1 = R^3 = OMe$, $R^2 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (83)	234, 257
$R^1 = R^2 = R^3 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (70-80)	234
C_{10}			
$R^1 + R^2 = OCH_2O$, $R^3 = i\text{-}Pr$	—	$R^5 = CHO$ (—)	258

TABLE I. BENZENES (*Continued*)

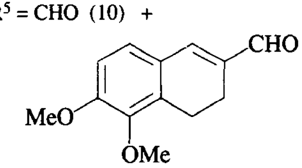
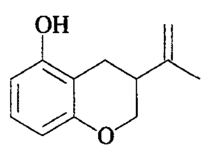
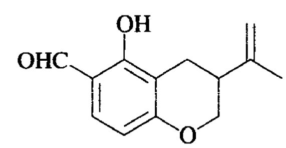
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{11}			
$R^1 = R^2 = OMe$, $R^3 = CH_2CH{=}CH_2$	MFA, $POCl_3$	$R^5 = CHO$ (10) +  (8)	237
$R^1 + R^2 = (CH_2)_4$, $R^3 = OMe$	MFA, $POCl_3$	$R^6 = CHO$ (—)	189
$R^1 + R^2 = N(Et)(CH_2)_2$, $R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (65)	225
$R^1 + R^2 = N(Et)(CH_2)_2$, $R^3 = Me$	1. DMF, $POCl_3$ 2. $EtNO_2$ 3. $LiAlH_4$ 4. Pd, H_2	$R^4 = CH_2CH(Me)NH_2$ (65)	225
C_{12}			
	—	 (—)	259
C_{13}			
$R^1 + R^2 = CH(Me)(CH_2)_2CH(Me)$, $R^3 = OMe$	DMF, $POCl_3$	$R^6 = CHO$ (60)	260
C_{15}			
$R^1 + R^2 = N(Bn)(CH_2)_2$, $R^3 = Cl$	DMF, $POCl_3$	$R^4 = CHO$ (98)	225

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C2. R^1, R^2, R^4 Substituents		
C_7			
$R^1 + R^2 = OCH_2O$, $R^4 = OH$	—	$R^5 = CHO$ (—)	261
C_8			
$R^1 + R^2 = OCH_2O$, $R^4 = SeMe$	MFA, $POCl_3$	$R^5 = CHO$ (65)	262
$C_{8\text{-}11}$			
$R^1 + R^2 = OCH_2O$, $R^4 = SR$		$R^5 = CHO$	262
R			
Me	DMF, $POCl_3$	(75)	
	MFA, $POCl_3$	(86)	
	$4\text{-}ClC_6H_4N(Me)CHO$, $POCl_3$	(70)	
	$4\text{-}O_2NC_6H_4N(Me)CHO$, $POCl_3$	(50)	
	$4\text{-}MeC_6H_4N(Me)CHO$, $POCl_3$	(91)	
	$4\text{-}MeOC_6H_4N(Me)CHO$, $POCl_3$	(93)	
	$4\text{-}i\text{-}PrC_6H_4N(Me)CHO$, $POCl_3$	(90)	
	$1,3,5\text{-}Me_3C_6H_2N(Me)CHO$, $POCl_3$	(78)	
	$4\text{-}t\text{-}BuC_6H_4N(Me)CHO$, $POCl_3$	(89)	
Et	MFA, $POCl_3$	(80)	
n-Pr	MFA, $POCl_3$	(81)	
i-Pr	MFA, $POCl_3$	(79)	
n-Bu	MFA, $POCl_3$	(80)	
i-Bu	MFA, $POCl_3$	(80)	
s-Bu	MFA, $POCl_3$	(79)	
C_9			
$R^1 + R^2 = OCH_2CH_2$, $R^4 = OMe$	MFA, $POCl_3$	$R^5 = CHO$ (56)	263
$R^1 = R^4 = Me$, $R^2 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (80)	217, 234
$R^1 = Me$, $R^2 = R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (87)	234, 264
$R^1 = R^2 = OMe$, $R^4 = Me$	DMF, $POCl_3$	$R^5 = CHO$ (35-40)	186
$R^1 = R^2 = R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (88)	234
$R^1 = R^2 = OMe$, $R^4 = SMe$	MFA, $POCl_3$	$R^5 = CHO$ (85)	48

TABLE I. BENZENES (*Continued*)

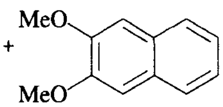
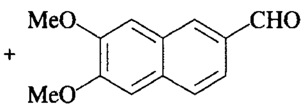
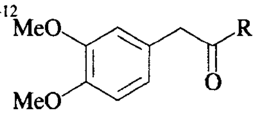
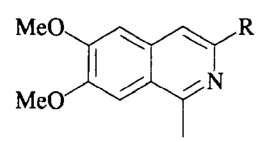
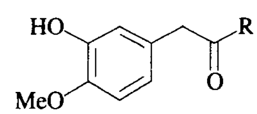
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$R^1 = R^4 = OMe$, $R^2 = SMe$	MFA, $POCl_3$	$R^5 = CHO$ (53)	48, 265
$R^1 = SMe$, $R^2 = R^4 = OMe$	MFA, $POCl_3$	$R^5 = CHO$ (96)	48
$R^1 + R^2 = O(CH_2)O$, $R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (77)	266, 267
C_{10}			
$R^1 = R^4 = OMe$, $R^2 = NMe_2$	DMF, $POCl_3$	$R^5 = CHO$ (47)	204
$R^1 + R^2 = OCH(Me)CH_2$, $R^4 = OMe$	MFA, $POCl_3$	$R^5 = CHO$ (78)	263
C_{11}			
$R^1 = R^2 = OMe$, $R^4 = CH_2CH{=}CH_2$	MFA, $POCl_3$, 8 h	$R^5 = CHO$ (5) +  **I** (3) +  **II** (15)	237
	MFA, $POCl_3$, 72 h	**I** (8) + **II** (39)	237
$R^1 = CH_2CH{=}CH_2$, $R^2 = R^4 = OMe$	MFA, $POCl_3$	$R^5 = CHO$ (63)	237
$R^1 + R^2 = (CH_2)_4$, $R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (—)	186
	MFA, $POCl_3$	$R^5 = CHO$ (—)	189
$R^1 + R^2 = (CH_2)_2N(Et)$, $R^4 = Me$	DMF, $POCl_3$	$R^5 = CHO$ (51)	225
$R^1 = Me$, $R^2 = OMe$, $R^4 = i\text{-Pr}$	DMF, $POCl_3$	$R^5 = CHO$ (76)	186
$R^1 = i\text{-Pr}$, $R^2 = R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (76)	264
$C_{11\text{-}12}$ 	$MeCONH_2$, $POCl_3$	 **I** +  **II**	45

TABLE I. BENZENES (*Continued*)

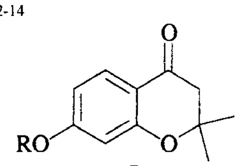
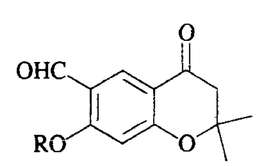
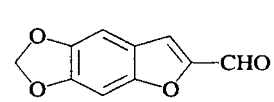
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R			
Me		**I** (9)	
Et		**I** (7) + **II** (8)	
C_{12}			
$R^1 + R^2 = (CH_2)_2C(Me)_2O$, $R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (79)	268
$R^1 + R^2 = CH{=}CHC(Me)_2$, $R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (89)	269
$R^1 = R^4 = OMe$, $R^2 = (CH_2)_2CO_2Me$	—	$R^5 = CHO$ (85)	270
$R^1 + R^2 = (CH_2)_4$, $R^4 = OEt$	MFA, $POCl_3$	$R^3 = CHO$ (—)	189
$C_{12\text{-}14}$ 	DMF, $POCl_3$		247
R			
Me		(78)	
Et		(80)	
Pr		(78)	
C_{13}			
$R^1 = R^2 = OMe$, $R^4 = (CH_2)_2N(Me)COCF_3$	DMF, $POCl_3$	$R^5 = CHO$ (45)	271
$R^1 + R^2 = OCH_2O$, $R^4 = OCH_2CH(OEt)_2$	DMF, $POCl_3$	 (15)	240
$R^1 + R^2 = CH(Me)(CH_2)_2CH(Me)$ $R^4 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (69)	272

TABLE I. BENZENES (*Continued*)

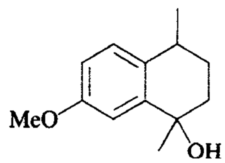
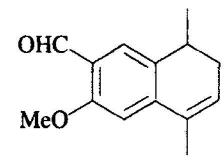
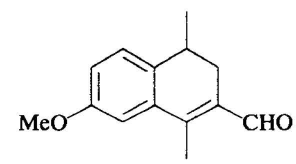
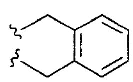
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (28) +  (28)	260
R^1 = *i*-C_5H_{11}, R^2 = R^4 = OMe	DMF, $POCl_3$	R^5 = CHO (84)	268
R^1 + R^2 =  R^4 = OMe	MFA, $POCl_3$	R^5 = CHO (82)	50
C_{16}			
R^1 = $COCH_2C_6H_4$Me-4, R^2 = R^4 = OMe	DMF, $POCl_3$	R^5 = CHO (60)	273
R^1 = CH=CHPh, R^2 = R^4 = OMe	DMF, $POCl_3$	R^5 = CHO (39)	209
R^1 + R^2 = $(CH_2)_2N(Bn)$, R^4 = Me	1. DMF, $POCl_3$ 2. $MeNO_2$ 3. $LiAlH_4$ 4. H_2, Pd	R^5 = $(CH_2)_2NH_2$ (70)	255

TABLE I. BENZENES (*Continued*)

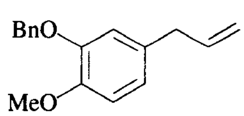
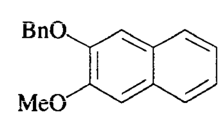
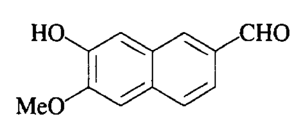
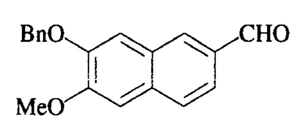
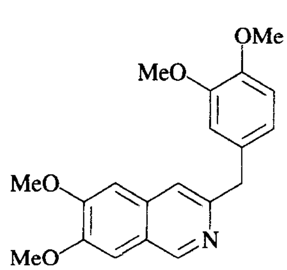
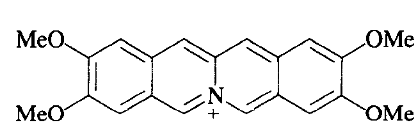
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	MFA, $POCl_3$	 (3) +  (24) +  (9)	237
C_{20}			
	1. DMF, $POCl_3$ 2. ClO_4^-	 ClO_4^- (—)	46

TABLE I. BENZENES (*Continued*)

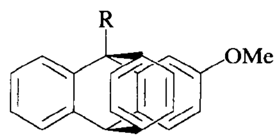
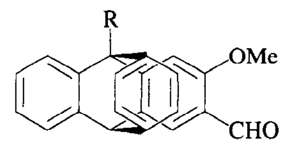
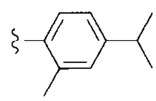
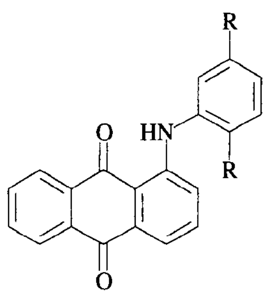
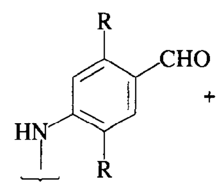
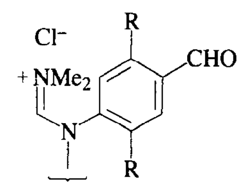
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{21-31}			
	MFA, $POCl_3$		50
R			
H		(82)	
		(79)	
C_{22}			
	DMF, $POCl_3$	 + 	211
		I + II	
R			
Me		I (37) + II (8)	
OMe		I (100)	
C_{24}			
R^1 = OMe, R^4 = Me, R^2 = $N(CH_2CO_2C_6H_{13})_2$	—	R^5 = CHO (—)	49

TABLE I. BENZENES (*Continued*)

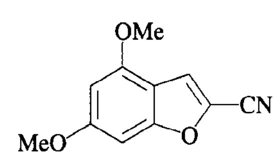
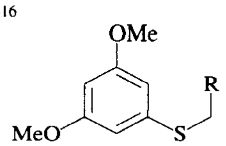
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C3. R^1, R^3, R^5 Substituents	
C_8			
R^1 = Br, R^3 = R^5 = OMe	DMF, $POCl_3$	R^2 = CHO (84)	274
R^1 = OH, R^3 = R^5 = OMe	DMF, $POCl_3$	R^2 = CHO (35) + R^4 = CHO (45)	275
	DMF, $POCl_3$	R^2 = CHO (11) + R^4 = CHO (52) + R^6 = CHO (1)	276
C_9			
R^1 = R^3 = R^5 = Me	DMF, $(CF_3SO_2)_2O$	R^2 = CHO (60)	47
R^1 = R^3 = Me, R^5 = OMe	DMF, $POCl_3$	R^2 = CHO (70)	217
R^1 = Me, R^3 = R^5 = OMe	DMF, $POCl_3$	R^2 = CHO (84)	234
R^1 = R^3 = R^5 = OMe	DMF, $POCl_3$	R^2 = CHO (94)	274, 186
C_{10}			
R^1 = R^3 = OMe, R^5 = OCH_2CN	DMF, $POCl_3$	R^2 = CHO (7-13) + R^6 = CHO (29-36) +  (0-61)	236
R^1 = NMe_2, R^3 = R^5 = Me	DMF, $POCl_3$ (2 eq)	R^4 = CHO (69) + R^2 = R^4 = CHO (—)	33
	DMF, $POCl_3$ (>2 eq)	R^2 = R^4 = CHO (81)	33
C_{10-16}			
	DMF, $POCl_3$		44

TABLE I. BENZENES (*Continued*)

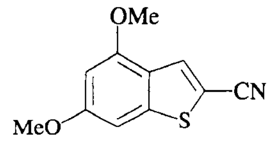
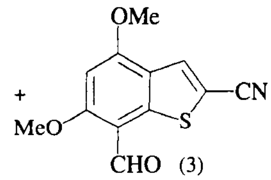
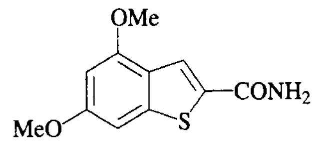
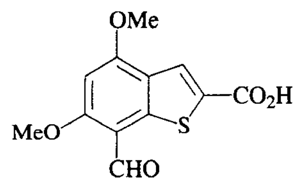
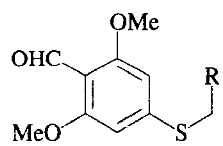
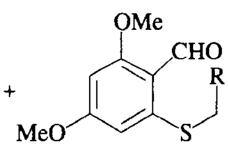
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R / CN		 (12) +  (3)	
		+  (22)	
CO_2H		 (56)	
CO_2Et		 (25) +  (35) +	

TABLE I. BENZENES (*Continued*)

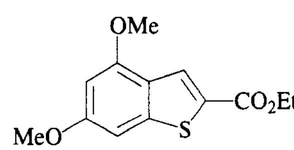
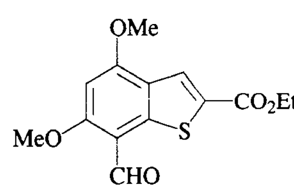
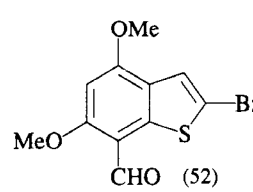
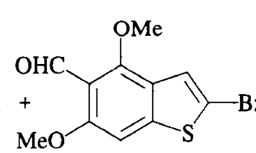
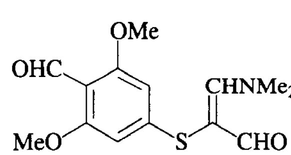
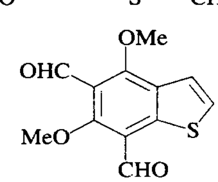
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 (4) +	
		 (16)	
COPh		 (52) +  (2)	
$CH(OEt)_2$		 (12) +	
		 (18)	

TABLE I. BENZENES (*Continued*)

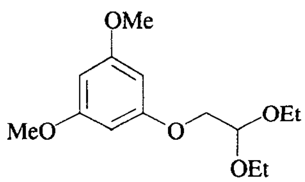
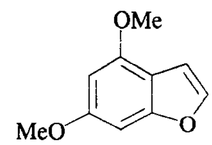
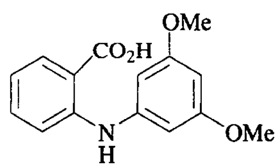
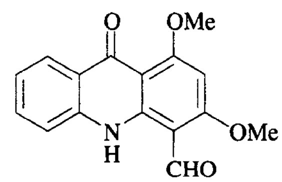
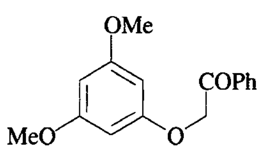
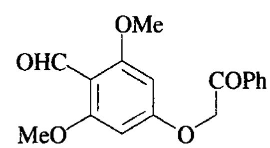
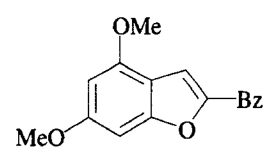
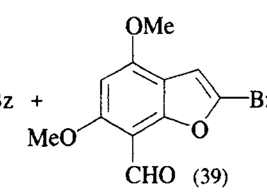
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
$R^1 = CH_2CO_2Et$, $R^3 = R^5 = OMe$	—	$R^2 = CHO$ (—)	277
C_{14}			
$R^1 = OH$, $R^3 = R^5 = N(CH_2CH_2)_2O$	DMF, $POCl_3$	$R^2 = CHO$ (—)	278
	DMF, $POCl_3$	 (58)	240
C_{15}			
	DMF, $POCl_3$	 (15)	279
C_{16}			
	DMF, $POCl_3$	 (14) +  (39) +  (39)	43

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{20}			
$R^1 = R^3 = Cl$, $R^5 = N(Bn)_2$	DMF, $POCl_3$	$R^2 = CHO$ (66)	244
C_{28}			
$R^1 = CH_2O_2CPh$, $R^3 = R^5 = OBn$	DMF, $POCl_3$	$R^2 = CHO$ (66)	280
	D. Tetrasubstituted Benzenes		
	D1. R^1, R^2, R^3, R^4 Substituents		
C_{10}			
$R^1 = R^2 = R^3 = R^4 = OMe$	MFA, $POCl_3$	$R^5 = CHO$ (94)	281-283
C_{16}			
$R^1 = R^2 = R^3 = OMe$, $R^4 = OBn$	MFA, $POCl_3$	$R^5 = CHO$ (23) + $R^6 = CHO$ (33)	284
	D2. R^1, R^2, R^3, R^5 Substituents		
C_{10}			
$R^1 + R^2 = OCH_2O$, $R^3 = OMe$, $R^5 = (CH_2)_2Cl$	DMF, $POCl_3$	$R^4 = CHO$ (46) + $R^6 = CHO$ (23)	285, 286
$R^1 = R^2 = R^3 = R^5 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (86)	234, 287
$R^1 = R^3 = R^5 = OMe$, $R^2 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (73)	274
$R^1 = R^2 = R^3 = Me$, $R^5 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (70)	217
$R^1 = OMe$, $R^2 = R^3 = R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (93)	234
$R^1 = R^2 = R^3 = OMe$, $R^5 = OEt$	—	$R^4 = CHO$ (—)	288
$R^1 = R^3 = R^5 = OMe$, $R^2 = OEt$	—	$R^4 = CHO$ (—)	288
C_{14}			
$R^1 = R^2 = R^3 = OMe$, $R^5 = CH_2CH(OAc)Me$	MFA, $POCl_3$	$R^4 = CHO$ (77)	289

TABLE I. BENZENES (*Continued*)

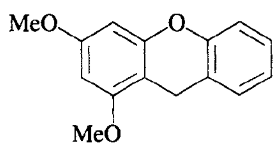
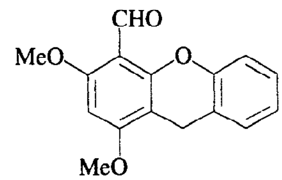
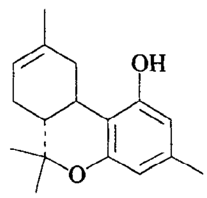
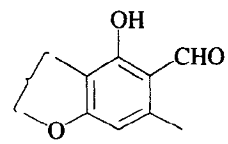
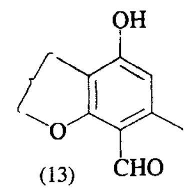
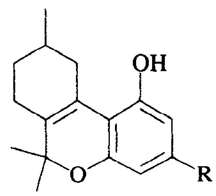
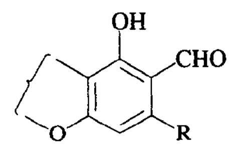
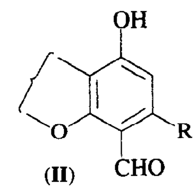
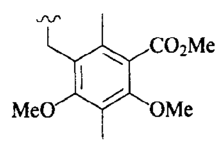
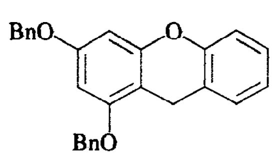
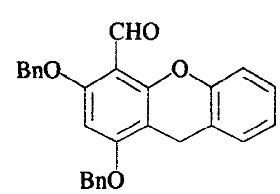
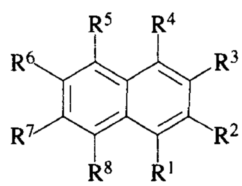
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	MFA, $POCl_3$	 (23)	290
C_{17}			
	DMF, $POCl_3$	 (36) +  (13)	291
C_{17-21}			
	DMF, $POCl_3$	 (I) +  (II)	291
R			
Me	DMF, $POCl_3$	**I** (43) + **II** (9)	
	MFA, $POCl_3$	**I** (32) + **II** (21)	
n-C_5H_{11}	DMF, $POCl_3$	**I** (35) + **II** (12)	

TABLE I. BENZENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{20}			
$R^1 = R^3 = OH$, $R^5 = Me$, R^2 = 	DMF, $POCl_3$	$R^4 = CHO$ (75)	292
C_{21}			
$R^1 = OMe$, $R^2 = CO_2Me$, $R^3 = n\text{-}C_5H_{11}$, $R^5 = OBn$	DMF, $POCl_3$	$R^4 = CHO$ (80)	293
C_{22}			
$R^1 = Me$, $R^2 = CO_2Bn$, $R^3 = OBn$, $R^5 = OMe$	DMF, $POCl_3$	$R^6 = CHO$ (63) + $R^3 = OH$, $R^6 = CHO$ (3)	294
$R^1 = R^3 = OMe$, $R^2 = R^5 = OBn$	DMF, $POCl_3$	$R^4 = CHO$ (61)	287
$R^1 = R^3 = OBn$, $R^2 = R^5 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (27)	287
C_{27}			
	MFA, $POCl_3$	 (88)	290
$R^1 = OMe$, $R^2 = CO_2Bn$, $R^3 = n\text{-}C_5H_{11}$, $R^5 = OBn$	DMF, $POCl_3$	$R^4 = CHO$ (100)	293
	D3. R^1, R^2, R^4, R^5 Substituents		
C_{10}			
$R^1 = OMe$, $R^2 = R^4 = R^5 = Me$	DMF, $POCl_3$	$R^6 = CHO$ (66)	217

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	E. Pentasubstituted Benzenes		
C_9			
$R^1 = R^3 = R^5 = OH$, $R^4 = Me$, $R^2 = CO_2Me$	DMF, $POCl_3$	$R^6 = CHO$ (68)	295
C_{11}			
$R^1 + R^2 = OCH_2O$, $R^3 = OMe$, $R^4 + R^5 = OCH(Me)CH_2$	MFA, $POCl_3$	$R^6 = CHO$ (60)	296
$R^1 + R^2 = OCH_2O$, $R^3 = R^4 = OMe$, $R^5 = CH_2CHBrMe$	MFA, $POCl_3$	$R^6 = CHO$ (40)	296
$R^1 = OMe$, $R^2 = R^3 = R^4 = R^5 = Me$	DMF, $POCl_3$	$R^6 = CHO$ (68)	217

TABLE II. NAPHTHALENES



R^1 - R^8 = H except as indicated

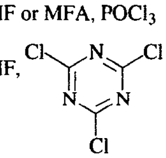
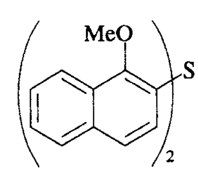
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Naphthalene		
C_{10}			
	DMF, Tf_2O	R^1 = CHO (50)	47
	B. Monosubstituted Naphthalenes		
	B1. R^1 Substituents		
C_{10}			
R^1 = OH	Me_2NN=CHCHO, $POCl_3$ or $COCl_2$	R^4 = CH=CHN=NMe_2^+ Cl^- or $POCl_2^-$	40
C_{11}			
R^1 = OMe	DMF or MFA, $POCl_3$	R^4 = CHO (81)	297
	DMF, 	R^4 = CHO (47)	36
	DMF, $POCl_3$	R^4 = CHO (81)	297
	DMF, $SOCl_2$	R^2 = CHO (37) +  (26)	42

TABLE II. NAPHTHALENES (*Continued*)

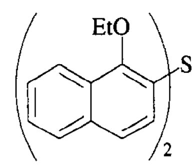
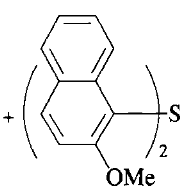
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $(Cl_2PO)_2O$	R^4 = CHO (96)	26
C_{12}			
$R^1 = NMe_2$	MFA, $POCl_3$	R^4 = CHO (47)	36, 2
	DMF, $POCl_3$ (3:1)	R^4 = CHO (33) + $R^2 = R^4$ = CHO (30)	56
	DMF, $POCl_3$ (3:2)	R^4 = CHO (8) + $R^2 = R^4$ = CHO (76)	56
	MFA, $POCl_3$	R^4 = CHO (20)	56
	Et_2NCHO, $POCl_3$ (3:1)	R^4 = CHO (18) + $R^2 = R^4$ = CHO (19)	56
	Et_2NCHO, $POCl_3$ (3:2)	R^4 = CHO (40) + $R^2 = R^4$ = CHO (17)	56
	i-Pr_2NCHO, $POCl_3$ (3:1)	R^4 = CHO (59) + $R^2 = R^4$ = CHO (6)	56
	i-Pr_2NCHO, $POCl_3$ (3:2)	R^4 = CHO (46) + $R^2 = R^4$ = CHO (20)	56
R^1 = OEt	DMF, $SOCl_2$	R^4 = CHO (19) +  (19)	42
C_{14}			
$R^1 = NEt_2$	DMF, $POCl_3$	R^4 = CHO (—)	191
	B2. R^2 Substituents		
C_{10}			
R^2 = OH	MFA, $POCl_3$	R^1 = CHO (—)	189, 298
	H_2NCHO, $AlCl_3$	R^1 = CHO (—)	299
C_{11}			
R^2 = OMe	1. MFA, $POCl_3$ 2. NH_2OH	R^1 = CN (20)	197
	DMF, $SOCl_2$	R^1 = CHO (31) +  (18)	42

TABLE II. NAPHTHALENES (*Continued*)

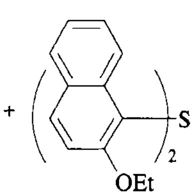
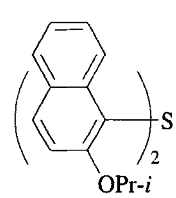
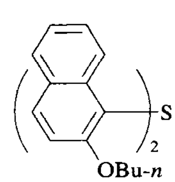
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, SO_2Cl_2	R^1 = CHO (—)	193
	DMF, $(Cl_2PO)_2O$	R^1 = CHO (90)	26
R^2 = SMe	MFA, $POCl_3$	R^1 = CHO (34)	300
C_{12}			
R^2 = OEt	MFA, $POCl_3$	R^1 = CHO (84)	179, 301, 302
	DMF, $SOCl_2$	R^1 = CHO (16) +  (12)	42
R^2 = SEt	—	R^1 = CHO (—)	303
C_{13}			
R^2 = OPr-*i*	DMF, $SOCl_2$	 (10)	42
C_{14}			
R^2 = OBu-*n*	DMF, $SOCl_2$	 (11)	42
$R^2 = NEt_2$	DMF, $POCl_3$	R^6 = CHO (—)	191

TABLE II. NAPHTHALENES (*Continued*)

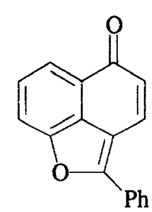
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C. Disubstituted Naphthalenes		
	C1. R^1, R^2 Substituents		
C_{11}			
$R^1 = OH, R^2 = Me$	$Me_2NN{=}CHCHO$, $POCl_3$ or $COCl_2$	$R^4 = CH{=}CHN{=}NMe_2^+\ Cl^-$ or $POCl_2^-$	40
	C2. R^1, R^3 Substituents		
C_{12}			
$R^1 = Me, R^3 = OMe$	DMF, $POCl_3$	R^4 = CHO (66)	304
	C3. R^1, R^4 Substituents		
C_{12}			
$R^1 = OMe, R^4 = Me$	DMF or MFA, $POCl_3$	R^2 = CHO (22)	297
$R^1 = R^4 = OMe$	DMF, $POCl_3$	R^2 = CHO (100)	306, 305
	C4. R^1, R^5 Substituents		
C_{10}			
$R^1 = R^5 = OH$	MFA, $POCl_3$	R^4 = CHO (—)	189
	1. MFA, $POCl_3$ 2. Et_3N, $PhNO_2$	 (47)	59
C_{12}			
$R^1 = R^5 = OMe$	DMF, $POCl_3$	R^4 = CHO (93)	306, 307
	MFA, $POCl_3$	R^4 = CHO (81)	308

TABLE II. NAPHTHALENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C5. R^1, R^6 Substituents		
C_{12}			
$R^1 = R^6 = OMe$	—	R^4 = CHO (—)	309
	DMF, $POCl_3$	R^4 = CHO (61) + unknown isomer (7)	57
	MFA, $POCl_3$	R^5 = CHO (54)	58
	C6. R^1, R^7 Substituents		
C_{12}			
$R^1 = R^7 = OMe$	DMF, $POCl_3$	R^4 = CHO (76) + R^8 = CHO (2)	310
	C7. R^1, R^8 Substituents		
C_{12}			
$R^1 + R^8 = (CH_2)_2$	MFA, $POCl_3$	R^5 = CHO (85)	311
C_{14}			
$R^1 = R^8 = NMe_2$	DMF, $POCl_3$ (0.5 eq)	R^4 = CHO (35)	312
	DMF, $POCl_3$ (1 eq)	$R^4 = R^5$ = CHO (50) + $R^2 = R^5$ = CHO (3)	312
	C8. R^2, R^3 Substituents		
C_{11}			
$R^2 = OH, R^3 = CO_2H$	MFA, $POCl_3$	R^1 = CHO (—)	189
C_{12}			
$R^2 = R^3 = OMe$	DMF, $POCl_3$	R^1 = CHO (23)	313
	C9. R^2, R^6 Substituents		
C_{11}			
$R^2 = OMe, R^6 = Br$	MeNHCHO, $POCl_3$	R^1 = CHO (—)	314
C_{12}			
$R^2 = OMe, R^6 = Me$	MFA, $POCl_3$	R^1 = CHO (86)	315
$R^2 = R^6 = OMe$	DMF, $POCl_3$	R^1 = CHO (81) + $R^1 = R^5$ = CHO (5)	297

TABLE II. NAPHTHALENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C10. R^2, R^7 Substituents	
C_{10}			
$R^2 = R^7 = OH$	MFA, $POCl_3$	$R^1 = CHO$ (—)	189
C_{12}			
$R^2 = R^7 = OMe$	DMF, $POCl_3$	$R^1 = CHO$ (82)	316, 297
		D. Trisubstituted Naphthalenes	
		D1. R^1, R^2, R^6 Substituents	
C_{13}			
$R^1 = Me$, $R^2 = R^6 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (76)	297
		D2. R^1, R^2, R^7 Substituents	
C_{13}			
$R^1 = Me$, $R^2 = R^7 = OMe$	DMF, $POCl_3$	$R^8 = CHO$ (83)	297
		D3. R^1, R^4, R^5 Substituents	
C_{13}			
$R^1 = R^5 = OMe$, $R^4 = Me$	MFA, $POCl_3$	$R^8 = CHO$ (85)	308
		D4. R^1, R^4, R^6 Substituents	
C_{13}			
$R^1 = Me$, $R^4 = R^6 = OMe$	DMF, $POCl_3$	$R^5 = CHO$ (70)	310
		D5. R^1, R^4, R^8 Substituents	
C_{12}			
$R^1 = OH$, $R^4 = R^8 = OMe$	DMF, $POCl_3$	$R^1 = OCHO$ (62) + $R^2 = CHO$ (24)	306
C_{13}			
$R^1 = R^4 = R^8 = OMe$	DMF, $POCl_3$	$R^2 = CHO$ (13) + $R^5 = CHO$ (80)	306

TABLE II. NAPHTHALENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		E. Tetrasubstituted Naphthalenes	
		E1. R^1, R^4, R^5, R^6 Substituents	
C_{15}			
$R^1 = R^6 = Me$, $R^4 + R^5 = CH(Me)CH_2O$	MFA, $POCl_3$	$R^8 = CHO$ (91)	317
		E2. R^1, R^4, R^5, R^8 Substituents	
C_{14}			
$R^1 = R^4 = R^5 = OMe$, $R^8 = Me$	DMF, $POCl_3$	$R^2 = CHO$ (99)	318
$R^1 = R^4 = R^5 = R^8 = OMe$	—	$R^2 = CHO$ (99)	319

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS

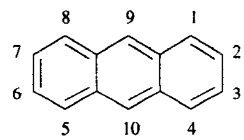
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$C_6/C_6/C_6$		
	A. 		
C_{14}			
1,5,10-Cl_3	MFA, $POCl_3$	1,5,10-Cl_3-9-CHO (—)	189
2,9-Cl_2	MFA, $POCl_3$	2,9-Cl_2-10-CHO (—)	189
—	DMF, $POCl_3$	9-CHO (63)	192
	MFA, $POCl_3$	9-CHO (92)	60, 179, 189, 301, 320
	DMF, PCl_3	9-CHO (49)	321
	DMF, PCl_5	9-CHO (50)	321
	DMF, $SOCl_2$	9-CHO (9) + $(9\text{-}C_{14}H_9)_2S$ (19)	42
	DMF, SO_2Cl_2	9-CHO (—)	193
	DMF, Tf_2O	9-CHO (98)	47
C_{15}			
9-Me	MFA, $POCl_3$	9-Me-10-CHO	311
2-OMe	MFA, $POCl_3$	2-OMe-1-CHO (40) + 2-OMe-3-CHO (23)	42, 322, 323, 50
C_{16}			
1,2-OMe_2-10-Cl	MFA, $POCl_3$	1,2-$(OMe)_2$-10-Cl-9-CHO (—)	189
2,6-OMe_2-10-Cl	MFA, $POCl_3$	2,6-$(OMe)_2$-10-Cl-9-CHO)—)	189
2-OMe-9-Me	MFA, $POCl_3$	2-OMe-9-Me-1-CHO (48)	50

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS (*Continued*)

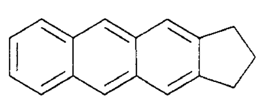
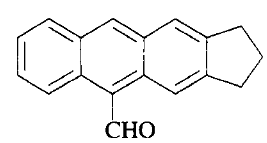
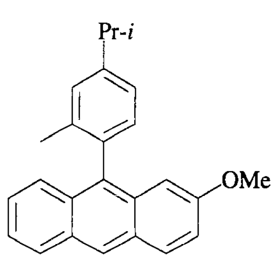
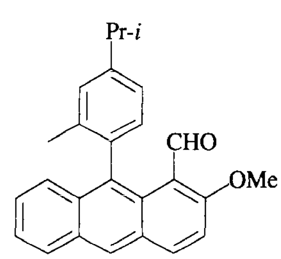
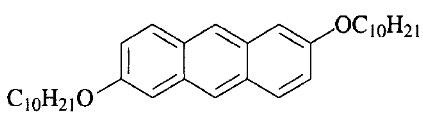
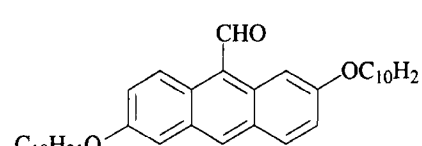
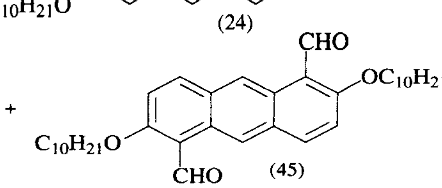
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	MFA, $POCl_3$	 (71)	324
C_{21}			
9-BzO	DMF, $POCl_3$	9-BzO-10-CHO (90)	325
2-OMc-9-Ph	MFA, $POCl_3$	2-OMe-9-Ph-1-CHO (50)	50
C_{24}			
	MFA, $POCl_3$	 (98)	50
C_{34}			
	MFA, $POCl_3$	 (24) +  (45)	326

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS (*Continued*)

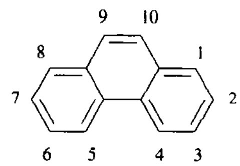
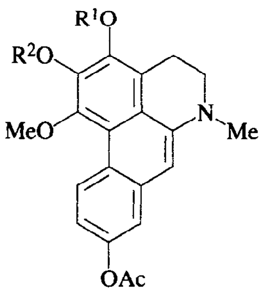
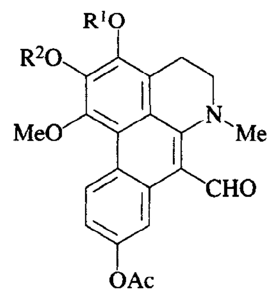
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	B. 		
C_{14}			
—	DMF, Tf_2O	3-CHO (25)	47
C_{15}			
3-OMe	DMF, $POCl_3$	3-OMe-9-CHO (48)	61
C_{23}			
	DMF, $POCl_3$		327
R^1 / R^2			
Me / COMe		(94)	
COMe / Me		(100)	

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS (*Continued*)

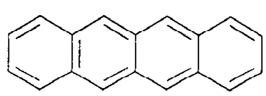
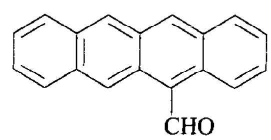
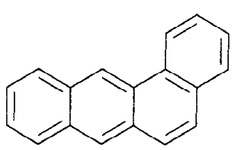
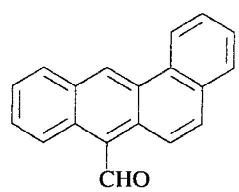
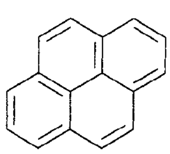
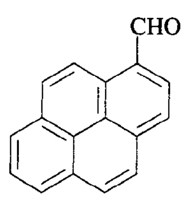
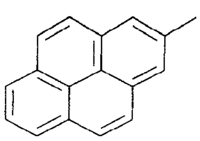
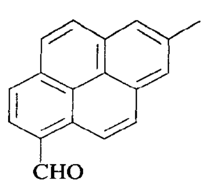
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$C_6/C_6/C_6/C_6$		
C_{16}			
	MFA, $POCl_3$	 (62)	328
	MFA, $POCl_3$	 (64)	60
	MFA, $POCl_3$	 (53)	329
C_{17}			
	MFA, $POCl_3$	 (80)	330

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS (*Continued*)

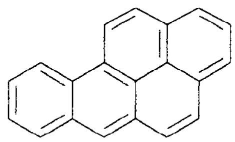
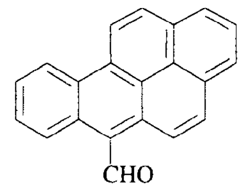
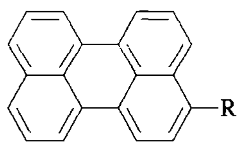
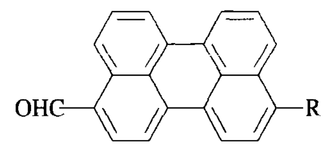
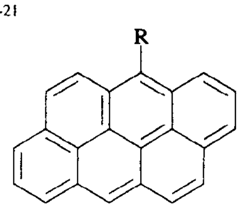
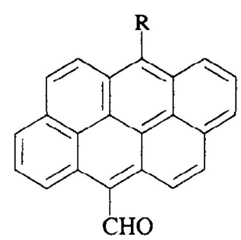
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_6/C_6/C_6/C_6/C_6$	
C_{20} 	MFA, $POCl_3$	 (90)	331
C_{20-21}  R: H, Me	MFA, $POCl_3$	 (63), (55)	332
		$C_6/C_6/C_6/C_6/C_6/C_6$	
C_{20-21}  R: H, Me	MFA, $POCl_3$	 (53), (49)	333

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS (*Continued*)

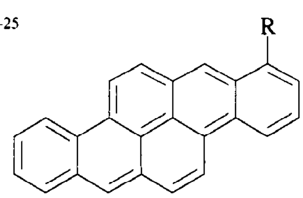
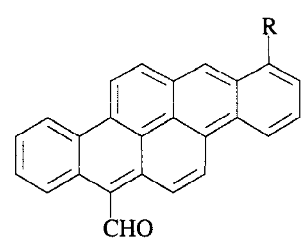
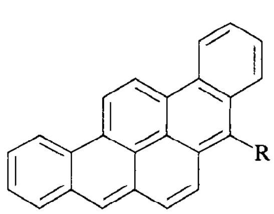
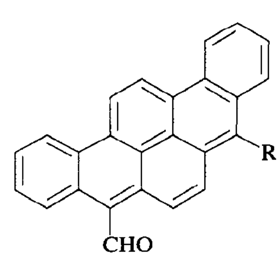
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{24-25}  R: H, Me	MFA, $POCl_3$	 (75), (81)	334
 R: H, Me	MFA, $POCl_3$	 (91), (46)	335

TABLE III. OTHER POLYCYCLIC BENZENOID HYDROCARBONS (*Continued*)

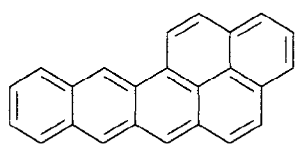
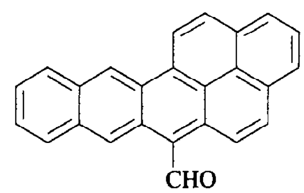
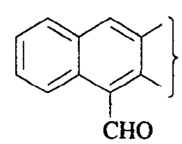
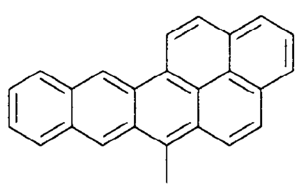
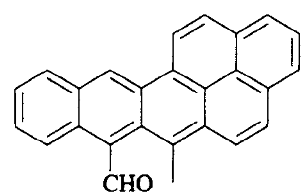
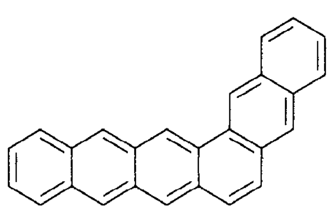
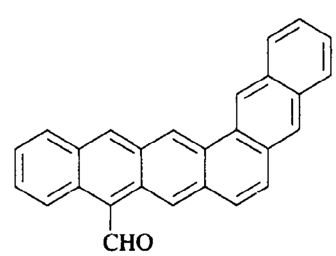
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{24} 	MFA, $POCl_3$	 (48) +  (3)	336
C_{25} 	MFA, $POCl_3$	 (27)	336
C_{26} 	MFA, $POCl_3$	 (20)	337

TABLE IV. CARBOCYCLIC ANIONS

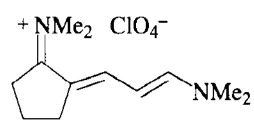
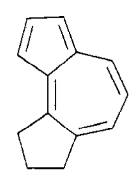
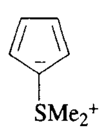
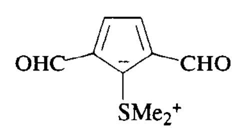
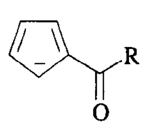
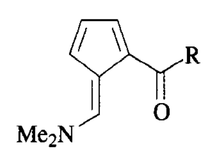
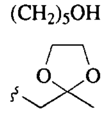
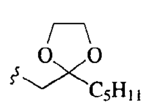
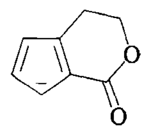
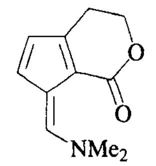
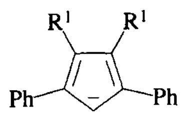
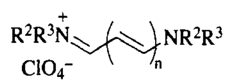
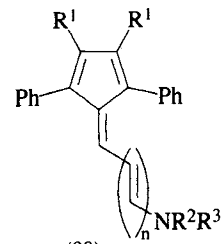
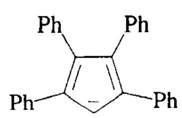
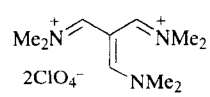
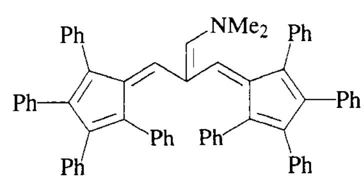
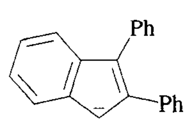
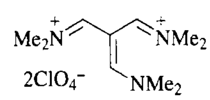
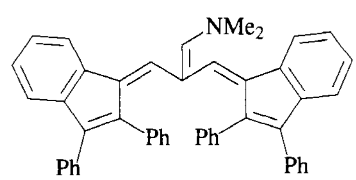
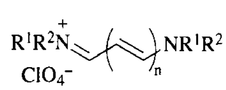
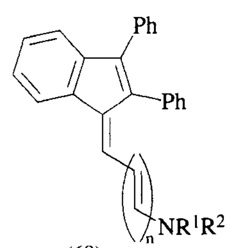
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		A. C_5	
C_5			
		 (28)	64
C_7			
	DMF, $POCl_3$	 (4)	338
$C_{7\text{-}15}$			
			
R			
Me	DMF, $POCl_3$, NaOMe	(93)	62, 339
OEt	DMF, $POCl_3$, NaOMe	(39)	62
$(CH_2)_5OH$	DMF, $POCl_3$	(54)	62
	DMF, $POCl_3$	(58)	62, 339
	DMF, $POCl_3$	(46)	62, 339

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_8 	DMF, $POCl_3$, NaOMe	 (66)	62, 339
C_{17-29} 			63

R^1	R^2	R^3	n	Yield (%)
H	Me	Me	0	(98)
H	Me	Me	1	(98)
Ph	Me	Me	0	(76)
	Me	Me	2	(97)
	$(CH_2)_5$		1	(81)
	$(CH_2)_5$		2	(85)
	Me	Ph	0	(57)
	Me	Ph	1	(70)
	Me	Ph	2	(90)

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{29} 		 (89)	63
		C_5/C_6	
C_{21} 		 (98)	63
			63

R^2	R^3	n	Yield (%)
Me	Me	0	(68)
Me	Me	1	(97)
Me	Me	2	(97)
$(CH_2)_5$		1	(80)
$(CH_2)_5$		2	(94)
Me	Ph	0	(53)
Me	Ph	1	(95)
Me	Ph	2	(91)

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

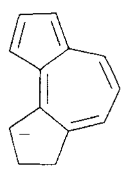
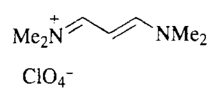
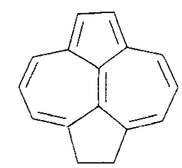
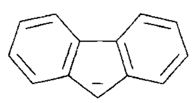
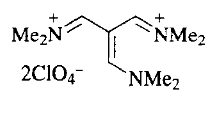
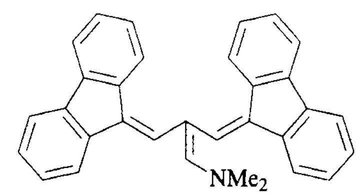
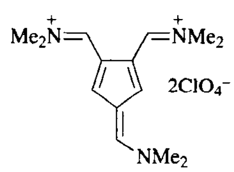
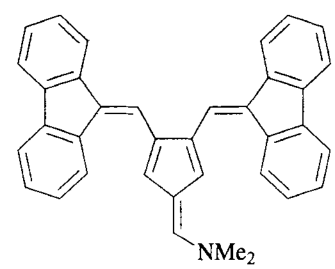
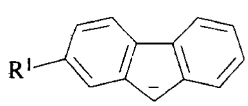
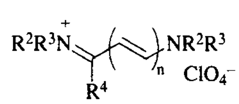
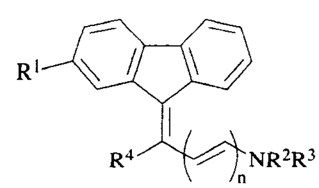
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_5/C_7		
C_{13} 		 (55)	64
	$C_5/C_6/C_6$		
C_{13} 		 (87)	63
		 (23)	63

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{13\text{-}14}$ 			63

R^1	R^2	R^3	R^4	n	Yield (%)
H	Me	Me	H	1	(85)
	Me	Me	H	2	(90)
	Me	Me	H	3	(90)
	Me	Me	Me	2	(91)
	$(CH_2)_5$		H	1	(80)
	$(CH_2)_5$		H	2	(90)
	Me	Ph	H	1	(87)
	Me	Ph	H	2	(37)
	Me	Me	Ph	2	(86)
NO_2	Me	Me	H	0	(87)
	Me	Me	H	1	(97)
	Me	Me	H	2	(98)
	Me	Ph	H	1	(87)
	Me	Ph	H	2	(92)
CN	Me	Me	H	0	(81)
	Me	Me	H	1	(90)
	Me	Ph	H	0	(68)
	Me	Ph	H	1	(94)
	Me	Ph	H	2	(91)

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

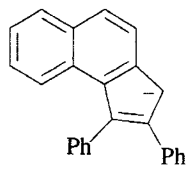
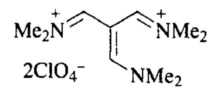
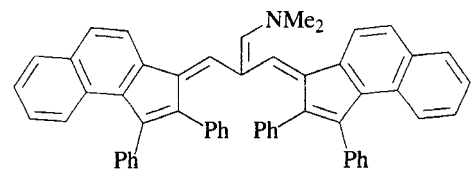
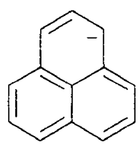
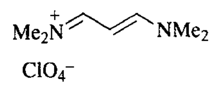
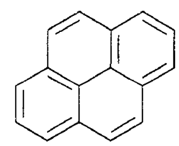
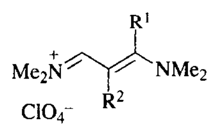
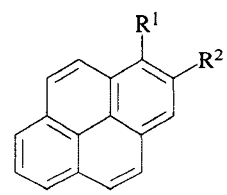
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{25} 		 (81)	63
	$C_6/C_6/C_6$		
C_{13} 		 (91)	65, 340
			65
	R^1 / R^2		
	H / Cl	(38)	
	H / NO_2	(30)	
	H / Me	(79)	
	Me / H	(88)	
	H / OMe	(63)	
	H / Et	(97)	

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

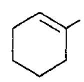
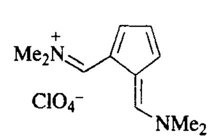
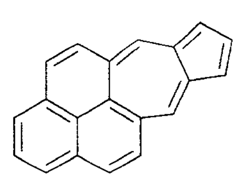
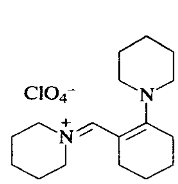
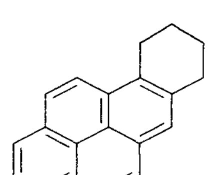
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	R^1 / R^2		
	Et / H	(87)	
	H / 	(95)	
	H / Ph	(74)	
	Ph / H	(67)	
	4-ClC_6H_4 / H	(87)	
	4-BrC_6H_4 / H	(79)	
	4-$MeOC_6H_4$ / H	(80)	
	H / 1-$C_{10}H_7$	(83)	
	H / 2-$C_{10}H_7$	(81)	
		 (61)	65
		 (83)	65

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

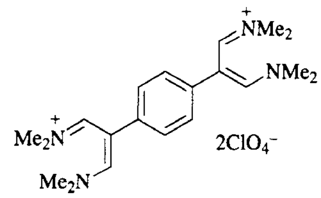
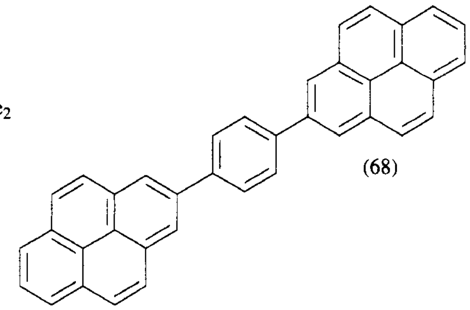
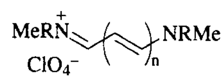
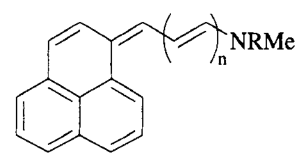
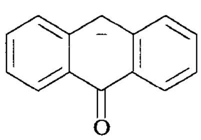
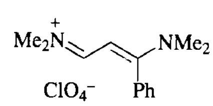
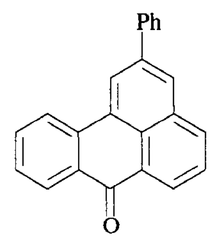
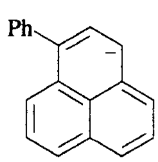
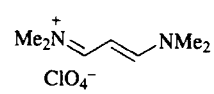
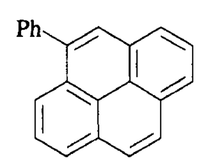
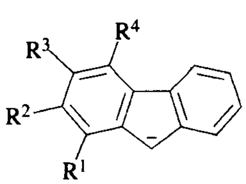
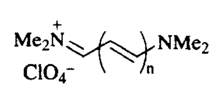
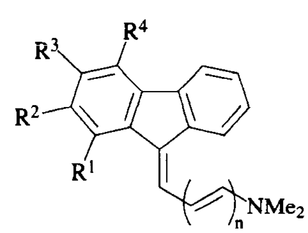
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 (68)	65
			65
	R = Me, n = 2	(72)	
	R = Me, n = 3	(62)	
	R = Ph, n = 1	(95)	
	R = Ph, n = 2	(90)	
C_{14}			
		 (87)	341

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{19}			
		 (94)	65
	$C_5/C_6/C_6/C_6$		
C_{17}			
			63

R^1	R^2	R^3	R^4	n	Yield (%)
CH=CHCH=CH		H	H	1	(95)
CH=CHCH=CH		H	H	2	(98)
H	CH=CHCH=CH		H	1	(70)
H	CH=CHCH=CH		H	2	(93)
H	H	CH=CHCH=CH		1	(96)
H	H	CH=CHCH=CH		2	(98)

TABLE IV. CARBOCYCLIC ANIONS (*Continued*)

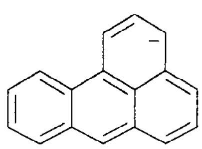
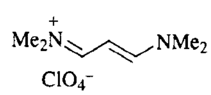
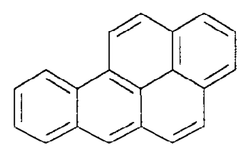
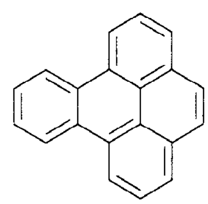
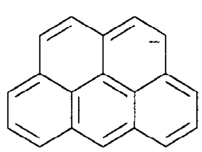
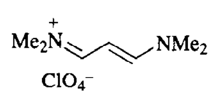
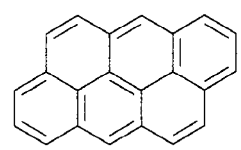
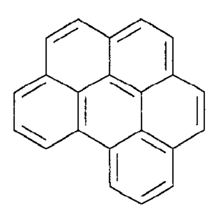
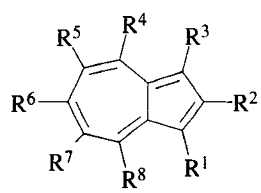
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$C_6/C_6/C_6/C_6$		
C_{17} 		 + (total 82) 	65
	$C_6/C_6/C_6/C_6/C_6$		
C_{19} 		 + (total 33) 	65

TABLE V. AZULENES



R^1 - R^8 = H except as indicated

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Azulene		
C_{10}			
	DMF, $POCl_3$	R^1 = CHO (90-95)	342, 66, 343, 344
	DMF, $POCl_3$, 70°	R^1 = CHO (50) + R^1 = R^3 = CHO (43)	344
	DMF, $POCl_3$, 85°	R^1 = R^3 = CHO (61)	66
	DMF, $POCl_3$	R^1 = $CH{=}NMe_2^+ Cl^-$ (77)	66
	—, PCl_5	R^1 = CHO (84)	345
	MFA, $POCl_3$	R^1 = CHO (85)	344
	DMA, $POCl_3$	R^1 = COMe (70)	66
	1. Me_2NCOBu-*n*, $POCl_3$ 2. $NaBH_4$, BF_3	R^1 = C_5H_{11}-*n* (78)	67
	$Me_2NCOC_{11}H_{23}$-*n*, $POCl_3$	R^1 = $COC_{11}H_{23}$-*n* (82)	66
	Me_2NCOCH_2Cl	R^1 = $COCH_2Cl$ (25)	346
	$Et_2NCO(CH_2)_2CO_2Et$, $POCl_3$	R^1 = $CO(CH_2)_2CO_2Et$ (44)	67
	$Et_2NCO(CH_2)_3CO_2Et$, $POCl_3$	R^1 = $CO(CH_2)_3CO_2Et$ (86)	67
	$Me_2NCO(CH_2)_6CO_2Et$, $POCl_3$	R^1 = $CO(CH_2)_6CO_2Et$ (80)	66
	Me_2NCOPh, $POCl_3$	R^1 = COPh (22)	66
	1. PhN(Me)CH=CHCHO, $POCl_3$ 2. ClO_4^- 3. OH^-	R^1 = CH=CHCHO (95-97)	68
	1. $PhN(Me)(CH{=}CH)_2CHO$, $POCl_3$ 2. ClO_4^- 3. OH^-	R^1 = $(CH{=}CH)_2CHO$ (95-97)	68

TABLE V. AZULENES (*Continued*)

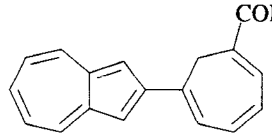
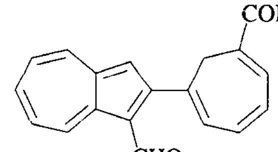
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	B. Monosubstituted Azulenes		
	B1. R^1 Substituents		
C_{11}			
$R^1 = Me$	DMF, $POCl_3$	$R^3 = CHO$ (95)	344, 345, 66
C_{14}			
$R^1 = Bu$-*t*	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
$R^1 = (CH_2)_4OH$	$Et_2NCO(CH_2)_2CO_2Et$, $POCl_3$	$R^1 = (CH_2)_4Cl$, $R^3 = CO(CH_2)_2CO_2Et$ (67)	67
C_{15}			
$R^1 = C_5H_{11}$-*n*	1. Me_2NCOBu-*n*, $POCl_3$ 2. $NaBH_4$, BF_3	$R^3 = C_5H_{11}$-*n* (78)	67
$R^1 = (CH_2)_5OH$	$Et_2NCO(CH_2)_3CO_2Et$, $POCl_3$	$R^1 = (CH_2)_5Cl$, $R^3 = CO(CH_2)_3CO_2Et$ (48)	67
C_{17}			
$R^1 = Bn$	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
C_{18}			
$R^1 = CH(Me)Ph$	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
C_{19}			
$R^1 = C(Me)_2Ph$	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
C_{23}			
$R^1 = CHPh_2$	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
C_{24}			
$R^1 = C(Me)Ph_2$	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
C_{29}			
$R^1 = CPh_3$	DMF, $POCl_3$	$R^3 = CHO$ (80-100)	347
	B2. R^2 Substituents		
C_{19}			
	DMF, $POCl_3$	 (80)	348

TABLE V. AZULENES (*Continued*)

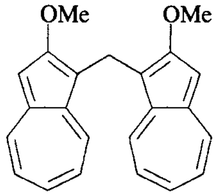
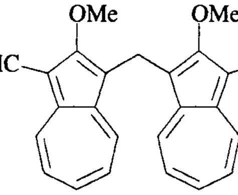
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	B3. R^6 Substituents		
C_{18}			
$R^6 = C_8H_{17}$-*n*	DMF, $POCl_3$	$R^1 = CHO$ (24)	349
	C. Disubstituted Azulenes		
	C1. R^1, R^2 Substituents		
C_{21}			
	DMF, $POCl_3$	 (59)	350
	C2. R^1, R^5 Substituents		
C_{15}			
$R^1 = Et$, $R^5 = i$-Pr	DMF, $POCl_3$	$R^3 = CHO$ (—)	351
	DMA, $POCl_3$	$R^3 = COMe$ (—)	352
	C3. R^4, R^7 Substituents		
C_{12}			
$R^4 = R^7 = Me$	—, $POCl_3$	$R^1 = CHO$ (91)	344
C_{13}			
$R^4 = Me$, $R^7 = Et$ + $R^4 = Et$, $R^7 = Me$	DMF, $POCl_3$	$R^1 = CHO$ (68) + $R^3 = CHO$ (13)	353
C_{14}			
$R^4 = Me$, $R^7 = i$-Pr	DMF, $POCl_3$	$R^1 = CHO$ (—)	345
$R^4 = Me$, $R^7 = i$-Pr + $R^4 = i$-Pr, $R^7 = Me$	DMF, $POCl_3$	$R^1 = CHO$ (61) + $R^3 = CHO$ (15)	353

TABLE V. AZULENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C4. R^4, R^8 Substituents		
C_{12}			
$R^4 = R^8 = Me$	DMF, $POCl_3$	$R^1 = CHO$ (94)	344
	D. Trisubstituted Azulenes		
	D1. R^1, R^4, R^7 Substituents		
C_{13}			
$R^1 = R^4 = R^7 = Me$	DMF, $POCl_3$	$R^3 = CHO$ (96)	344
C_{15}			
$R^1 = R^4 = Me$, $R^7 = i$-Pr	DMF, $POCl_3$	$R^3 = CHO$ (96)	344, 345
	DMF or MFA, $POCl_3$	$R^3 = CHO$ (—)	354
	MFA, $POCl_3$	$R^3 = CHO$ (87)	344
	MFA, $POCl_3$	$R^3 = CHO$ (29) + $R^5 = CHO$ (trace)	355
	D2. R^2, R^4, R^6 Substituents		
C_{15}			
$R^2 = R^4 = Me$, $R^6 = i$-Pr	DMF, $POCl_3$	$R^1 = CHO$ (90)	344
	D3. R^2, R^4, R^7 Substituents		
C_{15}			
$R^2 = R^4 = Me$, $R^7 = i$-Pr	DMF, $POCl_3$	$R^1 = CHO$ (98)	344
	MFA, $POCl_3$	$R^1 = CHO$ (88)	344
	DMF or MFA, $POCl_3$	$R^1 = CHO$ (—)	354
	DMF, $POCl_3$, 70°	$R^1 = R^3 = CHO$ (94)	344
	D4. R^2, R^4, R^8 Substituents		
C_{15}			
$R^2 = i$-Pr, $R^4 = R^8 = Me$	DMF, $POCl_3$	$R^1 = CHO$ (98)	344
	MFA, $POCl_3$	$R^1 = CHO$ (84)	344
	DMF or MFA, $POCl_3$	$R^1 = CHO$ (—)	354

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	D5. R^3, R^5, R^8 Substituents		
C_{15}			
$R^3 = R^8 = Me$, $R^5 = i$-Pr	1. PhN(Me)CH=CHCHO, $POCl_3$ 2. ClO_4^- 3. OH^-	$R^1 = CH{=}CHCHO$ (—)	68
	1. $PhN(Me)(CH{=}CH)_2CHO$, $POCl_3$ 2. ClO_4^- 3. OH^-	$R^1 = (CH{=}CH)_2CHO$ (—)	68
	D6. R^4, R^6, R^8 Substituents		
C_{15}			
$R^4 = R^6 = R^8 = Me$	DMF, $POCl_3$	$R^1 = CHO$ (99)	345, 66
	DMF, PCl_5	$R^1 = CHO$ (92)	66
	DMF, $COCl_2$	$R^1 = CHO$ (87)	345
	DMF, $AlCl_3$	$R^1 = CHO$ (50)	345
	DMF, $POCl_3$	$R^1 = CH{=}NMe_2^+\ Cl^-$ (83)	356, 357
	PhN(Me)CH=CHCHO, $POCl_3$	$R^1 = CH{=}CHCH{=}N(Me)Ph^+\ Cl^-$ (—)	357
	E. Tetrasubstituted Azulenes		
	E1. R^1, R^2, R^4, R^7 Substituents		
C_{16}			
$R^1 = R^2 = R^4 = Me$, $R^7 = i$-Pr	DMF, $POCl_3$	$R^3 = CHO$ (92)	3 44
	E2. R^1, R^2, R^4, R^8 Substituents		
C_{16}			
$R^1 = R^4 = R^8 = Me$, $R^2 = i$-Pr	DMF, $POCl_3$	$R^3 = CHO$ (72)	344
	MFA, $POCl_3$	$R^3 = CHO$ (48)	344

TABLE V. AZULENES (*Continued*)

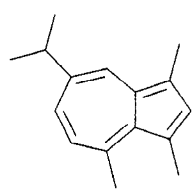
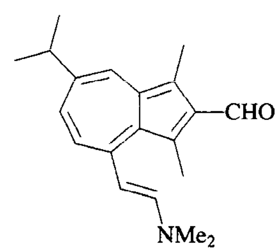
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
E3. R^1, R^3, R^4, R^7 Substituents			
C_{16}			
	DMF, $POCl_3$	 (76)	358

TABLE VI. OTHER POLYCYCLIC NONBENZENOID HYDROCARBONS

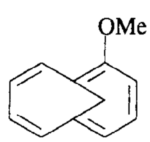
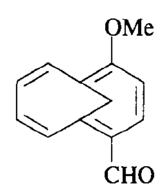
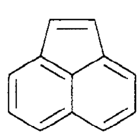
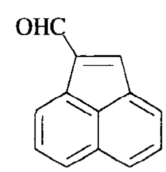
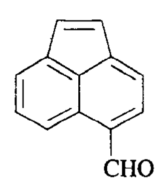
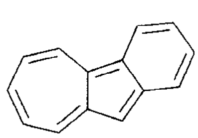
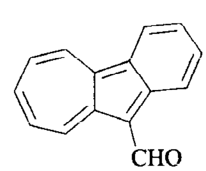
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_7/C_7	
C_{12} 	DMF, $POCl_3$	 (38)	69
		$C_5/C_6/C_6$	
C_{12} 	DMF, $POCl_3$	 (11)	359
	DMF, Tf_2O		47
		$C_5/C_6/C_7$	
C_{14} 	DMF, $POCl_3$	 (91)	344

TABLE VI. OTHER POLYCYCLIC NONBENZENOID HYDROCARBONS (*Continued*)

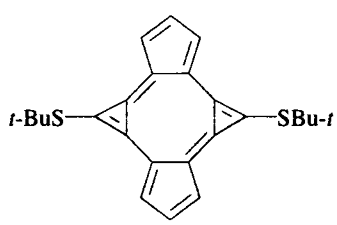
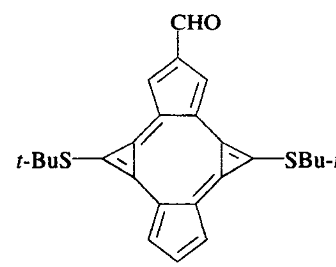
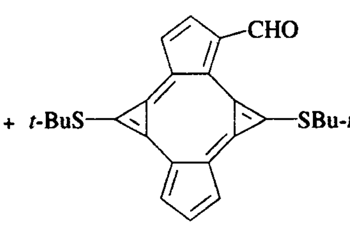
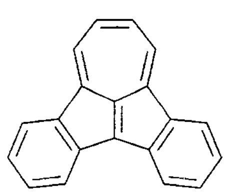
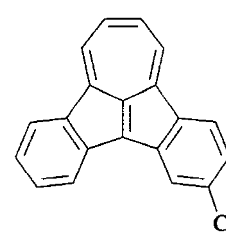
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$C_3/C_3/C_5/C_5/C_8$		
C_{24}			
	1. DMF, $POCl_3$ 2. $NaClO_4$ 3. $NaHCO_3$	 (69)	70
		+  (13)	
	$C_5/C_5/C_6/C_6/C_7$		
C_{20}			
	DMF, $POCl_3$	 (84)	360

TABLE VII. CARBOCYCLIC ORGANOMETALLICS

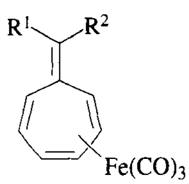
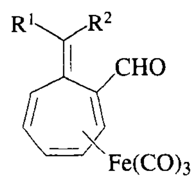
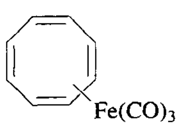
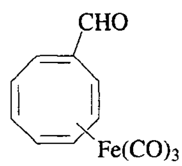
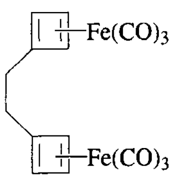
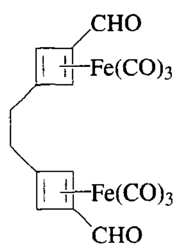
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_7	
$C_{17\text{-}18}$			
	DMF, $POCl_3$		
R^1 / R^2			
Ph / H		(70)	72, 361
4-MeC_6H_4 / H		(70)	72, 361
Ph / Me		(60)	361
		C_8	
C_{11}			
	DMF, $POCl_3$	 (60)	362
		C_4/C_4	
C_{16}			
	MFA, $POCl_3$	 (50)	363

TABLE VII. CARBOCYCLIC ORGANOMETALLICS (*Continued*)

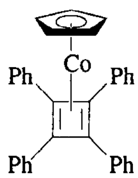
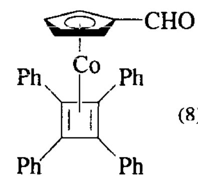
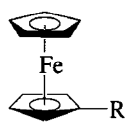
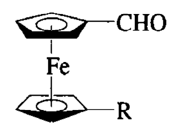
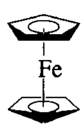
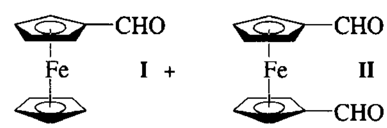
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_4/C_5		
C_{33}			
	MFA, $POCl_3$	 (8)	73
	C_5/C_5		
C_{10}			
	MFA, $POCl_3$		369
R			
Cl		(24)	
Br		(42)	
		 I + II	
		I II	
	MFA, $POCl_3$ (xs)	(0) (55)	71
	MFA, $POCl_3$	(77) (0)	368, 71, 365,366, 367,369

TABLE VII. CARBOCYCLIC ORGANOMETALLICS (*Continued*)

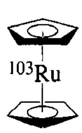
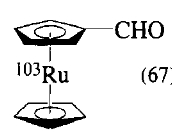
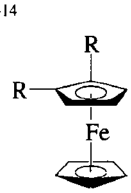
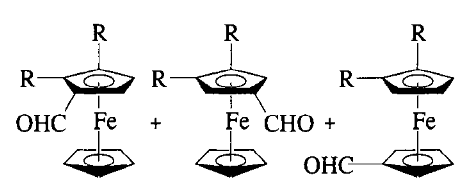
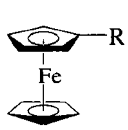
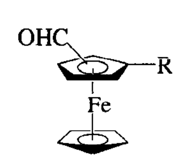
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	—	 (67)	370
C_{12-14}			
	MFA, $POCl_3$	 I + II + III	371
R		I II III	
Me		(19) (50) (19)	
$(CH_2)_4$		(20) (45) (11)	
	MFA, $POCl_3$		372
R			
Et		(58)	
$(CH_2)_2CO_2Me$		(65)	

TABLE VII. CARBOCYCLIC ORGANOMETALLICS (*Continued*)

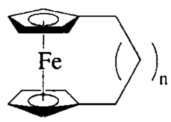
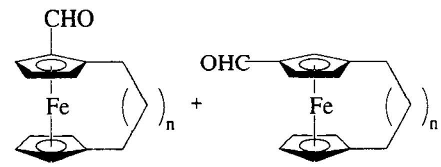
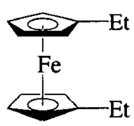
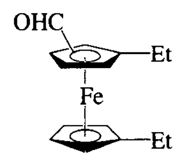
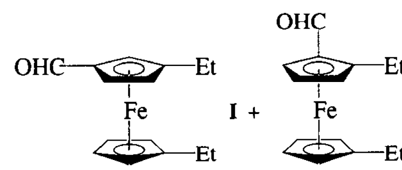
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{13\text{-}14}$ 		 I + II	
n		I / II	
1	DMF, $POCl_3$	(4) (60)	373
	MFA, $POCl_3$	(0) (60)	372
	MeNHCHO, $POCl_3$	(—) (60)	373
2	DMF, $POCl_3$	(3) (64)	373
C_{14} 	MFA, $POCl_3$		372
		 I + II	
		I / II	
	DMF, $POCl_3$	(70) (18)	373
	MFA, $POCl_3$	(53) (6)	374
	MeNHCHO, $POCl_3$, CH_2Cl_2	(70)	373
	MeNHCHO, $POCl_3$	(92) (8)	373

TABLE VII. CARBOCYCLIC ORGANOMETALLICS (*Continued*)

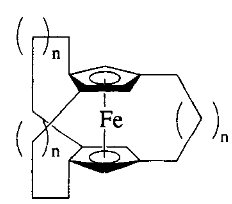
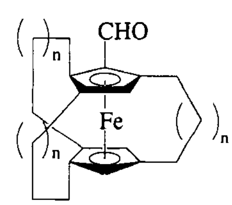
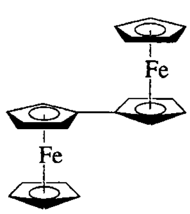
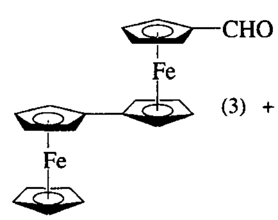
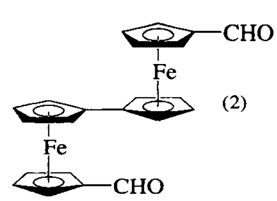
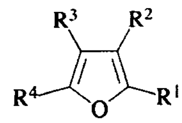
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{19\text{-}22}$ 	DMF, $POCl_3$		
n			
1		(91)	375
2		(96)	376
		$C_5/C_5/C_5/C_5$	
C_{20} 	MFA, $POCl_3$	 (3) +	377
		 (2)	

TABLE VIII. FURANS



R^1 - R^4 = H except as indicated

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Furan		
C_4			
	DMF, $POCl_3$	R^1 = CHO (64)	378
	DMF, $(Cl_2PO)_2O$	R^1 = CHO (71)	26
	$Me_2N^{14}CHO$, $POCl_3$	R^1 = ^{14}CHO (68)	76, 379, 380
	Me_2NCDO, $POCl_3$	R^1 = CDO (35)	76
	B. Monosubstituted Furans		
	B1. R^1 Substituents		
C_5			
R^1 = Me	DMF, $POCl_3$	R^4 = CHO (76)	378
	DMF, $COCl_2$	R^4 = CHO (95)	381
	DMF, $(Cl_2PO)_2O$	R^4 = CHO (77)	26
	1. DMF, $POCl_3$ 2. NH_4SH 3. $BrCH_2CH{=}CH_2$, NaH	R^4 = $CH_2SCH_2CH{=}CH_2$ (50-60)	382
C_6			
R^1 = Et	DMF, $POCl_3$	R^4 = CHO (90)	384, 378, 383
C_7			
R^1 = *i*-Pr	DMF, $POCl_3$	R^4 = CHO (68)	76

TABLE VIII. FURANS (*Continued*)

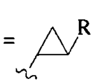
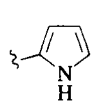
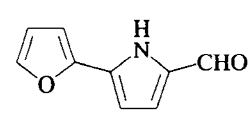
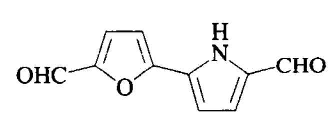
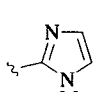
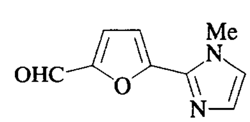
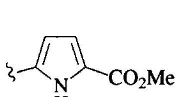
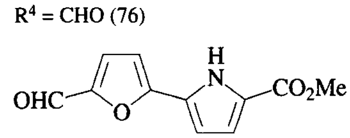
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{7-13}			
R^1 = 	DMF, $POCl_3$		385
R			
H		R^4 = CHO (45)	
Me		R^4 = CHO (63)	
Ph		R^4 = CHO (62)	
C_{8-17}			
R^1 = 	DMF, $POCl_3$	 (62) +	74
		 (14)	
R^1 = 	DMF, $POCl_3$	 (32)	386
R^1 = 4-ClC_6H_4	DMF, $POCl_3$	R^4 = CHO (80)	76
R^1 = 4-BrC_6H_4	DMF, $POCl_3$	R^4 = CHO (76)	76
R^1 = 	DMF, $POCl_3$	 (88)	74
R^1 = 1-$C_{10}H_7$	DMF, $POCl_3$	R^4 = CHO (82)	76
R^1 = 2-$C_{10}H_7$	DMF, $POCl_3$	R^4 = CHO (85)	76

TABLE VIII. FURANS (*Continued*)

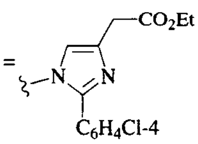
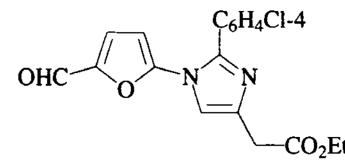
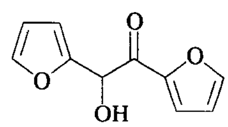
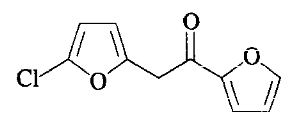
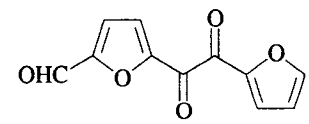
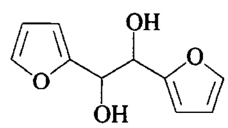
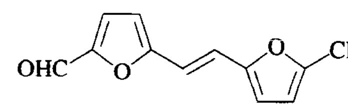
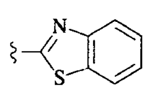
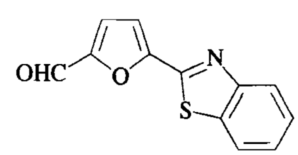
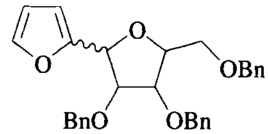
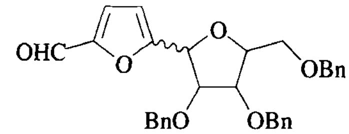
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^1 = 	DMF, $POCl_3$	 (49)	387
C_{10}			
	DMF, $POCl_3$	 (34) +  (26)	388
	DMF, $POCl_3$	 (52)	388
C_{11}			
R^1 = 	DMF, $POCl_3$	 (—)	389

TABLE VIII. FURANS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
$R^1 = CH_2OBn$	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH{=}CH_2$, NaH	$R^4 = CH_2SCH_2CH{=}CH_2$ (50-60)	382
C_{13}			
$R^1 = (CH_2)_2O_2CPh$	DMF, $POCl_3$	R^4 = CHO (86)	390
$R^1 = (CH_2)_7CO_2Me$	—	R^4 = CHO (—)	391
$C_{14\text{-}15}$			
$R^1 = CH{=}C(CO_2Me)Ar$	DMF, $POCl_3$	R^4 = CHO	392
Ar			
4-ClC_6H_4		(70)	
4-MeC_6H_4		(68)	
4-$MeOC_6H_4$		(91)	
C_{16}			
$R^1 = (CH_2)_2C_{10}H_7$-1	DMF, $POCl_3$	R^4 = CHO (69)	393
C_{30}			
	DMF, $POCl_3$	 α anomer (64) β anomer (96)	394

B2. R^2 Substituents

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_5			
R^2 = Me	DMF, $POCl_3$	R^1 = CHO (75) + R^4 = CHO (8)	76, 395
	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH{=}CH_2$, NaH	$R^4 = CH_2SCH_2CH{=}CH_2$ (50-60)	382

TABLE VIII. FURANS (*Continued*)

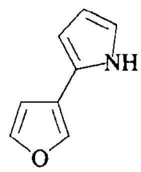
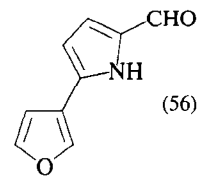
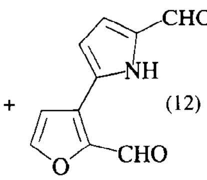
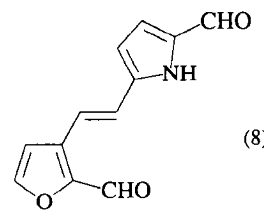
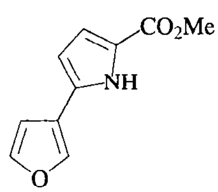
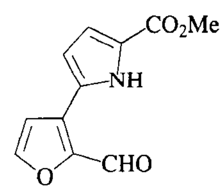
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_7			
R^2 = *i*-Pr	DMF, $POCl_3$	R^1 = CHO (61)	76
C_8			
	DMF, $POCl_3$	 (56) +  (12) +  (8)	74
C_{10}			
	DMF, $POCl_3$	 (56)	74

TABLE VIII. FURANS (*Continued*)

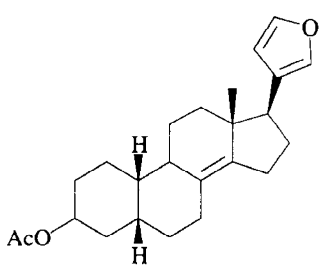
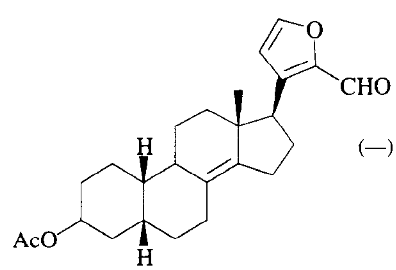
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{24}			
	DMF, $POCl_3$	 (—)	396
	C. Disubstituted Furans		
	C1. R^1, R^2 Substituents		
C_6			
R^1 = Me, R^2 = CN	DMF, $POCl_3$	R^4 = CHO (10-15)	397
R^1 = R^2 = Me	DMF, $POCl_3$	R^4 = CHO (96)	398, 399, 400
	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH{=}CH_2$, NaH	R^4 = $CH_2SCH_2CH{=}CH_2$ (50-60)	382
	DMA, $POCl_3$	R^4 = COMe (67)	400
C_7			
R^1 = Me, R^2 = COMe	DMF, $POCl_3$	R^4 = CHO (20)	397
C_8			
R^1 = Me, R^2 = CO_2Et	DMF, $POCl_3$	R^4 = CHO (79)	397
C_{10}			
R^1 = *n*-Pr, R^2 = CO_2Et	DMF, $POCl_3$	R^4 = CHO (85)	397
R^1 = R^2 = *i*-Pr	DMF, $POCl_3$	R^4 = CHO (68)	76
C_{12}			
R^1 = Me, R^2 = 4-$MeOC_6H_4$	DMF, $POCl_3$	R^4 = CHO (66)	397

TABLE VIII. FURANS (*Continued*)

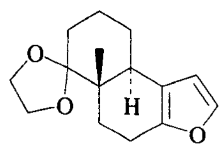
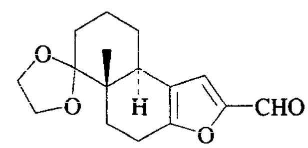
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{13}			
R^1 = Ph, R^2 = CO_2Et	DMF, $POCl_3$	R^4 = CHO (68)	397
R^1 = Me, R^2 = CH_2OBn	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH=CH_2$, NaH	R^4 = $CH_2SCH_2CH=CH_2$ (50-60)	382
C_{15}			
	DMF, $POCl_3$	 (86)	401, 402
	C2. R^1, R^3 Substituents		
C_6			
R^1 = R^3 = Me	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH=CH_2$, NaH	R^4 = $CH_2SCH_2CH=CH_2$ (50-60)	382
C_{11}			
R^1 = Me, R^3 = Ph	DMF, $POCl_3$	R^4 = CHO (84)	403
	C3. R^1, R^4 Substituents		
C_{16}			
R^1 = R^3 = Ph	DMF, $POCl_3$ DMF, $POCl_3$	R^4 = CHO (40) R^2 = CHO (40)	387 387

TABLE VIII. FURANS (*Continued*)

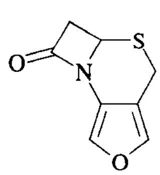
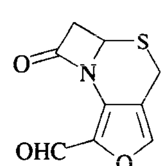
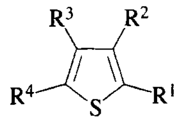
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C4. R^2, R^3 Substituents		
C_8			
	DMF, $POCl_3$	 (40)	404
C_{16}			
R^2 = R^3 = Ph	DMF, $POCl_3$	R^1 = CHO (80)	405
C_{18}			
R^2 = R^3 = 4-$MeOC_6H_4$	DMF, $POCl_3$	R^1 = CHO (—)	405
C_{20}			
R^2 = R^3 = CH_2OBn	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH=CH_2$, NaH	R^1 = $CH_2SCH_2CH=CH_2$ (50-60)	382
	D. Trisubstituted Furans **D1. R^1, R^2, R^3 Substituents**		
C_7			
R^1 = R^2 = R^3 = Me	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH=CH_2$, NaH	R^4 = $CH_2SCH_2CH=CH_2$ (50-60)	382
C_{15}			
R^1 = CH(Me)OBn, R^2 = R^3 = OMe	DMF, $POCl_3$	R^4 = CHO (13)	406

TABLE IX. THIOPHENES



R^1 - R^4 = H except as indicated

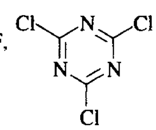
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Thiophene		
C_4			
	MFA, $POCl_3$	R^1 = CHO (76)	80, 79, 180, 407, 408
	DMF or MFA, $POCl_3$	R^1 = CHO (—)	409
	DMF, $POCl_3$	R^1 = CHO (72)	192, 409
	DMF, $(Cl_2PO)_2O$	R^1 = CHO (60)	26
	MFA, $(Cl_2PO)_2O$	R^1 = CHO (75)	26
	PhN(Et)CHO, $POCl_3$	R^1 = CHO (—)	80
	DMF, Ph_3PBr_2	R^1 = CHO (45)	35
	DMF, 	R^1 = CHO (5)	36
	Me_2NCDO, $POCl_3$	R^1 = CDO (30)	76
	1. MFA, $POCl_3$ 2. NH_2OH 3. Dehydrate	R^1 = CN (25)	197
	B. Monosubstituted Thiophenes **B1. R^1 Substituents**		
C_4			
R^1 = Cl	MFA, $POCl_3$	R^4 = CHO (59)	407, 79, 80, 408

TABLE IX. THIOPHENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF or MFA, $POCl_3$	R^4 = CHO (—)	409
	DMF, $POCl_3$	R^4 = CHO (43)	192, 409
R^1 = Br	MFA, $POCl_3$	R^1 = Cl, R^4 = CHO (58)	79
	MFA, $POCl_3$	R^4 = CHO (44)	80
	MFA, $POBr_3$	R^4 = CHO (70)	80, 79
C_5			
R^1 = Me	MFA, $POCl_3$	R^4 = CHO (80-85)	79, 80, 407
	DMF or MFA, $POCl_3$	R^4 = CHO (—)	409
	DMF, $POCl_3$	R^4 = CHO (66)	192, 409
C_{5-9}			
R^1 = OR		R^4 = CHO (66)	
R			
Me	MFA, $POCl_3$	(58)	410
	DMF, $(Cl_2PO)_2O$	(83)	26
	MFA, $(Cl_2PO)_2O$	(80)	26
Et	MFA, $POCl_3$	(55)	410
n-Pr	MFA, $POCl_3$	(59)	410
n-Bu	MFA, $POCl_3$	(40)	410
n-C_5H_{11}	MFA, $POCl_3$	(63)	410
C_6			
R^1 = NHAc	MFA, $POCl_3$	R^4 = CHO (—)	411
	DMF, $POCl_3$	R^4 = CHO (47)	192
R^1 = Et	MFA, $POCl_3$	R^4 = CHO (75-80)	79
	MFA, $POCl_3$	R^4 = CHO (—)	408

TABLE IX. THIOPHENES (*Continued*)

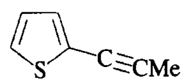
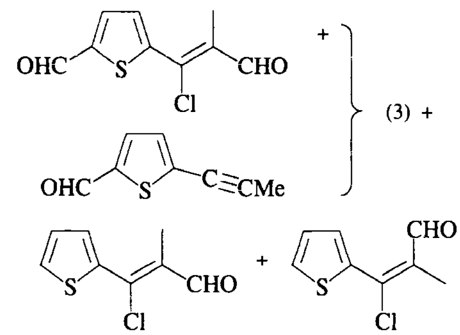
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{6-9}			
$R^1 = NR_2$	DMF, $POCl_3$	$R^4 = CHO$	412
R_2			
Me		(60)	
$(CH_2)_4$		(45)	
$(CH_2)_5$		(60)	
$[(CH_2)_2]O$		(80)	
C_7			
	MFA, $POCl_3$	 (3) + (31) (7)	413
$R^1 = n$-Pr	MFA, $POCl_3$	$R^4 = CHO$ (80-85)	79, 414
C_8			
$R^1 = n$-Bu	DMF or MFA, $POCl_3$	$R^4 = CHO$ (—)	415
$R^1 = i$-Bu	MFA, $POCl_3$	$R^4 = CHO$ (77)	408
$R^1 = t$-Bu	DMF, $POCl_3$	$R^4 = CHO$ (76)	80, 192

TABLE IX. THIOPHENES (*Continued*)

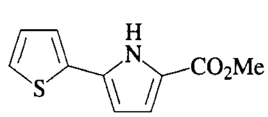
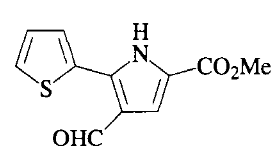
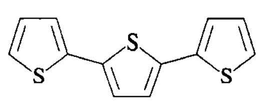
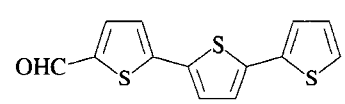
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{8-26}			
$R^1 = Ar$			
Ar			
2-Thienyl	DMF, $POCl_3$	$R^4 = CHO$ (48)	416
$3-ClC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (70)	417
$4-ClC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (81)	418
	DMF, $POCl_3$	$R^4 = CHO$ (71)	419
$4-BrC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (80)	418
Ph	MFA, $POCl_3$	$R^4 = CHO$ (87)	417, 418, 420
	DMF, $POCl_3$	$R^4 = CHO$ (68)	419
$3-MeC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (78)	417
$4-MeC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (83)	418
$4-MeOC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (85)	418, 421
$2,4-(Ph)_2C_6H_3$	MFA, $POCl_3$	$R^4 = CHO$ (—)	417
$3,5-(4-MeC_6H_4)_2C_6H_3$	MFA, $POCl_3$	$R^4 = CHO$ (82)	417
	DMF, $POCl_3$	 (85)	74
	DMF, $POCl_3$	 (75)	422, 416
C_9			
$R^1 = n-C_5H_{11}$	DMF or MFA, $POCl_3$	$R^4 = CHO$ (—)	415
$R^1 = i-C_5H_{11}$	DMF or MFA, $POCl_3$	$R^4 = CHO$ (—)	415

TABLE IX. THIOPHENES (*Continued*)

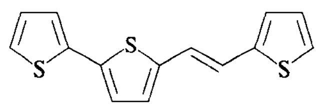
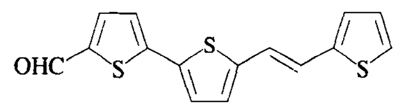
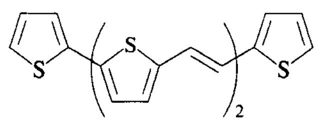
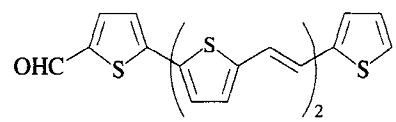
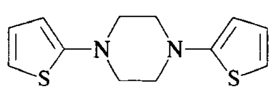
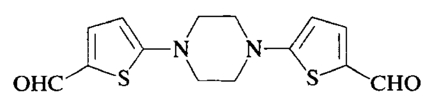
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{10}			
$R^1 = n\text{-}C_6H_{13}$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
$C_{10\text{-}13}$			
R^1 = CH=CHAr			
Ar			
2-Thienyl	DMF, $POCl_3$	R^4 = CHO (93)	423
$4\text{-}ClC_6H_4$	DMF, $POCl_3$	R^4 = CHO (—)	424
Ph	DMF, $POCl_3$	R^4 = CHO (72-90)	424, 425
$4\text{-}MeOC_6H_4$	DMF, $POCl_3$	R^4 = CHO (61)	425
	DMF, $POCl_3$	 (58)	423
	DMF, $POCl_3$	 (42)	423
C_{11}			
R^1 = Bn	MFA, $POCl_3$	R^4 = CHO (43)	408
$R^1 = CH_2C_6H_{11}$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
$R^1 = n\text{-}C_7H_{15}$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
C_{12}			
$R^1 = CH_2Bn$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
$R^1 = n\text{-}C_8H_{17}$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
	DMF, $POCl_3$	 (50)	412

TABLE IX. THIOPHENES (*Continued*)

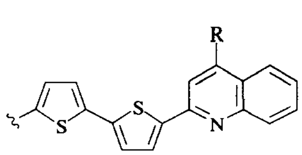
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{13}			
$R^1 = (CH_2)_3C_6H_{11}$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
C_{14}			
$R^1 = N(Et)CH=C(CO_2Et)_2$	MFA, —	R^4 = CHO (70)	426
$R^1 = n\text{-}C_{10}H_{21}$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
C_{15}			
$R^1 = CH_2(C_6H_4Bu\text{-}t\text{-}4)$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
$R^1 = n\text{-}C_{11}H_{23}$	MFA, $POCl_3$	R^4 = CHO (57)	414
C_{16}			
$R^1 = (CH_2)_3CH(C_6H_{11})Et$	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
$R^1 = n\text{-}C_{12}H_{25}$	MFA, $POCl_3$	R^4 = CHO (37)	414
$C_{16\text{-}17}$			
$R^1 = C(Ar^1)=CH(Ar^2)$	DMF or MFA, $POCl_3$	R^4 = CHO	424
Ar^1 — Ar^2			
Ph — $4\text{-}ClC_6H_4$		(—)	
$4\text{-}ClC_6H_4$ — Ph		(—)	
Ph — Ph		(—)	
$4\text{-}MeOC_6H_4$ — $4\text{-}ClC_6H_4$		(—)	
C_{18}			
$R^1 = n\text{-}C_{14}H_{29}$	MFA, $POCl_3$	R^4 = CHO (71)	414
$C_{21\text{-}23}$			
R^1 = 			
R			
H	DMF, $POCl_3$	R^4 = CHO (60)	427
OMe	DMF, $POCl_3$	R^4 = CHO (—)	427
CO_2H	DMF, $POCl_3$	R^4 = CHO (50)	427
CO_2Me	DMF, $POCl_3$	R^4 = CHO (92)	427

TABLE IX. THIOPHENES (*Continued*)

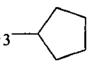
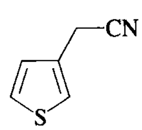
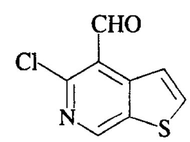
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{22}			
R^1 = $(CH_2)_{13}$— 	DMF or MFA, $POCl_3$	R^4 = CHO (—)	415
	B2. R^2 Substituents		
C_4			
R^2 = Br	DMF, $POCl_3$	R^1 = CHO (70)	76
C_5			
R^2 = Me	DMF, $POCl_3$	R^1 = CHO (33)	192, 76, 428
	DMF, $POCl_3$	R^1 = CHO (53) + R^4 = CHO (9)	429
	MFA, $POCl_3$	R^1 = CHO (83)	80
	MFA, $POCl_3$	R^1 = CHO (80-85)	79
R^2 = OMe	DMF, $COCl_2$	R^1 = CHO (99)	430
C_6			
R^2 = NHAc	DMF, $POCl_3$	R^1 = CHO (88)	78
	DMF, $POCl_3$ moderate conditions	R^1 = CHO (73)	431
	DMF, $POCl_3$ forcing conditions	R^1 = CHO (4) + R^2 = N=$CHNMe_2$ (7) + R^1 = CHO, R^2 = N=$CHNMe_2$ (15)	431
	DMF, $POCl_3$	 (34)	431
C_8			
R^2 = 2-Thienyl	—	R^4 = CHO (—)	432
R^2 = SBu-*n*	MFA, $POCl_3$	R^1 = CHO (72)	433
R^2 = SeBu-*n*	MFA, $POCl_3$	R^1 = CHO (70)	433

TABLE IX. THIOPHENES (*Continued*)

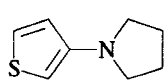
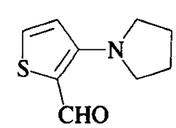
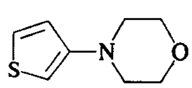
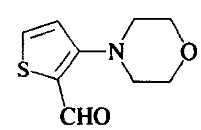
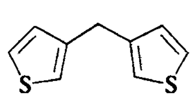
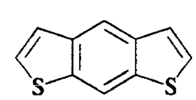
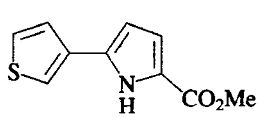
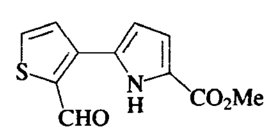
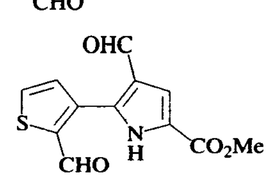
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (25)	412
	DMF, $POCl_3$	 (55)	412
C_9			
	DMF, $POCl_3$	 (33)	434
C_{10}			
R^2 = Ph	DMF, $POCl_3$	R^1 = CHO + R^4 = CHO (80) 94:6	77
R^2 = $(CH_2)_3CO_2Et$	—	R^1 = CHO (—)	435
	DMF, $POCl_3$	 (4) +  (85)	74

TABLE IX. THIOPHENES (*Continued*)

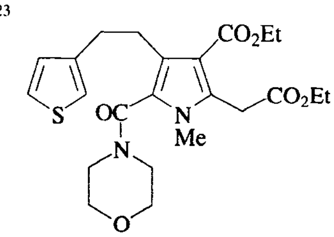
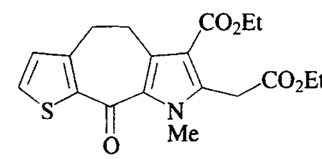
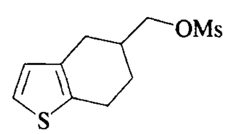
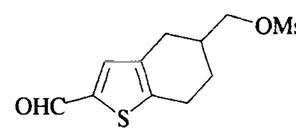
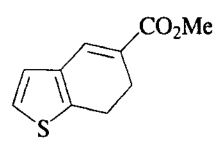
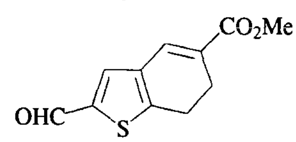
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{23}			
	$POCl_3$	 (56)	436
C. Disubstituted Thiophenes			
C1. R^1, R^2 Substituents			
C_6			
$R^1 = OMe$, $R^2 = CO_2Me$	DMF, $POCl_3$	$R^1 = Cl$, $R^4 = CHO$ (71)	437
$R^1 = SMe$, $R^2 = CO_2Me$	DMF, $POCl_3$	$R^4 = CHO$ (69)	437
C_7			
$R^1 = OMe$, $R^2 = CO_2Me$	DMF, $POCl_3$	$R^4 = CHO$ (60)	437
$R^1 = Et$, $R^2 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (58)	428
C_8			
$R^1 + R^2 = (CH_2)_4$	MFA, $POCl_3$	$R^4 = CHO$ (83)	438
C_{10}			
	DMF, $POCl_3$	 (65)	439
	DMF, $POCl_3$	 (88)	439

TABLE IX. THIOPHENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
$R^1 = Me$, $R^2 = CH_2OPh$	1. DMF, $POCl_3$ 2. NH_4SH 3. $LiAlH_4$ 4. $BrCH_2CH{=}CH_2$	$R^4 = CH_2SCH_2CH{=}CH_2$ (50-70)	440
C2. R^1, R^3 Substituents			
C_6			
$R^1 = CO_2H$, $R^3 = OMe$	DMF, $POCl_3$	$R^4 = CHO$ (25)	437
C_{12}			
$R^1 = R^3 = t\text{-Bu}$	DMF, $POCl_3$	$R^4 = CHO$ (—)	441
C_{13}			
$R^1 = Me$, $R^3 = (CH_2)_2(C_6H_3Br(Cl)\text{-}2,4)$	DMF, $POCl_3$	$R^4 = CHO$ (92)	442
C_{16}			
$R^1 = R^3 = Ph$	DMF, $POCl_3$	$R^4 = CHO$ (88)	443
	DMF or MFA, $POCl_3$	$R^4 = CHO$ (—)	417
C_{18}			
$R^1 = R^3 = 4\text{-}MeC_6H_4$	MFA, $POCl_3$	$R^4 = CHO$ (82)	417
C_{19}			
$R^1 = N(Me)Bn$, $R^3 = Bn$	DMF, $POCl_3$	$R^4 = CHO$ (74)	444
C3. R^1, R^4 Substituents			
C_6			
$R^1 = OMe$, $R^4 = CO_2H$	1. DMF, $POCl_3$ 2. MeOH	$R^1 = Cl$, $R^4 = CO_2Me$ (5)	437
$R^1 = R^4 = Me$	MFA, $POCl_3$	$R^2 = CHO$ (20)	80, 407

TABLE IX. THIOPHENES (*Continued*)

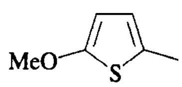
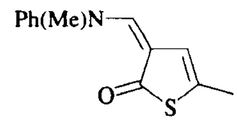
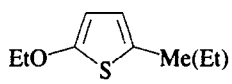
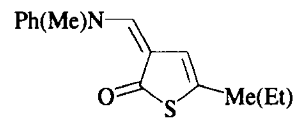
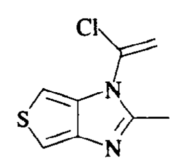
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	MFA, $POCl_3$	 (37)	83
C_7			
R^1 = Me, R^4 = NHAc	DMF, $POCl_3$	R^3 = CHO (62)	78
R^1 = Et, R^4 = OMe	DMF, $POCl_3$, 20°	R^3 = CHO (61)	83
C_{7-8}			
	MFA, $POCl_3$, 50-60°	 (53)	83
	C4. R^2, R^3 Substituents		
C_6			
$R^2 = R^3$ = Me	DMF, $POCl_3$	R^1 = CHO (63)	76
$R^2 = R^3$ = OMe	DMF, $POCl_3$	R^1 = CHO (69)	76
C_7			
$R^2 = SCH_2CO_2Me$, R^3 = Br	MFA, $POCl_3$	R^1 = CHO (—)	445
C_{8-18}			
$R^2 = R^3$ = NHCOR			
R			
CH_2Br	DMF, $POCl_3$, $Cl(CH_2)_2Cl$, 83°	R^1 = CHO (—)	
Me	DMF, $POCl_3$, $Cl(CH_2)_2Cl$, 83°	R^1 = CHO (35)	
	DMF, $POCl_3$ (xs), $Cl(CH_2)_2Cl$, 83°	 (—)	446

TABLE IX. THIOPHENES (*Continued*)

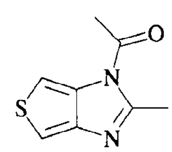
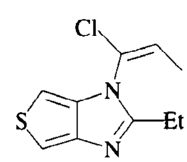
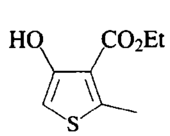
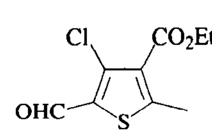
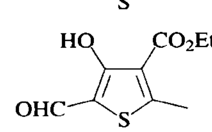
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$ (xs), 0°	 (33)	446
Et	DMF, $POCl_3$ (xs)	 (39)	446
	DMF, $POCl_3$, $Cl(CH_2)_2Cl$, 83°	R^1 = CHO (60)	446
t-Bu	DMF, $POCl_3$, $Cl(CH_2)_2Cl$, 83°	R^1 = CHO (90)	446
Ph	DMF, $POCl_3$, $Cl(CH_2)_2Cl$, 83°	R^1 = CHO (80)	446
C_{18}			
$R^2 = R^3 = 4\text{-}MeOC_6H_4$	DMF, $POCl_3$	R^1 = CHO (45)	76
	D. Trisubstituted Thiophenes		
	D1. R^1, R^2, R^3 Substituents		
C_8			
	DMF, $POCl_3$, 100°	 (53)	81, 82
	DMF, $POCl_3$, 30-50°	 (78)	82

TABLE IX. THIOPHENES (*Continued*)

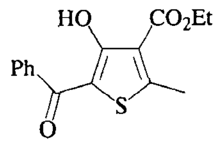
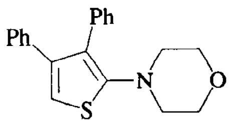
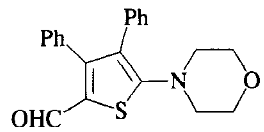
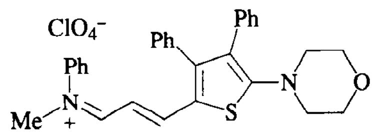
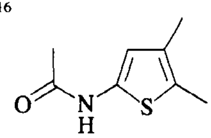
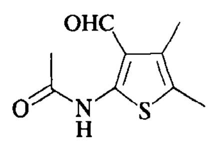
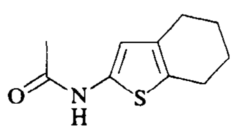
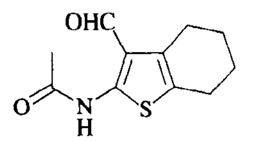
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	Me_2NCOPh, $POCl_3$	 (41)	82
C_{20} 	DMF, $POCl_3$	 (65)	447
	1. PhN(Me)CH=CHCHO, $POCl_3$ 2. $HClO_4$	 (7)	447
D2. R^1, R^2, R^4 Substituents			
C_{8-16} 	DMF, $POCl_3$	 (73)	448, 78
	DMF, $POCl_3$	 **I** (78)	448

TABLE IX. THIOPHENES (*Continued*)

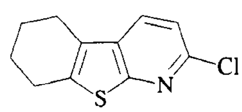
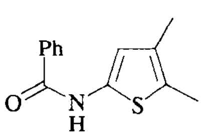
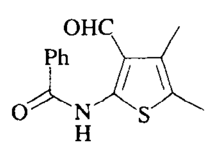
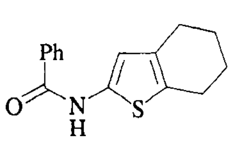
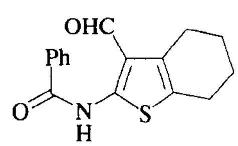
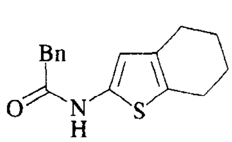
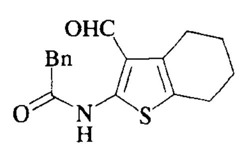
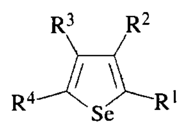
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$ (1:3)	**I** (79)	78
	DMF, $POCl_3$ (1:3), 1 h	**I** (8) +  **II** (80)	78
	DMF, $POCl_3$ (1:3), 15 min	**I** (76) + **II** (12)	78
	DMF, $POCl_3$	 (80)	448
	DMF, $POCl_3$	 (80)	448
	DMF, $POCl_3$	 (84)	448

TABLE X. SELENOPHENES



R^1 - R^4 = H except as indicated

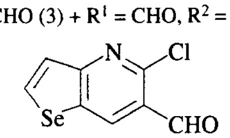
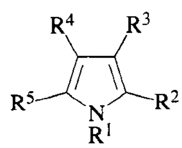
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		A. Selenophene	
C_4			
	DMF, $POCl_3$	R^1 = CHO (70)	84
		B. Monosubstituted Selenophenes	
		B1. R^1 Substituents	
C_5			
R^1 = Me	DMF, $POCl_3$	R^4 = CHO (88)	449
		B2. R^2 Substituents	
C_5			
R^2 = Me	DMF, $POCl_3$	R^1 = CHO (72)	450
C_6			
R^2 = NHAc	DMF, $POCl_3$	R^1 = CHO (3) + R^1 = CHO, R^2 = N=CHNMe$_2$ (24)	431
		+  (31)	
		C. Disubstituted Selenophenes	
		C1. R^1, R^3 Substituents	
C_{16-18}			
C2 R^1 = R^3 = Ar	MFA, $POCl_3$	R^4 = CHO	417
Ar			
Ph		(84)	
4-MeC_6H_4		(81)	
4-$MeOC_6H_4$		(69)	

TABLE XI. PYRROLES



R^1 - R^4 = H except as indicated

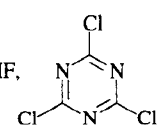
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Pyrrole		
C_4			
	DMF, $POCl_3$	R^2 = CHO (95)	181, 451-453
	DMF, Ph_3PBr_2	R^2 = CHO (40)	35
	DMF, Tf_2O	R^2 = CHO (75)	47
	DMF, 	R^2 = CHO (65)	36
	1. DMF, $(COCl)_2$ 2. MeCOCl, $AlCl_3$	R^2 = CHO, R^4 = COMe (80)	454
	1. DMF, $(COCl)_2$ 2. PhCOCl, $AlCl_3$	R^2 = CHO, R^4 = COPh (55)	454
	1. DMF, $(COCl)_2$ 2. Cl_3CCOCl, $AlCl_3$ 3. NaOMe, MeOH	R^2 = CHO, R^4 = CO_2Me (80)	454
	1. DMF, $(COCl)_2$ 2. EtOC(S)Cl, $AlCl_3$	R^2 = CHO, R^4 = COSEt (62)	454
	1. DMF, $(COCl)_2$ 2. $MeOCHCl_2$, $AlCl_3$	R^2 = R^4 = CHO (62)	454
	1. DMF, $(COCl)_2$ 2. NH_2OH 3. Dehydrate	R^2 = CN (64)	455

TABLE XI. PYRROLES (*Continued*)

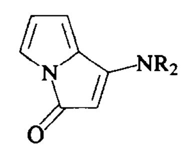
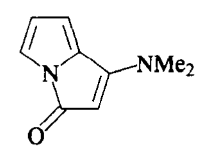
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. ClO_4^-	$R^2 = CH{=}NMe_2^+ ClO_4^-$ (62)	456
	1. DMF, $(COCl)_2$ 2. NaH 3. RLi	$R^2 = CHRNMe_2$	91
	R		
	t-Bu	(55)	
	s-Bu	(67-97)	
	n-Bu	(67-97)	
	Ph	(67-97)	
	DMA, $COCl_2$	$R^2 = COMe$ (—)	103
	DMA, $POCl_3$	$R^2 = COMe$ (49)	101
	Et_2NCOCH_2Cl, $POCl_3$	$R^2 = COCH_2Cl$ (54)	87
	Me_2NCOCH_2Cl, $POCl_3$	$R^2 = COCH_2Cl$ (75)	457
	$R_2NCOCH_2CO_2Et$, $POCl_3$		87
	R		
	Me	(29)	
	Et	(31)	
	$Me_2NCOCH_2NMe_2$, $POCl_3$	$R^1 = COCH_2CONMe_2$ (—) +  (6)	101

TABLE XI. PYRROLES (*Continued*)

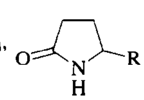
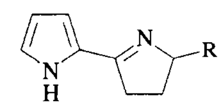
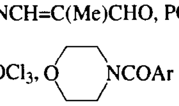
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$H_2NCO(CH_2)_2CO_2Me$, $POCl_3$	$R^2 = CO(CH_2)_2CO_2Me$ (73)	458
	$Et_2NCO(CH_2)_2CO_2Et$, $POCl_3$	$R^2 = CO(CH_2)_2CO_2Et$ (71)	87
	$POCl_3$, 		
	R		
	H	(80)	459
	Me	(84)	460
	CO_2Me	(51)	460
	CO_2Et	(47)	88
	$Me_2NCH{=}C(Me)CHO$, $POCl_3$	$R^2 = CH{=}C(Me)CHO$ (51)	38
	1. $POCl_3$,  2. $LiBH_4$ or $Na(CN)BH_3$	$R^2 = CH_2Ar$	461
	Ar		
	Ph	(90-92)	
	$4\text{-}MeC_6H_4$	(79-80)	
	$4\text{-}MeOC_6H_4$	(91-92)	
	$4\text{-}ClC_6H_4$	(80-82)	
	Me_2NCOPh, $POCl_3$	$R^2 = COPh$ (88)	86
	Et_2NCOPh, $POCl_3$	$R^2 = COPh$ (92)	86
	$Me_2NCO(C_6H_4NO_2\text{-}4)$, $POCl_3$	$R^2 = CO(C_6H_4NO_2\text{-}4)$ (91)	183

TABLE XI. PYRROLES (*Continued*)

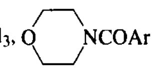
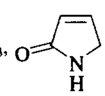
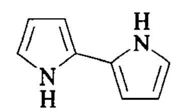
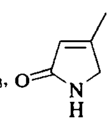
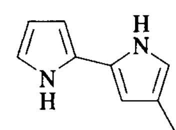
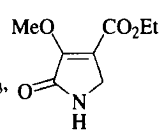
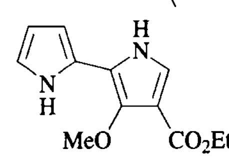
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$POCl_3$, 	R^2 = COAr	
	Ar		
	Ph	(88)	86, 183
	4-ClC_6H_4	(87)	183
	4-$O_2NC_6H_4$	(91)	183
	4-MeC_6H_4	(86)	183
	4-$MeOC_6H_4$	(88)	183
	1. Me_2NCOAr, $POCl_3$ 2. $NaClO_4$	R^2 = C(Ar)=NMe_2^+ ClO_4^-	462
	Ar		
	Ph	(66)	
	4-ClC_6H_4	(24)	
	4-$O_2NC_6H_4$	(24)	
	4-MeC_6H_4	(86)	
	4-$MeOC_6H_4$	(31)	
	$POCl_3$, 	 (—)	89
	$POCl_3$, 	 (79)	89
	$POCl_3$, 	 (65)	89

TABLE XI. PYRROLES (*Continued*)

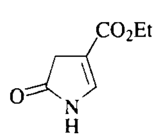
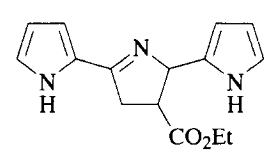
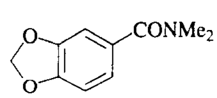
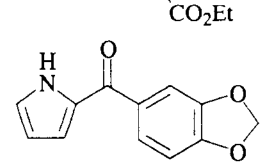
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$POCl_3$, 	 (36)	89
	$POCl_3$, 	 (80)	463
	B. Monosubstituted Pyrroles		
	B1. R[1] Substituents		
C_5			
R^1 = Me	DMF, $POCl_3$	R^2 = CHO (95)	453, 85, 452, 464, 465
	DMF, $POCl_3$	R^2 = CHO (84) + R^3 = CHO (6)	26
	DMF, $(Cl_2PO)_2O$	R^2 = CHO (88) + R^3 = CHO (5)	26
	$(Me_2N{=}CHCl)^+$ Cl^-	R^2 = CHO (88) + R^3 = CHO (5)	26
	1. DMF, $(COCl)_2$ 2. NH_2OH 3. Dehydrate	R^2 = CN (67)	455
	DMA, $COCl_2$	R^2 = COMe (—)	103
	DMA, $POCl_3$	R^2 = COMe (40) + R^3 = COMe (16)	87
	Et_2NCOMe, $POCl_3$	R^2 = COMe (59) + R^3 = COMe (25)	87
	Me_2NCOCH_2Cl, $POCl_3$	R^2 = $COCH_2Cl$ (40) + R^3 = $COCH_2Cl$ (40)	457
	Ph(Me)$NCOCH_2Cl$, $POCl_3$	R^2 = $COCH_2Cl$ (12) + R^3 = $COCH_2Cl$ (3)	457

TABLE XI. PYRROLES (*Continued*)

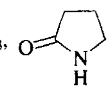
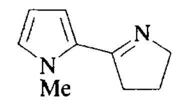
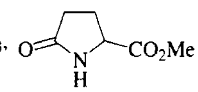
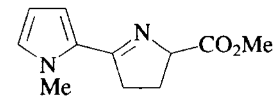
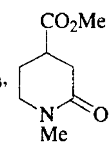
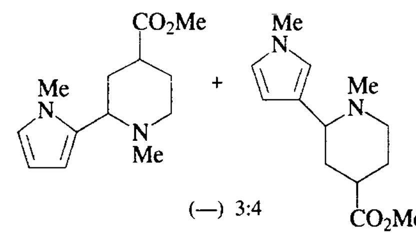
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$POCl_3$, 	 (34)	466
	$POCl_3$, 	 (69)	460, 466
	1. $POCl_3$,  2. $NaBH_4$	 (—) 3:4	467
	$Me_2NN{=}CHCHO$, $COCl_2$	$R^2 = CH{=}CHN{=}NMe_2^+\ Cl^-$ or $PO_2Cl_2^-$ (35)	40
	$Me_2NCH{=}CHCHO$, $POCl_3$	$R^2 = CH{=}CHCHO$ (49)	38
	$Me_2NCH{=}C(Me)CHO$, $POCl_3$	$R^2 = CH{=}C(Me)CHO$ (13)	38
	Me_2NCOPh, $POCl_3$	$R^2 = COPh$ (86)	86
	$Me_2NCO(C_6H_4Cl\text{-}4)$, $POCl_3$	$R^2 = CO(C_6H_4Cl\text{-}4)$ (20)	468
	1. DMF, $(COCl)_2$ 2. ArCOCl, $AlCl_3$	$R^2 = CHO$, $R^4 = COAr$	469
	Ar		
	Ph	(40)	
	$4\text{-}MeOC_6H_4$	(52)	
	$4\text{-}ClC_6H_4$	(44)	
	$4\text{-}FC_6H_4$	(60)	
	$4\text{-}O_2NC_6H_4$	(63)	

TABLE XI. PYRROLES (*Continued*)

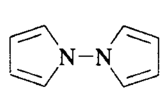
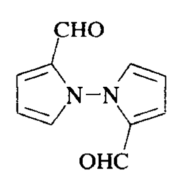
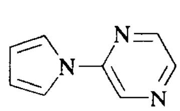
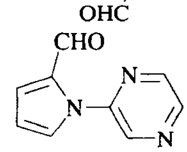
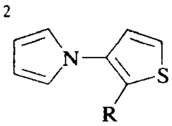
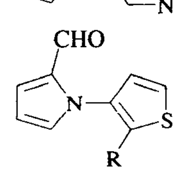
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_6			
$R^1 = COMe$	DMF, $POCl_3$	$R^2 = CHO$ (61)	85
$R^1 = Et$	DMF, $POCl_3$	$R^2 = CHO$ (58) + $R^3 = CHO$ (27)	85
	Me_2NCOCH_2Cl, $POCl_3$	$R^2 = COCH_2Cl$ (30) + $R^3 = COCH_2Cl$ (35)	457
$R^1 = NMe_2$	DMF, $POCl_3$	$R^2 = CHO$ (56)	470
C_7			
$R^1 = CO_2Et$	DMF, $POCl_3$	$R^2 = CHO$ (54)	85
$R^1 = i\text{-}Pr$	DMF, $POCl_3$	$R^2 = CHO$ (8) + $R^3 = CHO$ (71)	85
C_8			
$R^1 = t\text{-}Bu$	DMF, $POCl_3$	$R^2 = CHO$ (5) + $R^3 = CHO$ (64)	85
	DMF, $POCl_3$	 (56)	471
	—	 (56)	472
$C_{8\text{-}12}$			
	DMF, $POCl_3$		
R			
H		(—)	473
CO_2H		(60)	474, 473
CO_2Me		(72)	474, 473

TABLE XI. PYRROLES (*Continued*)

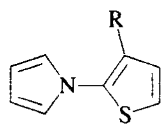
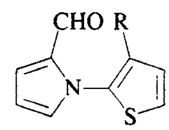
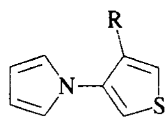
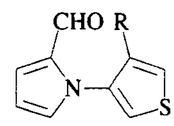
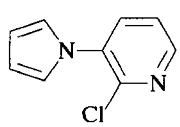
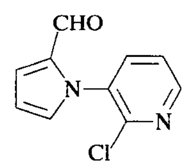
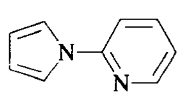
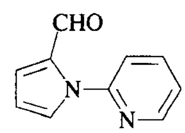
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMF, $POCl_3$		
R			
CN		(83)	474, 475
CO_2H		(49)	474
	DMF, $POCl_3$		474
R			
CN		(83)	
CO_2H		(49)	
	—	 (83)	472
	DMF, $POCl_3$	 (96)	476

TABLE XI. PYRROLES (*Continued*)

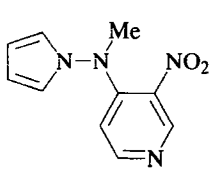
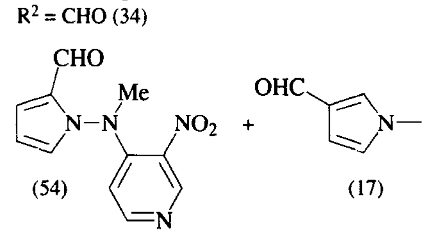
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{10}			
R^1 = 4-BrC_6H_4	DMF, $POCl_3$	R^2 = CHO (76) + R^3 = CHO (14)	85
R^1 = 2-$O_2NC_6H_4$	DMF, $POCl_3$	R^2 = CHO (100)	477
R^1 = 4-$O_2NC_6H_4$	DMF, $POCl_3$	R^2 = CHO (77) + R^3 = CHO (11)	85
R^1 = Ph	DMF, $POCl_3$	R^2 = CHO (84) + R^3 = CHO (8)	85
	DMA, $POCl_3$	R^2 = COMe (60) + R^3 = COMe (15)	182
	Me_2NCOCH_2Cl, $POCl_3$	R^2 = $COCH_2Cl$ (33) + R^3 = $COCH_2Cl$ (33)	457
	Ph(Me)$NCOCH_2Cl$, $POCl_3$	R^2 = $COCH_2Cl$ (1) + R^3 = $COCH_2Cl$ (9)	457
R^1 = SO_2Ph	DMF, $POCl_3$	R^2 = CHO (34)	478
		 (54) + (17)	479
C_{11}			
R^1 = COPh	DMF, $POCl_3$	R^2 = CHO (74)	85
R^1 = (2-CH_2Cl)C_6H_4	DMF, $POCl_3$, $Cl(CH_2)_2Cl$	R^2 = CHO (70)	480
	DMF, $POCl_3$	R^2 = CHO (20) + R^3 = CHO (19)	480
R^1 = 4-MeC_6H_4	DMF, $POCl_3$	R^2 = CHO (84) + R^3 = CHO (8)	85
R^1 = 4-$MeOC_6H_4$	DMF, $POCl_3$	R^2 = CHO (81) + R^3 = CHO (12)	85
	DMF, $POCl_3$	R^2 = CHO (86) + R^3 = CHO (10)	26, 85, 481
	DMF, $(Cl_2PO)_2O$	R^2 = CHO (80) + R^3 = CHO (18)	
	MFA, $(Cl_2PO)_2O$	R^2 = CHO (75) + R^3 = CHO (22)	
	Me_2NCOCH_2Cl, $POCl_3$	R^2 = $COCH_2Cl$ (27) + R^3 = $COCH_2Cl$ (48)	
	Ph(Me)$NCOCH_2Cl$, $POCl_3$	R^2 = $COCH_2Cl$ (1) + R^3 = $COCH_2Cl$ (9)	
R^1 = $CH_2(C_6H_4F$-2)	DMF, $POCl_3$	R^2 = CHO (100)	482, 483

TABLE XI. PYRROLES (*Continued*)

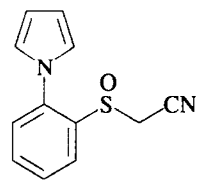
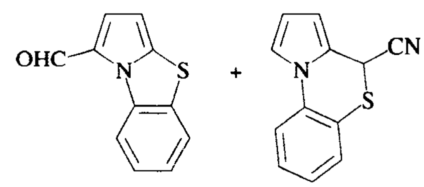
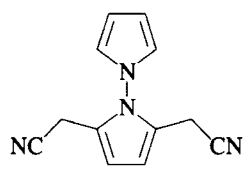
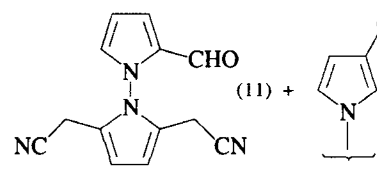
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	DMF, $POCl_3$	 (20) (20)	484
	DMF, $POCl_3$	 (11) + (15)	485, 486
$R^1 = C_6H_4CO_2Me$-2	DMF, $POCl_3$	R^2 = CHO (76)	487, 480
$R^1 = C_6H_2(Me)_2$-2,6-NO_2-3	DMF, $POCl_3$	R^2 = CHO (75) + R^3 = CHO (16)	85
$R^1 = C_6H_2(Me)_2$-2,6-NO_2-4	DMF, $POCl_3$	R^2 = CHO (30) + R^3 = CHO (7)	85
$R^1 = C_6H_3(Me)_2$-2,6	DMF, $POCl_3$	R^2 = CHO (65) + R^3 = CHO (6)	85
$R^1 = C_6H_3(OMe)_2$-2,5	DMF, $POCl_3$	R^2 = CHO (70)	488
$R^1 = CH_2C_6H_4SMe$-2	DMF, $POCl_3$	R^2 = CHO (86)	489
	1. DMF, $POCl_3$ 2. NH_2OH 3. Dehydrate	R^2 = CN (80)	489

TABLE XI. PYRROLES (*Continued*)

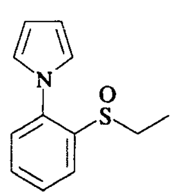
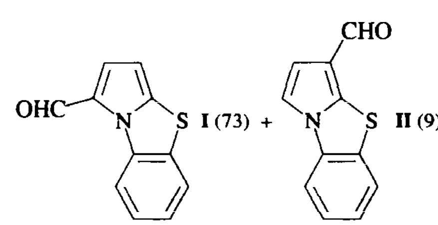
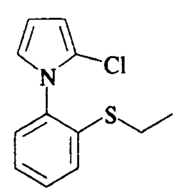
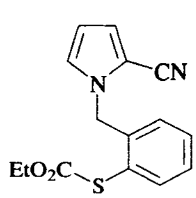
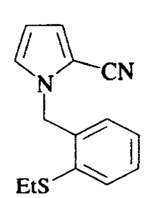
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 I (73) + II (9)	484
	DMF, $(COCl)_2$	 (32) + I (46) + II (10)	484
$R^1 = (CH_2)_6CO_2Me$	DMF, $POCl_3$	R^2 = CHO (70)	490
C_{13}			
$R^1 = (i\text{-}Pr)_3Si$	DMF, $(Cl_2PO)_2O$	R^2 = CHO (66) + R^3 = CHO (14)	26
	MFA, $(Cl_2PO)_2O$	R^2 = CHO (61-73) + R^3 = CHO (3-7)	26
C_{14}			
R^1 = 1-(8-nitronaphthyl)	DMF, $POCl_3$	R^2 = CHO (74)	491
	1. DMF, $(COCl)_2$ 2. NH_2OH 3. Dehydrate	 (70)	489

TABLE XI. PYRROLES (*Continued*)

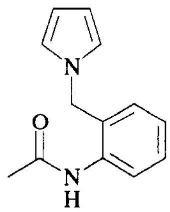
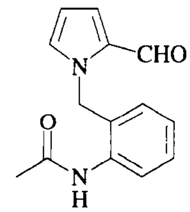
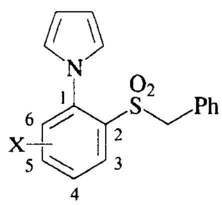
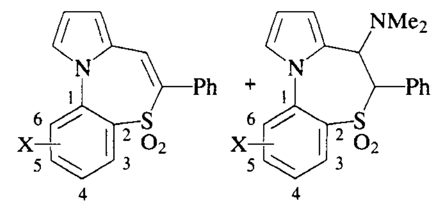
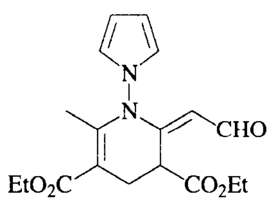
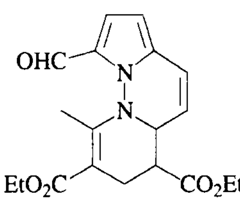
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	—	 (—)	492
C_{17} 	1. DMF, $(COCl)_2$ 2. NH_2OH 3. Dehydrate	 I II	493
X		I (II)	
4-Cl		(23) (0)	
5-Cl		(55) (0)	
4-NO_2		(46) (40)	
6-NO_2		(40) (42)	
C_{18} 	DMF, $POCl_3$	 (28)	494

TABLE XI. PYRROLES (*Continued*)

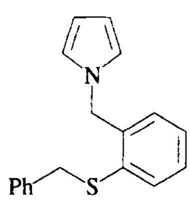
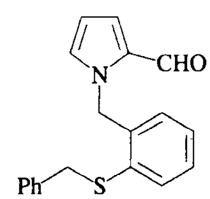
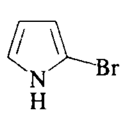
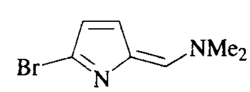
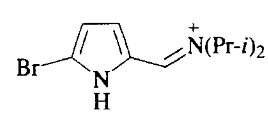
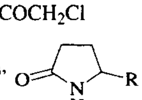
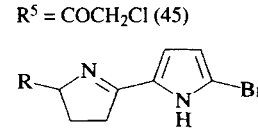
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{19} 	DMF, $POCl_3$ or $(COCl)_2$	 (84)	495
	B2. R^2 Substituents		
C_4 	1. DMF, $(COCl)_2$ 2. $NaHCO_3$	 (80)	90
	$(i\text{-Pr})_2NCHO$, $(COCl)_2$	 (95)	90
C_5 R^2 = Me	DMF, $POCl_3$	R^5 = CHO (90)	453
	DMA, $COCl_2$	R^5 = COMe (—)	103
	Me_2NCOCH_2Cl	R^5 = $COCH_2Cl$ (45)	457
	$POCl_3$, 		460
	R		
	H	(78)	
	Me	(78)	

TABLE XI. PYRROLES (*Continued*)

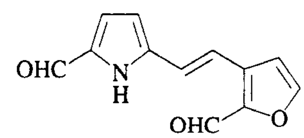
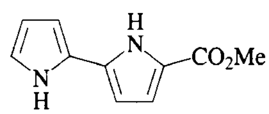
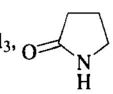
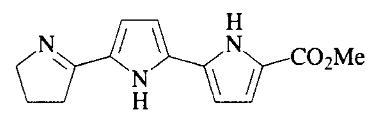
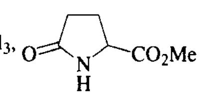
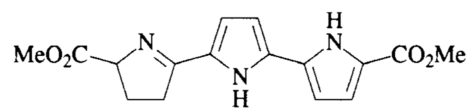
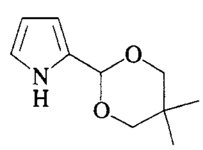
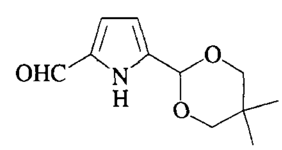
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_6			
$R^2 = COMe$	DMF, $POCl_3$	$R^5 = CHO$, $R^2 = CCl{=}CH_2$ (31)	496
C_8			
R^2 = 2-furyl	DMF, $POCl_3$	$R^5 = CHO$ (62) + $R^5, R^{5'} = CHO$ (14)	74, 75
R^2 = 3-furyl	DMF, $POCl_3$	$R^5 = CHO$ (56) + $R^5, R^{2'} = CHO$ (12) +  (8)	74
R^2 = 2-thienyl	DMF, $POCl_3$	$R^5 = CHO$ (85)	74, 75
R^2 = 3-thienyl	DMF, $POCl_3$	$R^5 = CHO$ (81)	74
C_{10}			
$R^2 = Ph$	DMF, $POCl_3$	$R^5 = CHO$ (71)	74
	$POCl_3$, 	 (25)	497
	$POCl_3$, 	 (76)	497
	DMF, $POCl_3$	 (56)	498

TABLE XI. PYRROLES (*Continued*)

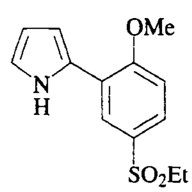
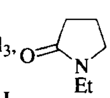
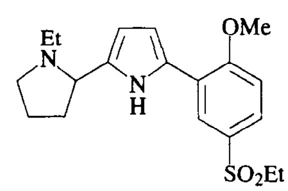
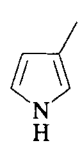
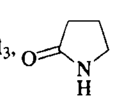
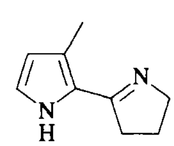
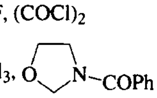
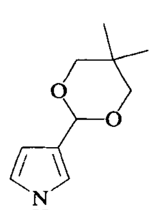
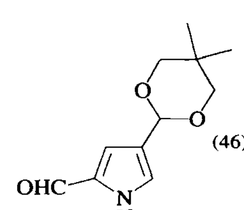
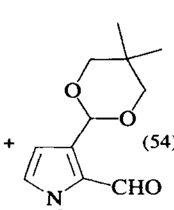
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. $POCl_3$,  2. $NaBH_4$	 (55)	499
	B3. R^3 Substituents		
C_5			
	$POCl_3$, 	 (40)	460
C_8			
$R^3 = CH_2CO_2Et$	DMF, $(COCl)_2$, HMPT	$R^2 = CHO$ (60) + $R^5 = CHO$ (40)	94
	DMF, $(COCl)_2$	$R^2 = CHO$ (40) + $R^5 = CHO$ (60)	94
	$POCl_3$, 	$R^2 = CHO$ (5) + $R^5 = CHO$ (31)	500
C_{10}			
	DMF, $POCl_3$	 (46) +  (54)	501

TABLE XI. PYRROLES (*Continued*)

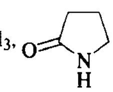
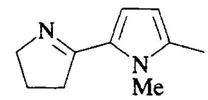
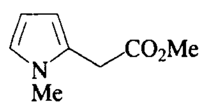
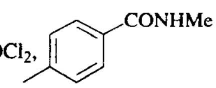
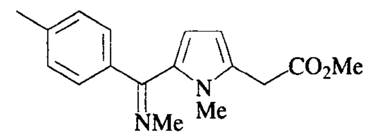
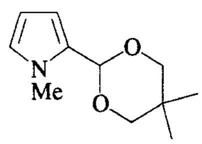
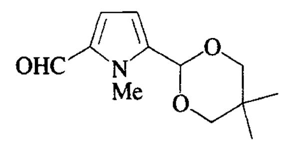
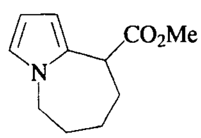
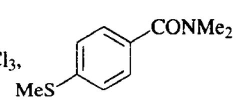
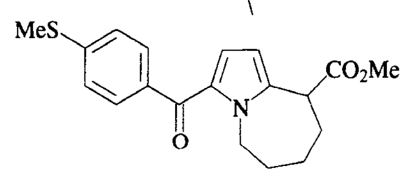
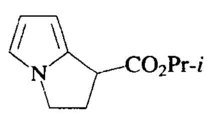
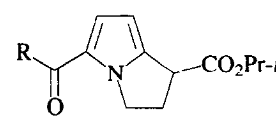
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	D. Disubstituted Pyrroles		
	C1. R^1, R^2 Substituents		
C_6			
$R^1 = R^2 = Me$	DMF, $POCl_3$	$R^5 = CHO$ (79)	453
	$POCl_3$, 	 (66)	466
C_8			
	1. $SOCl_2$,  2. H^+	 (30)	502
C_{11}			
	DMF, $POCl_3$	 (95)	501
	$POCl_3$, 		503
	Me_2NCOR, $POCl_3$		503

TABLE XI. PYRROLES (*Continued*)

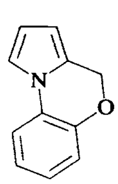
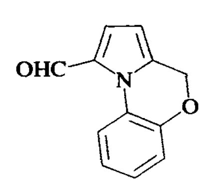
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	R		
	c-C_4H_8	(88)	
	t-Bu	(25)	
	Ph	(85)	
	2-ClC_6H_4	(19)	
	3-ClC_6H_4	(70)	
	4-ClC_6H_4	(91)	
	3-FC_6H_4	(66)	
	4-FC_6H_4	(98)	
	2-MeC_6H_4	(37)	
	3-MeC_6H_4	(90)	
	4-MeC_6H_4	(66)	
	3-$MeOC_6H_4$	(66)	
	4-$MeOC_6H_4$	(100)	
	Bn	(70)	
	3-$EtOC_6H_4$	(45)	
	4-$EtOC_6H_4$	(52)	
	4-i-$PrOC_6H_4$	(93)	
	2-$C_{10}H_7$	(88)	
	4-PhC_6H_4	(50)	
C_{12}			
	DMF, $POCl_3$	 (40)	482

TABLE XI. PYRROLES (*Continued*)

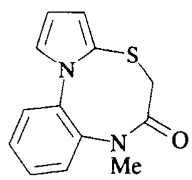
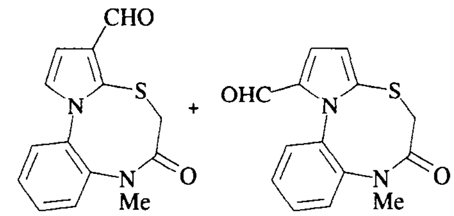
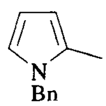
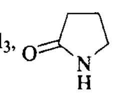
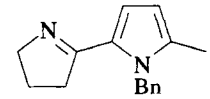
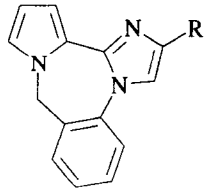
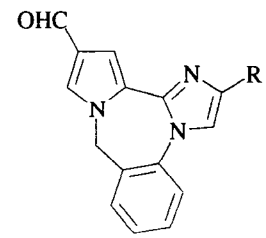
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (32)	504
	$POCl_3$, 	 (21)	466
$C_{12\text{-}17}$			
	DMF, $POCl_3$	 R = H (90) R = CO_2Et (16)	505
C_{13}			
R^1 = Me, R^2 = $CO(C_6H_4Me\text{-}4)$	DMF, $(COCl)_2$	R^3 = CHO (trace) + R^5 = CHO (95)	506

TABLE XI. PYRROLES (*Continued*)

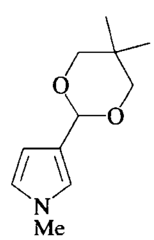
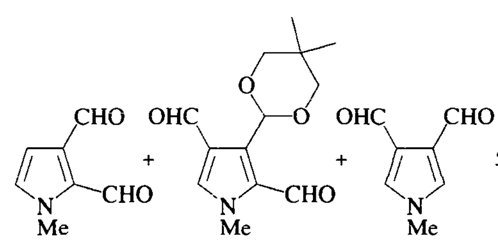
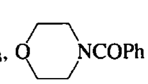
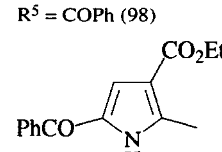
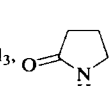
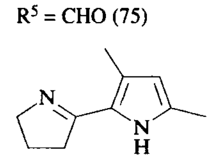
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C2. R^1, R^3 Substituents		
C_{11}			
	1. DMF, $POCl_3$ 2. Hydrolysis	 (total: 53)	501
	C3. R^2, R^3 Substituents		
C_8			
R^2 = Me, R^3 = CO_2Et	Me_2NCOPh, $POCl_3$	R^5 = COPh (98)	86
	$POCl_3$, 	 (90)	86
C_{13}			
R^2 = CO_2Bn, R^3 = Me	DMF, $POCl_3$	R^4 = CHO (28) + R^5 = CHO (72)	507
	C4. R^2, R^4 Substituents		
C_6			
R^2 = R^4 = Me	PhNHCHO, $POCl_3$	R^5 = CHO (33)	233
	DMF, $POCl_3$	R^5 = CHO (75)	453, 508
	$POCl_3$, 	 (66)	88

TABLE XI. PYRROLES (*Continued*)

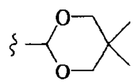
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_7			
$R^2 = CO_2Me$, $R^4 = Me$	DMF, $POCl_3$	$R^5 = CHO$ (88)	509
C_{11}			
$R^2 = Me$, $R^4 = 2\text{-}O_2N\text{-}3\text{-}ClC_6H_3$	DMF, $POCl_3$	$R^5 = CHO$ (—)	510
$R^2 = Me$, $R^4 = 3\text{-}O_2N\text{-}4\text{-}ClC_6H_3$	DMF, $POCl_3$	$R^5 = CHO$ (—)	510
C_{16}			
$R^2 = R^4 = Ph$	MFA, $POCl_3$	$R^5 = CHO$ (—)	511
$R^2 = R^4 =$ 	DMF, $POCl_3$	$R^5 = CHO$ (77)	501
C_{17} $R^2 = Ph$, $R^4 = 4\text{-}MeOC_6H_4$	MFA, $POCl_3$	$R^5 = CHO$ (—)	511
		C5. R^2, R^5 Substituents	
C_6			
$R^2 = R^5 = Me$	DMF, $POCl_3$	$R^3 = CHO$ (62)	513, 512
	DMF, $POCl_3$	$R^3 = CHO$ (18) + $R^3 = R^4 = CHO$ (9)	514, 515
	DMA, $POCl_3$	$R^3 = COMe$ (40)	516
	$Et_2NCOCH_2CO_2Et$, $POCl_3$	$R^3 = CH(NEt_2){=}CHCO_2Et$ (40)	87
	$Me_2NN{=}CHCHO$, $POCl_3$ or $COCl_2$	$R^3 = CH{=}CHN{=}NMe_2^+$ $POCl_2^-$ or Cl^- (70)	40
C_8			
$R^2 = Me$, $R^5 = CO_2Et$	—	$R^3 = CHO$ (—)	121
C_{10}			
$R^2 = 2$-furyl, $R^5 = CO_2Me$	DMF, $POCl_3$	$R^{2'} = CHO$ (88)	74, 75
$R^2 = 3$-furyl, $R^5 = CO_2Me$	DMF, $POCl_3$	$R^{2'} = CHO$ (56)	74
$R^2 = 2$-thienyl, $R^5 = CO_2Me$	DMF, $POCl_3$	$R^3 = CHO$ (85) + $R^{2'} = CHO$ (4)	74, 75
$R^2 = 3$-thienyl, $R^5 = CO_2Me$	DMF, $POCl_3$	$R^3 = CHO$ (85) + $R^{2'} = CHO$ (4)	74
C_{12}			
$R^2 = Ph$, $R^5 = CO_2Me$	DMF, $POCl_3$	$R^3 = CHO$ (62)	74

TABLE XI. PYRROLES (*Continued*)

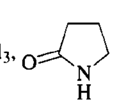
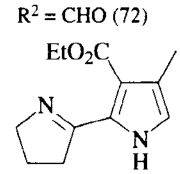
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C6. R^3, R^4 Substituents	
C_6			
$R^3 = R^4 = Me$	DMF, $POCl_3$	$R^2 = CHO$ (79)	453, 518
C_7			
$R^3 = Et$, $R^4 = CF_3$	DMF, $POCl_3$	$R^2 = CHO$ (86)	519
$R^3 = Me$, $R^4 = COMe$	DMF, $POCl_3$	$R^2 = CHO$ (4) + $R^2 = CHO$, $R^4 = C{\equiv}CH$ (34)	520
$R^3 = Me$, $R^4 = Et$	DMF, $POCl_3$	$R^2 = CHO$ (51) + $R^5 = CHO$ (33)	521
C_8			
$R^3 = Me$, $R^4 = CO_2Et$	DMF, $POCl_3$	$R^2 = CHO$ (72)	516
	$POCl_3$, 	 (66)	460
$R^3 = R^4 = Et$	$Me_2NCH{=}CHCHO$, $POCl_3$	$R^2 = CH{=}CHCHO$ (75)	522
$C_{8\text{-}12}$			
$R^3 = Ar$, $R^4 = NO_2$	DMF, $POCl_3$		523
Ar			
2-thienyl		$R^2 = CHO$ (82)	
$2,4\text{-}ClC_6H_3$		$R^2 = CHO$ (12)	
Ph		$R^2 = CHO$ (76)	
$4\text{-}MeOC_6H_4$		$R^2 = CHO$ (82)	
$2,4\text{-}(MeO)_2C_6H_3$		$R^2 = CHO$ (90)	
$3,5\text{-}(MeO)_2C_6H_3$		$R^2 = CHO$ (48) + $R^3 = 2\text{-}CHO\text{-}3,5\text{-}(MeO)_2C_6H_3$ (38)	
C_{10}			
$R^3 = Et$, $R^4 = n\text{-}C_3F_7$	DMF, $POCl_3$	$R^2 = CHO$ (70)	519
C_{16}			
$R^3 = R^4 = Ph$	DMF, $POCl_3$	$R^2 = CHO$ (83)	524

TABLE XI. PYRROLES (*Continued*)

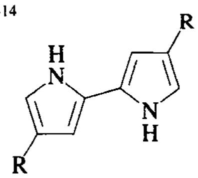
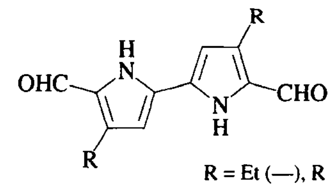
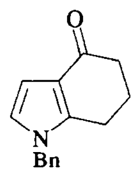
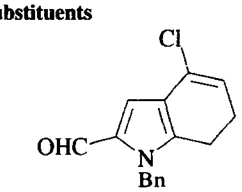
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C7. R^3, R^5 Substituents		
C_{12-14}			
	DMF, $POCl_3$	 R = Et (—), R = *n*-Pr (86)	517
	D. Trisubstituted Pyrroles		
	D1. R^1, R^2, R^3 Substituents		
C_{15}			
	DMF, $POCl_3$	 (50)	525
	D2. R^1, R^2, R^4 Substituents		
C_7			
$R^1 = R^2 = R^4 = Me$	DMF, $POCl_3$	$R^5 = CHO$ (18) + $R^3 = R^5 = CHO$ (—)	514
C_9			
$R^1 = R^4 = Me$, $R^2 = CH_2CO_2Me$	1. $MeNHCOC_6H_4R$-4, $SOCl_2$ 2. H^+	$R^5 = CH(=NMe)C_6H_4R$-4	402
	R		
	H	(61)	
	Cl	(69)	
	NO_2	(65)	
	Me	(61)	
	MeO	(64)	
C_{10}			
$R^1 = R^4 = Me$, $R^2 = CH_2CO_2Et$	$Me_2NCOC_6D_4$-4	$R^5 = CHO$ (—)	526

TABLE XI. PYRROLES (*Continued*)

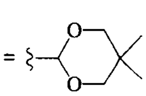
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$R^1 = Me$, $R^2 = CH_2CO_2Et$, $R^4 = SMe$	Me_2NCOAr, $POCl_3$	$R^5 = COAr$	527
	Ar		
	Ph	(—)	
	4-ClC_6H_4	(—)	
	4-FC_6H_4	(—)	
	4-MeC_6H_4	(—)	
	4-$EtOC_6H_4$	(—)	
	4-*n*-PrC_6H_4	(—)	
	4-*c*-PrC_6H_4	(—)	
C_{17}			
$R^1 = Me$, $R^2 = R^4 =$ 	DMF, $POCl_3$	$R^5 = CHO$ (80)	501
	D3. R^1, R^2, R^5 Substituents		
C_7			
$R^1 = R^2 = R^5 = Me$	DMF, $POCl_3$	$R^3 = CHO$ (44) + $R^3 = R^4 = CHO$ (—)	514, 515
C_{10-19}			
$R^1 = Ar$, $R^2 = R^5 = Me$	DMF, $POCl_3$	$R^3 = CHO$	
Ar			
1-pyrrolyl		(67)	
2-pyridyl		(14)	
2-ClC_6H_4		(89)	
Ph		(73) + $R^3 = R^4 = CHO$ (13)	
2-NCC_6H_4		(84)	
4-Me-2-pyridyl		(68)	
2-Cl-6-MeC_6H_3		(79)	
2-MeC_6H_4		(90)	
2-$MeOC_6H_4$		(91)	
2-$EtOC_6H_4$		(93)	
4-$Me_2NC_6H_4$		(60)	
8-quinolyl		(62)	
2-$BnOC_6H_4$		(86)	

TABLE XI. PYRROLES (*Continued*)

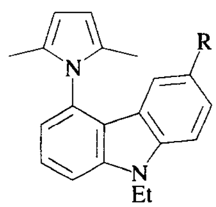
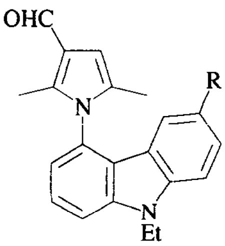
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{13}			
R^1 = Bn, R^2 = R^5 = Me	DMF, $POCl_3$	R^3 = CHO (83)	531
C_{16}			
R^1 = 1-pyrrolyl, R^2 = R^5 = CH_2CO_2Et	DMF, $POCl_3$	R^3 = CHO (41)	485
C_{17}			
R^1 = R^2 = Ph, R^5 = Me	DMF, $POCl_3$	R^4 = CHO (98)	530
C_{20-21}			
	DMF, $POCl_3$	 R = H (93), R = Me (67)	532
D4. R^1, R^3, R^4 Substituents			
C_7			
R^1 = R^3 = R^4 = Me	DMF, $POCl_3$	R^2 = CHO (70)	453
C_{19}			
R^1 = *i*-Pr, R^3 = R^4 = 2-FC_6H_4	Me_2NCH=CHCHO, $POCl_3$	R^2 = CH=CHCHO (—)	533
D5. R^1, R^3, R^5 Substituents			
C_7			
R^1 = R^3 = R^5 = Me	DMF, $POCl_3$	R^2 = CHO (65)	453
D6. R^2, R^3, R^4 Substituents			
C_7			
R^2 = R^3 = R^4 = Me	DMF, $POCl_3$	R^2 = CHO (81)	453, 508, 534

TABLE XI. PYRROLES (*Continued*)

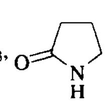
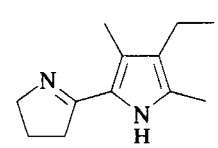
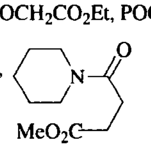
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_8			
R^2 = R^4 = Me, R^3 = COMe	DMF, $POCl_3$, 80°	R^5 = CHO (34) + R^3 = C≡CH, R^5 = CHO (32)	535
	DMF, $POCl_3$, 0°	R^3 = C(Cl)=CH_2, R^5 = CHO (70)	535
R^2 = R^4 = Me, R^3 = Et	DMF , $POCl_3$	R^5 = CHO (76)	536, 508, 534
	Et_2NCOCH_2Cl, $POCl_3$	R^5 = $COCH_2Cl$ (34)	87
	$Et_2NCOCH_2CO_2Et$, $POCl_3$	R^5 = C(NEt_2)=$CHCO_2Et$ (36)	87
	$POCl_3$, 	 (76)	87
R^2 = R^3 = Me, R^4 = Et	DMF, $POCl_3$	R^5 = CHO (—)	534
C_9			
R^2 = R^4 = Me, R^3 = CO_2Et	DMF, $POCl_3$	R^5 = CHO (93)	508, 516
	DMA, $POCl_3$	R^5 = COMe (67)	516
	Et_2NCOCH_2Cl, $POCl_3$	R^5 = $COCH_2Cl$ (75)	87
	$Et_2NCOCH_2CO_2Et$, $POCl_3$	R^5 = $COCH_2CO_2Et$ (61)	87
	$POCl_3$, 	R^5 = $CO(CH_2)_2CO_2Me$ (40)	516
	R_2NCOAr, $POCl_3$	R^5 = COAr	
	R — Ar		
	Me — 2-pyrrolyl	(86)	183, 537
	Me — 2-furyl	(81)	183, 537
	Me — 2-thienyl	(87)	183, 537
	Me — 3-pyridyl	(85)	183

TABLE XI. PYRROLES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	R Ar		
	Me Ph	(99)	86, 537, 538
	Me 3-ClC_6H_4	(88)	183, 537
	Me 4-ClC_6H_4	(90)	183, 537
	Me 3-$O_2NC_6H_4$	(90)	183, 537
	Me 4-$O_2NC_6H_4$	(96)	183, 537
	Me 4-MeC_6H_4	(82)	537
	Me 4-$MeOC_6H_4$	(86)	537
	Et Ph	(95)	538, 86
	$(CH_2)_3$ Ph	(10)	538
	$(CH_2)_4$ Ph	(93)	538
	$(CH_2)_5$ Ph	(97)	538, 516
	$[(CH_2)_2]_2O$ Ph	(99)	86, 537-539
	$[(CH_2)_2]_2O$ 4-ClC_6H_4	(87)	183, 537
	$[(CH_2)_2]_2O$ 4-MeC_6H_4	(85)	183, 537
	$[(CH_2)_2]_2O$ 4-$MeOC_6H_4$	(90)	183, 537
	$[(CH_2)_2]_2NMe$ Ph	(96)	538
	$POCl_3$, PhCONNCOPh	R^5 = COPh (94)	538
	1. $O[(CH_2)_2]_2NCOAr$, $POCl_3$ 2. $LiBH_4$ or $Na(CN)BH_3$	$R^5 = CH_2Ar$	461
	Ar		
	Ph	(90-93)	
	4-ClC_6H_4	(89-90)	
	4-MeC_6H_4	(87-88)	
	4-$MeOC_6H_4$	(91-93)	

TABLE XI. PYRROLES (*Continued*)

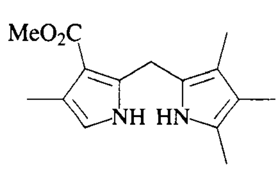
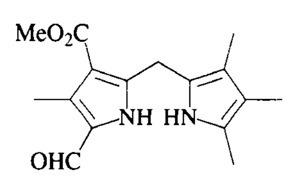
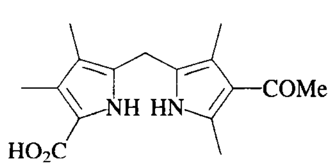
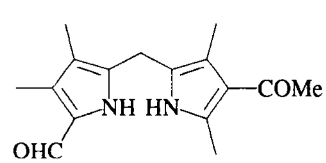
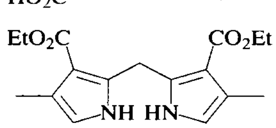
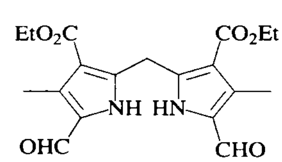
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{11}			
$R^2 = R^4 = CO_2Et$, R^3 = Me	DMF, $POCl_3$	R^5 = CHO (59)	516
C_{12}			
$R^2 = R^4$ = Me, R^3 = Ph	DMF, PhCOCl	R^5 = CHO (88)	466
C_{14}			
$R^2 = CO_2Et$, R^3 = Me, R^4 = Ar	DMF, $POCl_3$	R^5 = CHO	510
Ar			
2-O_2N-3-ClC_6H_3		(—)	
3-O_2N-4-ClC_6H_3		(—)	
4-$O_2NC_6H_4$		(91)	
R^2 = Me, $R^3 = CO_2Et$, R^4 = Ph	MFA, $POCl_3$	R^5 = CHO (—)	540
$R^2 = CO_2Bu$-*t*, $R^3 = (CH_2)_2CO_2Me$, R^4 = Me	DMF, $POCl_3$	R^5 = CHO (75)	92, 541
C_{15}			
	DMF, PhCOCl	 (13)	542
C_{16}			
	1. Decarboxylate 2. DMF, PhCOCl	 (74)	542
C_{17}			
	DMF, $POCl_3$	 (100)	93, 516

TABLE XI. PYRROLES (*Continued*)

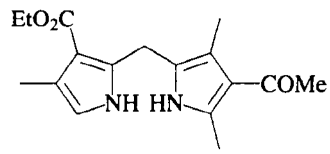
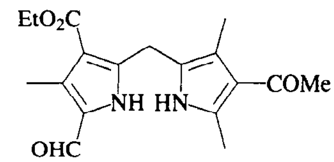
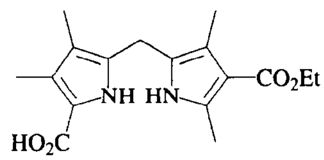
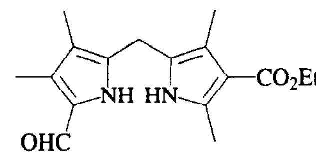
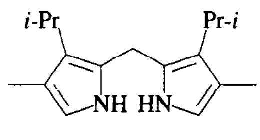
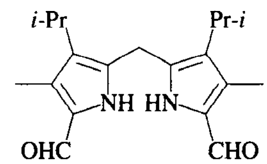
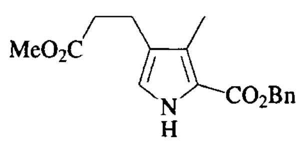
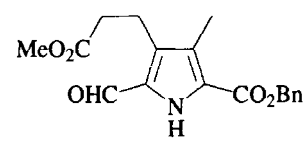
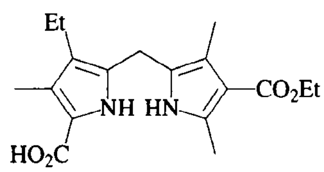
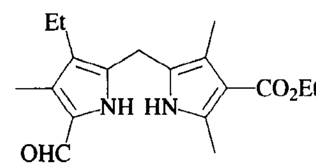
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, PhCOCl	 (27)	542
	1. Decarboxylate 2. DMF, PhCOCl	 (71)	542
	DMF, $POCl_3$	 (66)	543
	DMF, $POCl_3$	 (89)	544
C_{18}			
	1. Decarboxylate 2. DMF, PhCOCl	 (56)	542

TABLE XI. PYRROLES (*Continued*)

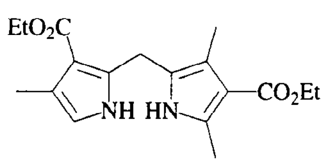
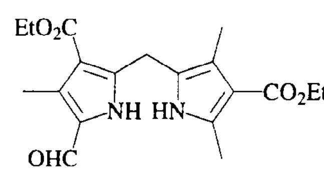
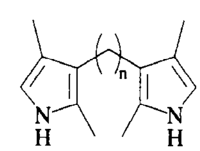
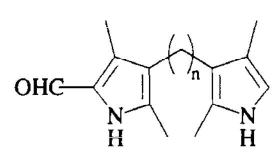
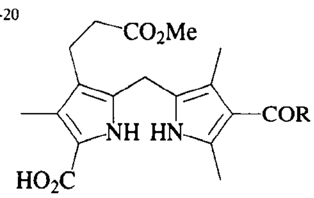
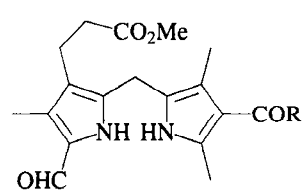
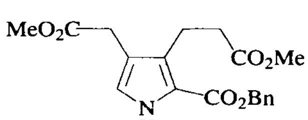
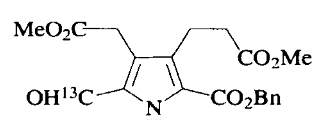
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, PhCOCl	 (22)	542
$C_{18\text{-}23}$			
	DMF, $POCl_3$		
n			
6		(66)	545
11		(91)	546
$C_{19\text{-}20}$			
	1. Decarboxylate 2. DMF, PhCOCl	 R = Me (68) R = OEt (64)	542
C_{19}			
	$Me_2N^{13}CHO$, —	 (—)	548

TABLE XI. PYRROLES (*Continued*)

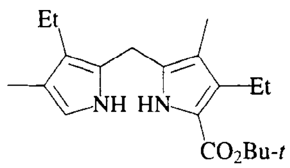
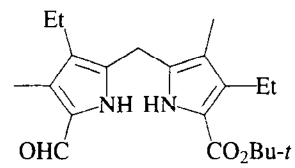
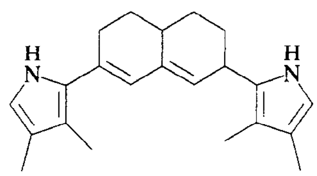
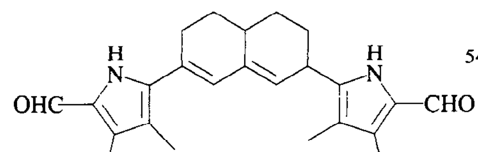
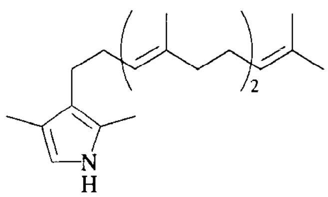
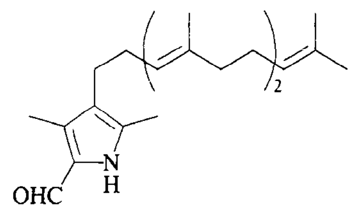
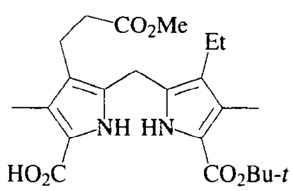
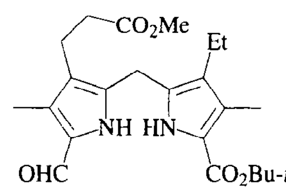
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{20} 	—	 (—)	548
C_{22} 	DMF, $POCl_3$	 (71)	549
C_{23} 	—	 (74)	550
	1. Decarboxylate 2. DMF, PhCOCl	 (66)	551

TABLE XI. PYRROLES (*Continued*)

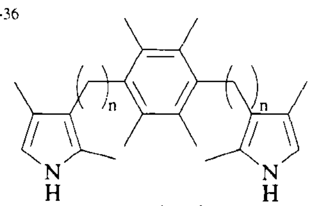
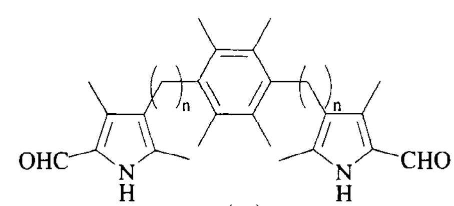
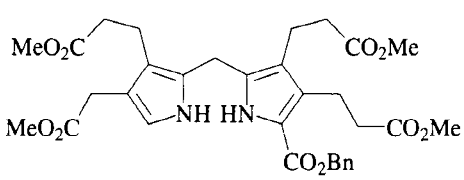
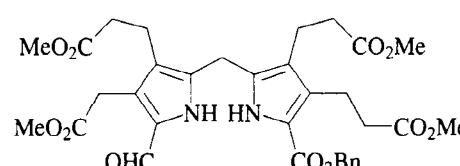
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{30\text{-}36}$  n = 4, 5, 7	DMF, $POCl_3$	 (—)	552, 553
	—	 (—)	554
D6. R^2, R^3, R^5 Substituents			
C_7			
$R^2 = R^3 = R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (99)	513
C_9			
$R^2 = CO_2Et$, $R^3 = R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (95)	508, 555
	PhNHCHO, $POCl_3$	$R^4 = CHO$ (—)	233
$R^3 = CO_2Et$, $R^2 = R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (93)	516
	PhNHCHO, $POCl_3$	$R^4 = CHO$ (20)	233
C_{11}			
$R^2 = R^3 = CO_2Et$, $R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (81)	556
C_{14}			
$R^2 = CO_2Et$, $R^3 = Ph$, $R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (97)	555
$R^2 = CO_2Bn$, $R^3 = R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (93)	557

TABLE XI. PYRROLES (*Continued*)

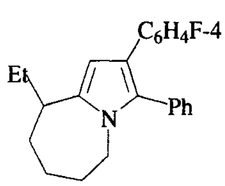
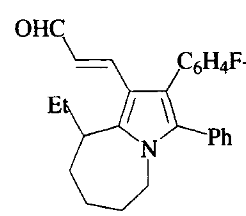
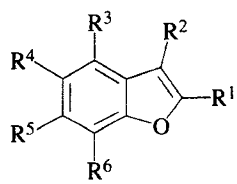
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	E. Tetrasubstituted Pyrroles		
	E1. R^1, R^2, R^3, R^4 Substituents		
C_{10}			
$R^1 = R^2 = R^4 = Me$, $R^3 = CO_2Et$	Me_2NCOPh, $POCl_3$	$R^5 = COPh$ (78)	86
C_{16}			
$R^1 = Bn$, $R^2 = R^4 = Me$, $R^3 = CO_2Et$	Me_2NCOPh, $POCl_3$	$R^5 = COPh$ (20)	86
	E2. R^1, R^2, R^3, R^5 Substituents		
C_{13}			
$R^1 = Ph$, $R^2 = R^3 = R^5 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (83)	530
C_{18}			
$R^1 = R^5 = Ph$, $R^2 = R^3 = Me$	DMF, $POCl_3$	$R^4 = CHO$ (77)	530
C_{23}			
	$Me_2NCH{=}CHCHO$, $POCl_3$	 (—)	558

TABLE XII. BENZO[*b*]FURANS



R^1 - R^6 = H except as indicated.

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Benzo[*b*]furan		
C_8			
	DMF, $POCl_3$	R^1 = CHO (62)	95, 156
	B. Monosubstituted Benzo[*b*]furans		
	B1. R^1 Substituents		
C_8			
R^1 = Me	DMF, $POCl_3$	R^2 = CHO (78)	156
C_{10}			
R^1 = Et	DMF, $POCl_3$	R^2 = CHO (70)	156
	B2. R^4 Substituents		
C_9			
R^4 = OMe	DMF, $POCl_3$	R^1 = CHO (38)	559
	C. Disubstituted Benzo[*b*]furans		
	C1. R^1, R^4 Substituents		
C_9			
R^1 = Et, R^4 = Cl	DMF, $POCl_3$	R^2 = CHO (76)	298
C_{11}			
R^1 = Et, R^4 = Me	DMF, $POCl_3$	R^2 = CHO (84)	560
R^1 = Et, R^4 = OMe	DMF, $POCl_3$	R^2 = CHO (76)	298
C_{15}			
R^1 = Ph, R^4 = OMe	DMF, $POCl_3$	R^2 = CHO (75)	561

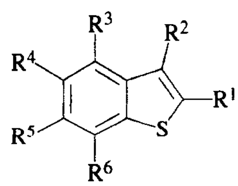
TABLE XII. BENZO[*b*]FURANS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C2. R^2, R^3 Substituents		
C_{10}			
R^2 = Me, R^3 = OMe	DMF, $POCl_3$	R^1 = CHO (80)	
	C3. R^2, R^4 Substituents		
C_{10}			
R^2 = Me, R^4 = OMe	DMF, $POCl_3$	R^1 = CHO (50)	98
C_{11}			
R^2 = NHAc, R^4 = OMe	DMF, $POCl_3$	R^1 = CHO (50)	562
C_{15}			
R^2 = Ph, R^4 = OMe	DMF, $POCl_3$	R^1 = CHO (98)	561
	C4. R^2, R^5 Substituents		
C_{10}			
R^2 = R^5 = Me	DMF, $POCl_3$	R^1 = CHO (75)	563
R^2 = Me, R^5 = OMe	DMF, $POCl_3$	R^1 = CHO (90)	98
	C5. R^2, R^6 Substituents		
C_{10}			
R^2 = Me, R^6 = OMe	DMF, $POCl_3$	R^1 = CHO (85)	98
	C6. R^3, R^5 Substituents		
C_9			
R^3 = Me, R^5 = Cl	DMF, $POCl_3$	R^1 = CHO (97)	564
	D. Trisubstituted Benzo[*b*]furans		
	D1. R^1, R^2, R^4 Substituents		
C_{21}			
R^1 = R^2 = Ph, R^4 = OMe	DMF, $POCl_3$	R^5 = CHO (78)	565
	D2. R^1, R^2, R^5 Substituents		
C_{21}			
R^1 = R^2 = Ph, R^5 = OMe	DMF, $POCl_3$	R^4 = CHO (60)	565

TABLE XII. BENZO[*b*]FURANS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	D3. R^1, R^3, R^6 Substituents		
C_{11}			
R^1 = R^6 = Me, R^3 = OMe	DMF, $POCl_3$	R^2 = CHO (79)	98
C_{12}			
R^1 = Et, R^3 = Me, R^6 = OMe	DMF, $POCl_3$	R^5 = CHO (84)	98
	D4. R^2, R^3, R^5 Substituents		
C_{12}			
R^2 = Et, R^3 = R^5 = Me	DMA, $POCl_3$	R^1 = COMe (26)	566
	D5. R^2, R^3, R^6 Substituents		
C_{11}			
R^2 = R^3 = Me, R^6 = OMe	DMF, $POCl_3$	R^1 = CHO (67)	98
R^2 = Me, R^3 = R^6 = OMe	DMF, $POCl_3$	R^1 = CHO (70)	98
	D6. R^2, R^5, R^6 Substituents		
C_{11}			
R^2 = Me, R^5 = R^6 = OMe	DMF, $POCl_3$	R^1 = CHO (87)	98
	D7. R^3, R^4, R^5 Substituents		
C_{10}			
R^3 = R^5 = Me, R^4 = Cl	DMF, $POCl_3$	R^1 = CHO (93)	564

TABLE XIII. BENZO[*b*]THIOPHENES



R^1 - R^6 = H except as indicated.

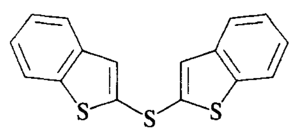
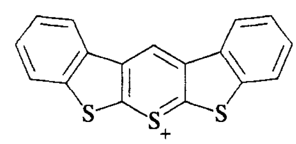
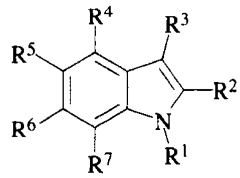
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		A. Benzo[*b*]thiophene	
C_8			
	MFA, $POCl_3$	R^2 = CHO (7)	96
		B. Monosubstituted Benzo[*b*]thiophenes	
		B1. R^1 Substituents	
C_{12} R^1 = *N*-morpholinyl	DMF, $POCl_3$	R^2 = CHO (80)	412
C_{16} 	DMF, $POCl_3$	 Cl^- (37)	434
		B2. R^2 Substituents	
C_8			
R^2 = NH_2	DMF, $POCl_3$	R^1 = CHO, R^2 = N=CHNMe_2 (—)	567
C_9			
R^2 = OMe	MFA, $POCl_3$, <45°	R^1 = CHO (40-45)	100
	MFA, $POCl_3$, 90°	R^1 = CHO, R^2 = Cl (90)	100
C_{10}			
R^2 = NHAc	DMF, $POCl_3$	R^1 = CHO (31)	568
	DMF, $POCl_3$	R^1 = CHO, R^2 = N=CHNMe_2 (35)	569

TABLE XIII. BENZO[*b*]THIOPHENES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{11}			
R^2 = N=CHNMe_2	DMF, $POCl_3$	R^1 = CHO (85)	567
		B3. R^3 Substituents	
C_9			
R^3 = OMe	DMF, $POCl_3$	R^6 = CHO (98)	99
	MFA, $POCl_3$	R^6 = CHO (70)	100
		C. Disubstituted Benzo[*b*]thiophenes	
		C1. R^2, R^3 Substituents	
C_{10}			
R^2 = Me, R^3 = OMe	DMF, $POCl_3$	R^1 = CHO (35) + R^6 = CHO (62)	99
		C2. R^2, R^5 Substituents	
C_{10}			
R^2 = OH, R^5 = OEt	MFA, $POCl_3$	R^1 = CHO (—)	189
		C3. R^4, R^5 Substituents	
C_{10}			
R^4 + R^5 = CH_2OCH_2	MFA, $POCl_3$	R^1 = CHO (66)	570
		D. Trisubstituted Benzo[*b*]thiophenes	
		D1. R^2, R^4, R^6 Substituents	
C_9			
C_2 R^2 = OH, R^4 = Me, R^6 = Cl	MFA, $POCl_3$	R^1 = CHO (—)	189

TABLE XIV. INDOLES



R^1 - R^7 = H except as indicated.

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Indole		
C_8			
	DMF, $POCl_3$	R^3 = CHO (100)	572, 571, 97
	MFA, $POCl_3$	R^3 = CHO (53)	573
	DMF, $(Cl_2PO)_2O$	R^3 = CHO (97)	26
	DMF, PCl_3	R^3 = CHO (95)	321
	DMF, PCl_5	R^3 = CHO (97)	321
	DMF, $SOCl_2$	R^3 = CHO (65)	321
	DMF, BCl_3	R^3 = CHO (80)	574
	DMF, $C_3N_3Cl_3$[a]	R^3 = CHO (31)	36
	DMF, Ph_3PBr_2	R^3 = CHO (78)	55
	DMF, MeCOCl	R^3 = CHO (48)	575
	DMF, MeCOBr	R^3 = CHO (89)	575
	DMF, PhCOCl	R^3 = CHO (85)	575
	1. DMF, $POCl_3$ 2. NH_2OH 3. Dehydrate	R^3 = CN (54-59)	197
	1. *N*-Formylmorpholine, $POCl_3$ 2. NH_2OH 3. Dehydrate	R^3 = CN (31)	197
	1. DMF, $POCl_3$ 2. HBF_4	R^3 = $CH{=}NMe_2^+$ BF_4^- (56)	576

TABLE XIV. INDOLES (*Continued*)

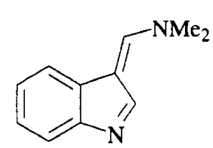
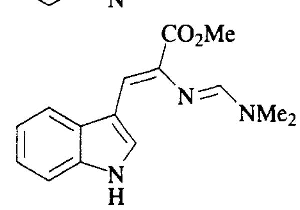
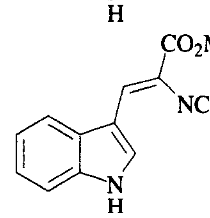
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. base	 (61)	572
	1. DMF, $POCl_3$ 2. Na_2CO_3 3. $CNCH_2CO_2Me$, DMF, MeOH	 (80)	577
	1. DMF, $POCl_3$ 2. Na_2CO_3 3. $CNCH_2CO_2Me$, DMF	 (60)	577
	DMA, $COCl_2$	R^1 = COMe + R^3 = COMe (—) 2:98	103
	DMA, $POCl_3$	R^3 = COMe (45)	578
	MeNHCOMe, $POCl_3$	R^3 = COMe (22)	101
	Me_2NCOCH_2Cl, $POCl_3$	R^3 = $COCH_2Cl$ (37)	101
	Me_2NCOEt, $POCl_3$	R^3 = COEt (86)	101
	Me_2NCOPh, $POCl_3$	R^3 = COPh (51)	101, 578

TABLE XIV. INDOLES (*Continued*)

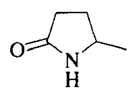
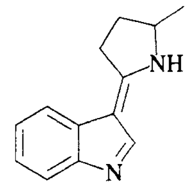
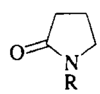
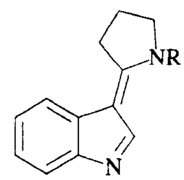
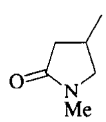
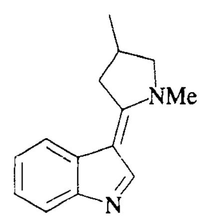
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$POCl_3$, 	 (—)	102
	$POCl_3$, 		
	R		
	H	(89)	579
	Me	(85)	102
	Et	(95)	579, 102
	Bu	(75)	579, 102
	Bn	(50)	579, 102
	$POCl_3$, 	 (53)	579, 102

TABLE XIV. INDOLES (*Continued*)

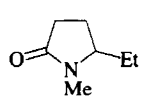
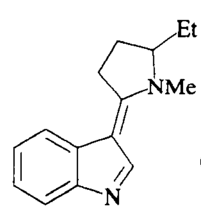
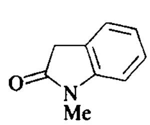
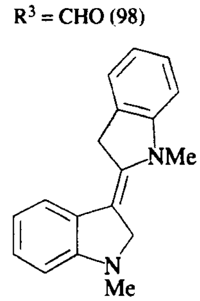
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	$POCl_3$, 	 (—)	102
	$Me_2NN=CHCHO$, $COCl_2$	$R^3 = CH=CHN=NMe_2^+ Cl^-$ (90)	40
	B. Monosubstituted Indoles		
	B1. R^1 Substituents		
C_9			
$R^1 = Me$	DMF, $POCl_3$	$R^3 = CHO$ (87)	580
	DMF, $(Cl_2PO)_2O$	$R^3 = CHO$ (98)	26
	$POCl_3$, 	 (85)	581
$R^1 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (91)	582
C_{10}			
$R^1 = OAc$	DMF, $POCl_3$	$R^1 = OH$, $R^3 = CHO$ (6) + $R^2 = Cl$, $R^3 = CHO$ (53)	583
$R^1 = Et$	DMA, $POCl_3$	$R^3 = COMe$ (76)	101

TABLE XIV. INDOLES (*Continued*)

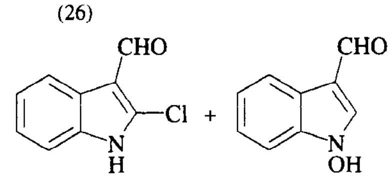
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{14}			
R^1 = Ar		R^3 = CHO	
Ar			
2-$O_2NC_6H_4$	DMF, $POCl_3$	(92)	584
	DMF, PCl_3	(60)	321
	DMF, PCl_5	(60)	321
	DMF, $SOCl_2$	(24)	321
3-$O_2NC_6H_4$	DMF, $POCl_3$	(90)	584
	DMF, PCl_3	(60)	321
	DMF, PCl_5	(60)	321
	DMF, $SOCl_2$	(24)	321
4-$O_2NC_6H_4$	DMF, $POCl_3$	(98)	584, 585
	DMF, PCl_3	(60)	321
	DMF, PCl_5	(60)	321
	DMF, $SOCl_2$	(26)	321
R^1 = OTBDMS	—	 I (39) + II (32)	586
C_{15}			
R^1 = O_2CPh	1. DMF, $POCl_3$ (3 eq), 47 h 2. NaOH	**I** (98)	586
	1. DMF, $POCl_3$ (2 eq), 3 h 2. NaOH	**I** (14) + **II** (57)	586
C_{21}			
R^1 = OTs	—	**I** (67)	586
C_{22}			
R^1 = tetraacetyl-β-D-arabinose	DMF, $POCl_3$	R^3 = CHO (86)	587
R^1 = tetraacetyl-β-D-glucose	DMF, $POCl_3$	R^3 = CHO (85)	588

TABLE XIV. INDOLES (*Continued*)

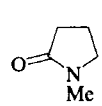
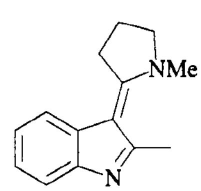
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	B2. R^2 Substituents		
C_9			
R^2 = Me	DMF, $POCl_3$	R^3 = CHO (96)	589, 590
	DMF, $(Cl_2PO)_2O$	R^3 = CHO (88)	26
	DMF, PhCOCl	R^3 = CHO (88)	575
	DMA, $POCl_3$	R^3 = COMe (98)	101
	DMA, $POCl_3$	R^1 = COMe + R^3 = COMe (—) 2:98	103
	Me_2NCOBu-*t*, $POCl_3$	R^3 = COBu-*t* (49)	101
	$Me_2NCOCH(Me)Et$, $POCl_3$	R^3 = COCH(Me)Et (18)	101
	Me_2NCOPr-*i*, $POCl_3$	R^3 = COPr-*i* (62)	101
	$Me_2NCOCH(Et)Pr$-*i*, $POCl_3$	R^3 = COCH(Et)Pr-*i* (24)	101
	$POCl_3$, 	 (96)	579, 102
R^2 = $CONHNH_2$	DMF, $POCl_3$	R^2 + R^3 = $CONHNHCH_2$ (77)	591
C_{10}			
R^2 = CH_2CN	DMA, $POCl_3$	R^3 = COMe (—)	592
R^2 = Et	DMF, $POCl_3$	R^3 = CHO (70)	589
R^2 = CH_2CO_2Me	MFA, $POCl_3$	R^3 = CHO (—)	593
R^2 = $NHCO_2Et$	DMF, $POCl_3$	R^3 = CHO (88)	594
R^2 = *n*-Pr	DMF, $POCl_3$	R^3 = CHO (75)	589
R^2 = *i*-Pr	DMF, $POCl_3$	R^3 = CHO (88)	589
C_{12}			
R^2 = CO_2Et	DMF, $POCl_3$	R^3 = CHO (—)	591
	MFA, $POCl_3$	R^3 = CHO (100)	26

TABLE XIV. INDOLES (*Continued*)

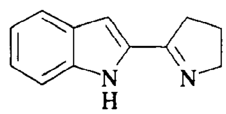
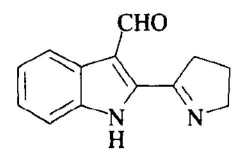
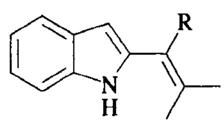
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^2 = 2-furyl	DMF, $POCl_3$, 30°	R^3 = CHO (85)	595
	DMF, $POCl_3$ (xs), 100°	R^3 = $R^{5'}$ = CHO (63)	595
R^2 = *t*-Bu	DMF, $POCl_3$	R^3 = CHO (80)	590
	DMF, $POCl_3$	 (30)	596
C_{12-18} 			
R			
H	DMF, $POCl_3$, rt	R^3 = CHO (94)	235
	DMF, $POCl_3$, rt to reflux	2-methylcarbazole (80)	235
	DMF, $POCl_3$, heat	2-methylcarbazole or R^3 = CHO (high)	597
Me	DMF, $POCl_3$, rt	R^3 = CHO (96)	235
	DMF, $POCl_3$, rt to reflux	1,2-dimethylcarbazole (1)	235
Ph	DMF, $POCl_3$, rt	R^3 = CHO (98)	235
	DMF, $POCl_3$, rt to reflux	1-phenyl-2-methylcarbazole (3)	235
C_{13}			
R^2 = $C(Me)_2CH{=}CH_2$	—	R^3 = CHO (—)	598
C_{14}			
R^2 = C_6H_{11}	DMF, $POCl_3$	R^3 = CHO (79)	589
R^2 = CH_2(piperidyl-4)	DMF, $POCl_3$	R^3 = CHO (52)	599

TABLE XIV. INDOLES (*Continued*)

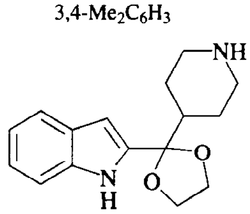
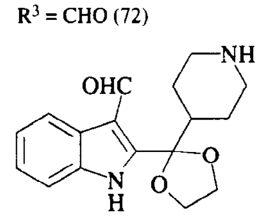
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{14-15}			
R^2 = Ar			
Ar			
3-Cl-4-FC_6H_3	DMF, $POCl_3$	R^3 = CHO (68)	600
4-FC_6H_4	DMF, $POCl_3$	R^3 = CHO (76)	600
Ph	DMF, $POCl_3$	R^3 = CHO (97)	589
	MFA, $POCl_3$	R^3 = CHO (—)	601
	DMF, $POCl_3$	R^3 = $CH{=}NMe_2^+ Cl^-$ (—)	602
	DMF, PCl_3	R^3 = CHO (60)	321
	DMF, PCl_5	R^3 = CHO (60)	321
	DMF, $SOCl_2$	R^3 = CHO (20)	321
	DMF, PhCOCl	R^3 = CHO (96)	575
3,4-$Me_2C_6H_3$	DMF, $POCl_3$	R^3 = CHO (72)	600
C_{16} 	DMF, $POCl_3$	 (85)	599
R^2 = $NHCO_2Bn$	DMF, $POCl_3$	R^3 = CHO (66) + R^2 = $N{=}CHNMe_2$, R^3 = CHO (17)	594
	DMF, $POCl_3$	R^3 = CHO (67)	603
	Me_2NCOR, $POCl_3$	R^3 = COR	594
	R		
	Me	(41)	
	i-Pr	(46)	
	4-ClC_6H_4	(69)	
	Ph	(72)	
	4-$MeOC_6H_4$	(67)	
	Et_2NCOCH_2Cl, $POCl_3$	R^3 = $COCH_2Cl$ (73)	594, 604

TABLE XIV. INDOLES (*Continued*)

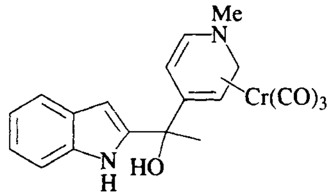
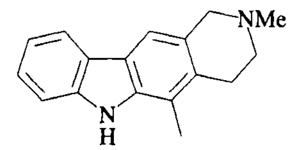
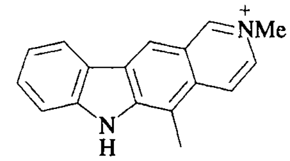
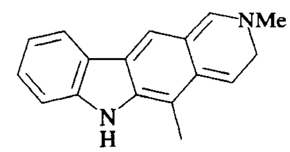
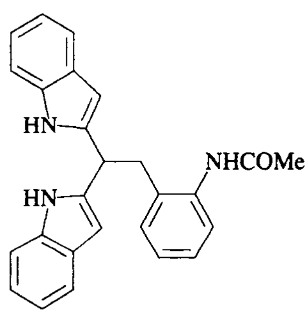
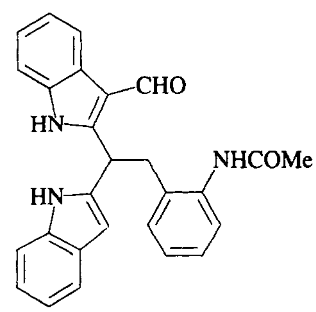
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	1. DMF, $POCl_3$ 2. $NaBH_4$	 (89)	605
	DMF, $POCl_3$	 $H_2PO_4^-$ (64) +	606
		 (27)	
C_{26}			
	DMF, $POCl_3$	 (11)	607

TABLE XIV. INDOLES (*Continued*)

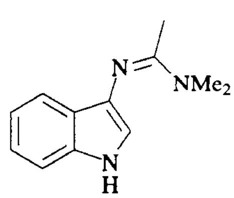
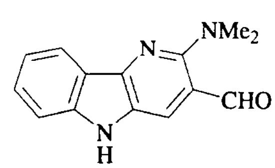
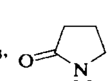
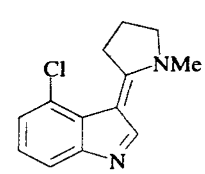
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		B3. R^3 Substituents	
C_8			
$R^3 = NH_2$	—	$R^2 = CHO$, $R^3 = N{=}CHNMe_2$ (—)	608
	Et_2NCHO, $POCl_3$	$R^2 = CHO$, $R^3 = N{=}CHNEt_2$ (48)	106
C_9			
$R^3 = Me$	DMF, $POCl_3$	$R^1 = CHO$ (71) + $R^2 = CHO$ (22)	104, 105
	DMA, $POCl_3$	$R^1 = COMe$ + $R^2 = COMe$ (—) 5:95	103
C_{11}			
	DMF, $POCl_3$	 (15)	106
C_{12}			
$R^3 = t$-Bu	DMF, $POCl_3$	$R^1 = COMe$ (—)	103
C_{14}			
$R^3 = 4\text{-}FC_6H_4$	DMF, $POCl_3$	$R^2 = CHO$ (38)	108
		B4. R^4 Substituents	
C_8			
$R^4 = Cl$	DMF, $POCl_3$	$R^3 = CHO$ (66)	609
	$POCl_3$, 	 (49)	579, 102

TABLE XIV. INDOLES (*Continued*)

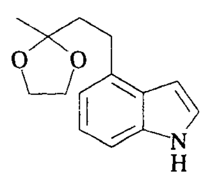
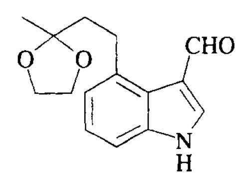
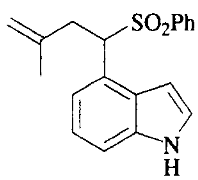
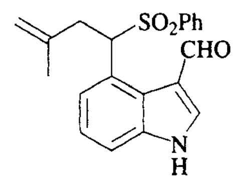
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^4 = Br	DMF, $POCl_3$	R^3 = CHO (67)	609
R^4 = I	DMF, $POCl_3$	R^3 = CHO (100)	609
C_9			
R^4 = Me	DMA, $POCl_3$	R^1 = COMe + R^3 = COMe (—) 5:95	103
C_{11}			
R^4 = SCH_2CO_2Me	DMF, $POCl_3$	R^3 = CHO (95)	610
C_{13}			
R^4 = 3-Pyridyl	DMF, $POCl_3$	R^3 = CHO (92)	611
C_{14}			
	DMF, $POCl_3$		612
C_{19}			
	DMF, $POCl_3$	 (96)	613
	B5. R^5 Substituents		
C_8			
R^5 = F	—	R^3 = CHO (—)	614
R^5 = Cl	DMF, $POCl_3$	R^3 = CHO (93)	615
R^5 = Br	DMF, $POCl_3$	R^3 = CHO (95)	616
	MFA, $POCl_3$	R^3 = CHO (13)	617
R^5 = I	DMF, $POCl_3$	R^3 = CHO (89)	618

TABLE XIV. INDOLES (*Continued*)

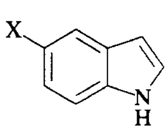
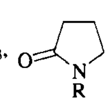
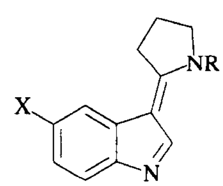
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{8-15}			
	$POCl_3$, 		
X	R		
F	Me	(69)	579, 102
Cl	Me	(76)	579, 102
	Bn	(79)	579, 102
Br	Me	(82)	579, 102
	Bn	(60)	579, 102
Me	Me	(93)	579, 102
MeO	Me	(88)	579
BnO	Me	(90)	579, 102
C_9			
R^5 = OMe	DMF, $POCl_3$	R^3 = CHO (94)	615, 97, 619-621
C_{10}			
R^5 = $COCH_2Cl$	Et_2NCOCH_2Cl, $POCl_3$	R^3 = $COCH_2Cl$ (30)	622
R^5 = COMe	Et_2NCOCH_2Cl, $POCl_3$	R^3 = $COCH_2Cl$ (—)	622
R^5 = Et	—	R^3 = CHO (—)	614
C_{12}			
R^5 = CH=$CHCO_2Me$	DMF, $POCl_3$	R^3 = CHO (72)	623
C_{15}			
R^5 = OBn	DMF, $POCl_3$	R^3 = CHO (86)	615, 621, 624
	DMA, $POCl_3$	R^3 = COMe (71)	101

TABLE XIV. INDOLES (*Continued*)

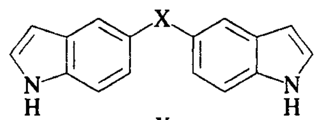
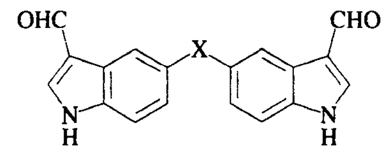
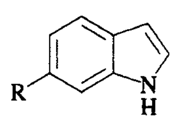
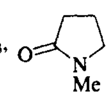
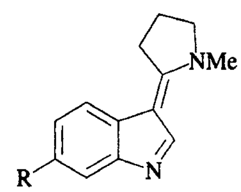
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{16-18}			
	DMF, $POCl_3$		
X			
O		(75)	625
SO_2		(65)	626
$(CH_2)_2$		(85)	627
	B6. R^6 Substituents		
C_8			
R^6 = Cl	DMF, $POCl_3$	R^3 = CHO (53)	619
R^6 = Br	DMF, $POCl_3$	R^3 = CHO (94)	628
R^6 = I	DMF, $POCl_3$	R^3 = CHO (87)	629
C_9			
R^6 = Me	DMF, $POCl_3$	R^3 = CHO (80)	619
R^6 = OMe	DMF, $POCl_3$	R^3 = CHO (92)	621, 615
C_{9-15}			
	$POCl_3$, 		
R			
Me		(—)	102
BnO		(88)	579, 102

TABLE XIV. INDOLES (*Continued*)

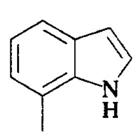
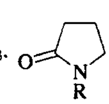
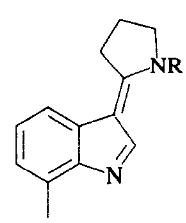
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
R^6 = CH=CHCO$_2$Me	DMF, $POCl_3$	R^3 = CHO (96)	623
C_{15}			
R^6 = OBn	DMF, $POCl_3$	R^3 = CHO (90)	621, 615
	DMF, PBr_3	R^3 = CHO (82)	615
	DMF, PCl_5	R^3 = CHO (27)	615
	B7. R^7 Substituents		
C_9			
	$POCl_3$, 		579
	R		
	Me	(93)	
	Bn	(97)	
R^7 = OMe	DMF, $POCl_3$	R^3 = CHO (92)	630
C_{11}			
R^7 = Pr	DMF, $POCl_3$	R^3 = CHO (71)	631
C_{12}			
R^7 = CH=CHCO$_2$Me	DMF, $POCl_3$	R^3 = CHO (96)	623
C_{13}			
R^7 = C_5H_{11}	DMF, $POCl_3$	R^3 = CHO (56)	631

TABLE XIV. INDOLES (*Continued*)

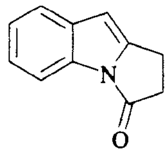
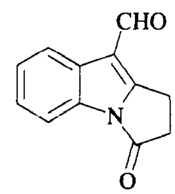
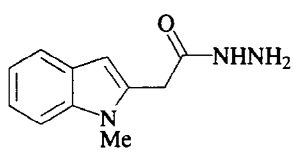
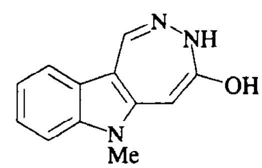
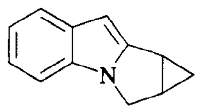
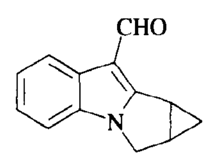
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C. Disubstituted Indoles		
	C1. R^1, R^2 Substituents		
C_{10}			
$R^1 = R^2 = Me$	MFA, $POCl_3$	$R^3 = CHO$ (—)	601
	DMF, $(Cl_2PO)_2O$	$R^3 = CHO$ (95)	26
	1. DMF, $POCl_3$ 2, NaSH	$R^3 = CHS$ (89)	632
	$PhNHCO(C_6H_4Cl\text{-}4)$, $POCl_3$	$R^3 = CO(C_6H_4Cl\text{-}4)$ (—)	633
C_{11}			
	—		634
$R^1 = OH$, $R^2 = CO_2Et$	DMF, $POCl_3$	$R^1 = H$, $R^3 = Cl$ (51)	635
	DMF, $POCl_3$	 (90)	636
C_{12}			
	MFA, $POCl_3$	 (91)	637, 638

TABLE XIV. INDOLES (*Continued*)

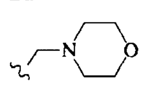
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{13}			
$R^1 = Me$, $R^2 = CH_2CO_2Et$	DMF, $POCl_3$	$R^3 = CHO$ (85)	636, 639
	DMA, $POCl_3$	$R^3 = COMe$ (75)	639
	Me_2NCOPh, $POCl_3$	$R^3 = COPh$ (85)	639
	$Me_2NCO(C_6H_4Cl\text{-}4)$, $POCl_3$	$R^3 = CO(C_6H_4Cl\text{-}4)$ (65)	639
C_{15}			
$R^1 = Me$, $R^2 = Ph$	MFA, $POCl_3$	$R^3 = CHO$ (—)	601
	DMF, $(Cl_2PO)_2O$	$R^3 = CHO$ (94)	26
	$PhNHCO(C_6H_4Cl\text{-}4)$, $POCl_3$	$R^3 = CO(C_6H_4Cl\text{-}4)$ (—)	633
$C_{15\text{-}16}$			
$R^1 = Me$, $R^2 = C{\equiv}CR$	—	$R^3 = CHO$	640
R			
Bu		(—)	
		(—)	
C_{20}			
$R^1 = Ar$, $R^2 = Ph$	DMF, $POCl_3$	$R^3 = CHO$	584
Ar			
$2\text{-}O_2NC_6H_4$		(68)	
$3\text{-}O_2NC_6H_4$		(95)	
$4\text{-}O_2NC_6H_4$		(98)	
C_{23}			
$R^1 = Bn$, $R^2 = NHCO_2Bn$	DMF, $POCl_3$	$R^3 = CHO$ (66) + $R^2 = N{=}CHNMe_2$, $R^3 = CHO$ (15)	594
	C2. R^1, R^3, Substituents		
C_{10}			
$R^1 = R^3 = Me$	DMF, $(Cl_2PO)_2O$	$R^2 = CHO$ (87)	26

TABLE XIV. INDOLES (*Continued*)

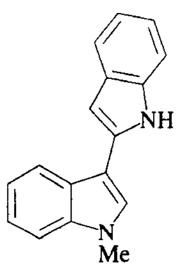
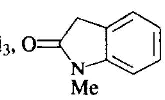
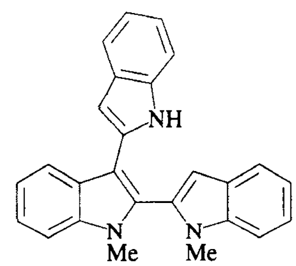
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
$R^1 = CH_2CH{=}CH_2$, R^3 = Me	DMF, $POCl_3$	R^2 = CHO (88)	107
C_{13}			
$R^1 = CH_2CH{=}CMe_2$, R^3 = Me	DMF, $POCl_3$	R^2 = CHO (88)	107
C_{15}			
R^1 = Me, $R^3 = 4\text{-}FC_6H_4$	DMF, $POCl_3$	R^2 = CHO (86)	108
C_{17}			
R^1 = *i*-Pr, $R^3 = 4\text{-}FC_6H_4$	DMF, $POCl_3$, 100°, 5 h	R^2 = CHO (50-56)	108
	DMF, $POCl_3$, 80°, 18 h	R^2 = CHO (39) + R^5 = CHO (14) + R^7 = CHO (7)	108
	PhN(Me)CH=CHCHO, $POCl_3$	R^2 = CH=CHCHO (83)	641
	$POCl_3$, 	 (80)	581
C3. R^1, R^6, Substituents			
C_9			
R^1 = Me, $R^6 = NO_2$	MFA, $POCl_3$	R^3 = CHO (—)	601
C4. R^2, R^3, Substituents			
C_{10}			
$R^2 = R^3$ = Me	Et_2NCHO, $POCl_3$	R^1 = CHO (—)	642
	DMF, $POCl_3$	R^1 = CHO (52)	104
	DMA, $POCl_3$	R^1 = COMe + R^6 = COMe (—) 97:3	103

TABLE XIV. INDOLES (*Continued*)

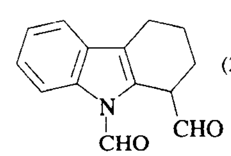
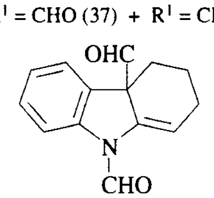
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
$R^2 + R^3 = (CH_2)_4$	Et_2NCHO, $POCl_3$	R^1 = CHO (—)	642
	DMF, $(Cl_2PO)_2O$	R^1 = CHO (17) +  (21)	26
	DMF, $POCl_3$	R^1 = CHO (37) + R^1 = CHO, R^7 = CHO (37) +  (18)	643
	DMA, $POCl_3$	R^1 = COMe + R^7 = COMe (—) 95:5	103
C5. R^2, R^5, Substituents			
C_9			
R^2 = Me, R^5 = Br	DMF, $POCl_3$	R^3 = CHO (75)	590
C_{10}			
$R^2 = CON_3$, R^5 = OMe	DMF, $POCl_3$	R^3 = CHO (80)	644
R^2 = Me, R^5 = OMe	DMF, $POCl_3$	R^3 = CHO (76)	646, 645
C_{11}			
$R^2 = CO_2Et$, R^5 = Br	MFA, $POCl_3$	R^3 = CHO (67)	617
$R^2 = CO_2Et$, R^5 = OH	DMF, $POCl_3$	R^3 = CHO (80)	647
	DMF, $POCl_3$, 120°	R^3 = CHO (77)	648
	DMF, $POCl_3$, 35°	R^5 = OCHO (77)	648
	MFA, $POCl_3$	$R^3 = R^4$ = CHO (3)	648

TABLE XIV. INDOLES (*Continued*)

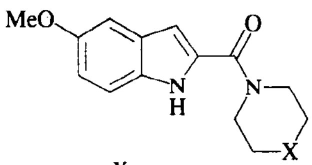
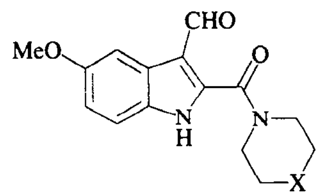
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12}			
$R^2 = CO_2Et$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (80)	647
$R^2 = CONMe_2$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (77)	649
C_{13}			
$R^2 = CO_2Et$, $R^5 = OEt$	DMF, $POCl_3$	$R^3 = CHO$ (85)	647
C_{14}			
$R^2 = 4\text{-}FC_6H_4$, $R^5 = F$	DMF, $POCl_3$	$R^3 = CHO$ (63)	600
$R^2 = CONEt_2$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (83)	649
$C_{14\text{-}15}$			
	DMF, $POCl_3$		649
X			
O		(52)	
CH_2		(96)	
NMe		(65)	
C_{15}			
$R^2 = CONH(CH_2)_3NMe_2$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (66)	649
C_{16}			
$R^2 = NHCO_2Bn$, $R^5 = Cl$	DMF, $POCl_3$	$R^3 = CHO$ (41)	594
C_{17}			
$R^2 = NHCO_2Bn$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (45)	594

TABLE XIV. INDOLES (*Continued*)

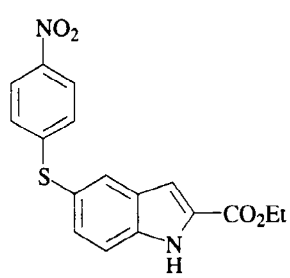
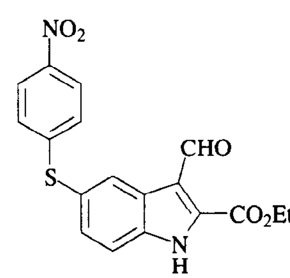
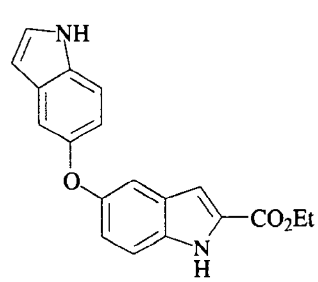
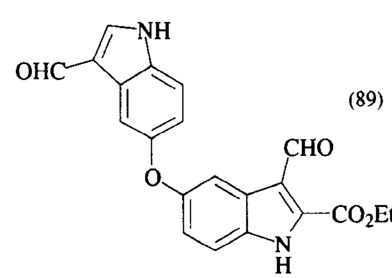
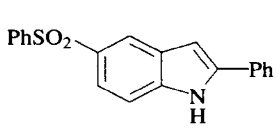
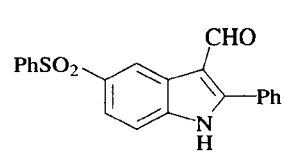
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	—	 (—)	650
C_{18}			
$R^2 = CO_2Et$, $R^5 = OBn$	DMF, $POCl_3$	$R^3 = CHO$ (95)	647
	MFA, $POCl_3$	$R^3 = CHO$ (96)	651
C_{19}			
	DMF, $POCl_3$	 (89)	625
C_{20}			
	—	 (—)	652

TABLE XIV. INDOLES (*Continued*)

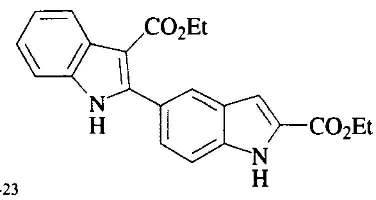
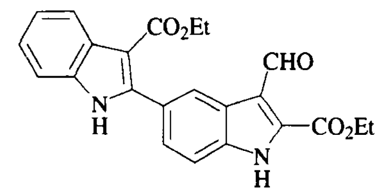
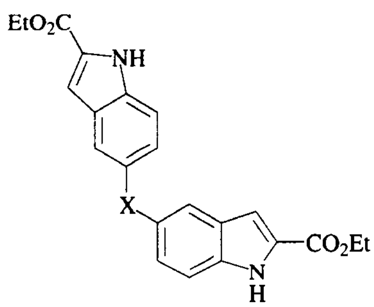
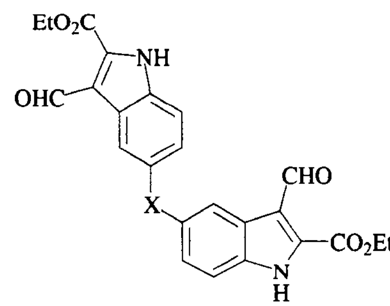
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{22}			
	DMF, $POCl_3$	 (22)	653
C_{22-23}			
	DMF, $POCl_3$		
X			
SO_2		(68)	626
CH_2		(85)	654
	C6. R^2, R^6 Substituents		
C_9			
R^2 = Me, R^6 = Br	DMF, $POCl_3$	R^3 = CHO (88)	629
C_{10}			
R^2 = Me, R^6 = OMe	DMF, $POCl_3$	R^3 = CHO (84)	655, 656
C_{14}			
R^2 = 4-FC_6H_4, R^6 = F	DMF, $POCl_3$	R^3 = CHO (59)	600

TABLE XIV. INDOLES (*Continued*)

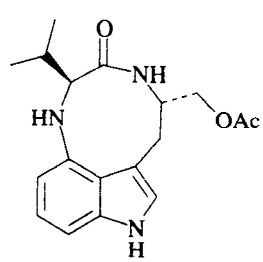
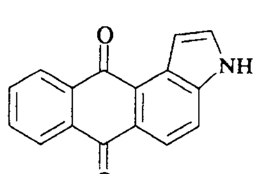
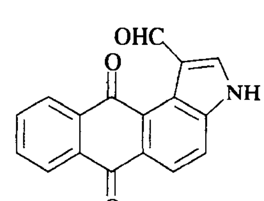
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C7. R^3, R^4 Substituents		
C_{19}			
	DMF, $POCl_3$	R^7 = CHO (65)	657
	MFA, $POCl_3$	R^7 = CHO (--)	657
	PhN(Me)CH=CHCHO, $POCl_3$	R^5 = CH=CHCHO (35) + R^7 = CH=CHCHO (6)	657
	C8. R^4, R^5 Substituents		
C_{10}			
R^4 + R^5 = $O(CH_2)_2O$	DMF, $POCl_3$	R^3 = CHO (60)	658
C_{16}			
	DMF, $POCl_3$	 (71)	659
	C9. R^4, R^6 Substituents		
C_{10}			
R^4 = R^6 = OMe	DMF, $POCl_3$	R^7 = CHO (56)	109

TABLE XIV. INDOLES (*Continued*)

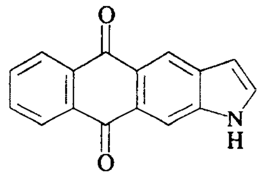
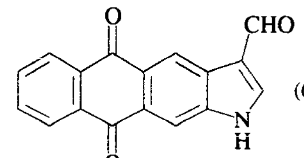
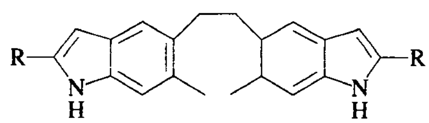
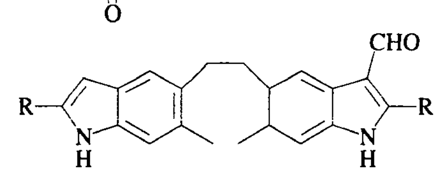
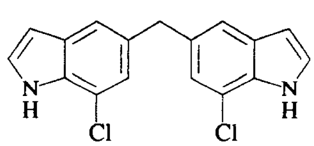
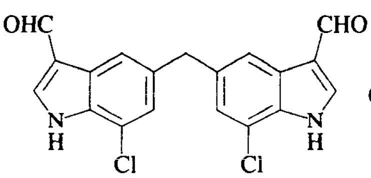
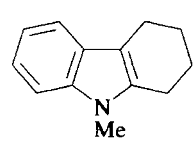
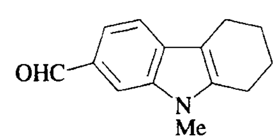
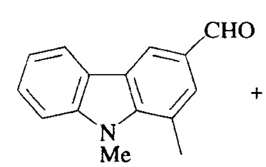
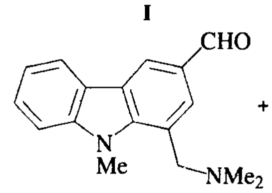
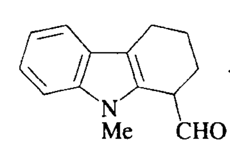
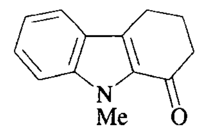
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C10. R^5, R^6 Substituents	
C_{16} 	DMF, $POCl_3$	 (68)	659
C_{24}  R = CO_2Et	DMF, $POCl_3$	 (75)	627
		C11. R^5, R^7 Substituents	
C_{15} R^5 = Br, R^7 = OTs	DMF, $POCl_3$	R^3 = CHO (—)	660
C_{17} 	DMF, $POCl_3$	 (95)	257
		C12. R^6, R^7 Substituents	
C_8 R^6 = Br, R^7 = I	DMF, $POCl_3$	R^3 = CHO (94)	629

TABLE XIV. INDOLES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		D. Trisubstituted Indoles	
		D1. R^1, R^2, R^3 Substituents	
C_{13} 		 I +  II +  III +  IV +  V	

Reagents	I	II	III	IV	V	Refs.
Et_2NCHO, $POCl_3$		(27)			(2)	661, 642
DMF (1 eq), $POCl_3$ (xs) 100°	(42)					110
DMF (xs), $POCl_3$ (2 eq) 100°		(50)				110
DMF (xs), $POCl_3$ (2 eq) rt, 6 h				(89)		110
DMF, $(Cl_2PO)_2O$ (1 eq), 80°		(17)	(11)			26
DMF, $(Cl_2PO)_2O$ (1.8 eq), 80°		(21)	(25)			26
DMF, $(Cl_2PO)_2O$ (xs), 0°				(96)		26

TABLE XIV. INDOLES (*Continued*)

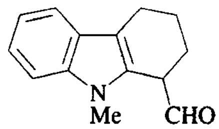
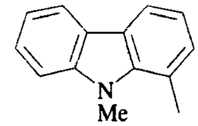
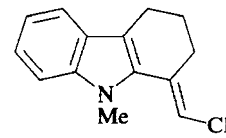
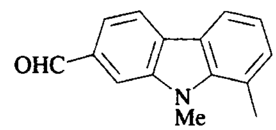
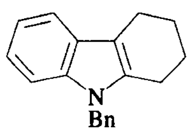
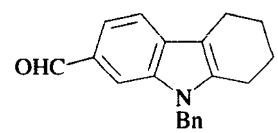
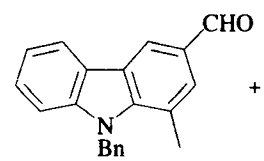
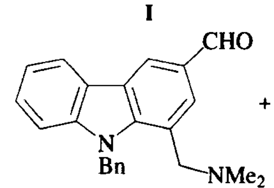
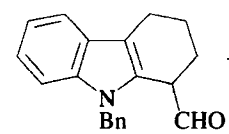
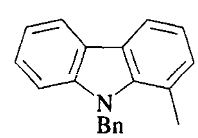
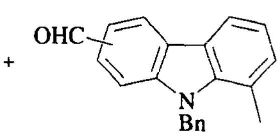
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{14} 	DMF (xs), $POCl_3$ (3 eq), rt, 3 h	 (73)	110
	DMF (xs), $POCl_3$ (3 eq), rt, 20 min	 (85)	110
	DMF (xs), $POCl_3$ (3 eq), 100°, 3 h	 (50)	110
C_{19} 		 I +  II +  III +  IV +	

TABLE XIV. INDOLES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 V +  VI	

Reagents	I	II	III	IV	V	VI	Refs.
DMF, $POCl_3$ (1 eq), 120°	(5)	(18)	(8)	(3)			662, 663
DMF, $POCl_3$ (3 eq), 120°		(38)	(26)		(1)		662
DMF, $POCl_3$ (3 eq), 0°				(90)			662, 663
N-Formylpyrrolidine, $POCl_3$, 0°				(81)			664
N-Formylpyrrolidine, $POCl_3$, 120°		(37)	(21)	(5)			664
Et_2NCHO, $POCl_3$, 0°				(57)			664, 642
Et_2NCHO, $POCl_3$, 120°		(26)	(6)	(25)		(15)	664
MFA, $POCl_3$, rt				(4)		(6)	664
MFA, $POCl_3$, 100°						(83)	664
i-Pr_2NCHO, $POCl_3$, 120°						(77)	664

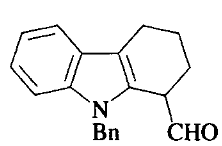
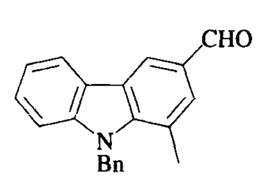
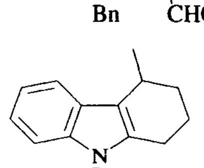
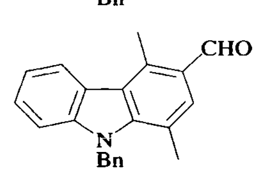
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{20} 	DMF, $POCl_3$ (1.2 eq)	 (60)	662
	DMF, $POCl_3$ (2.6 eq), 100°	 (38) +	662

TABLE XIV. INDOLES (*Continued*)

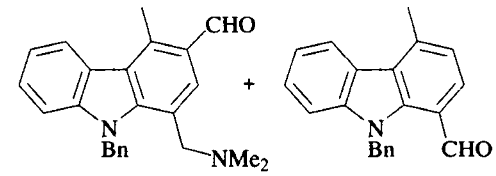
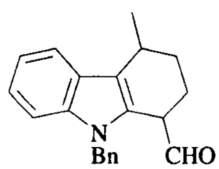
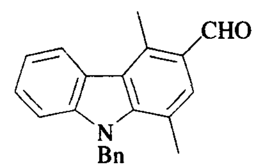
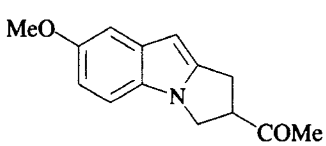
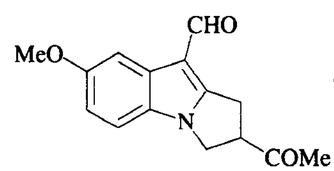
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 (15) I (9)	
	DMF, $POCl_3$ (2.6 eq), 0°	I (88)	662
C_{21} 	DMF, $POCl_3$ (1.2 eq)	 (44)	662
D2. R^1, R^2, R^5 Substituents			
C_{11} $R^1 = R^2 = Me$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (69)	645
C_{12} $R^1 = R^2 = Me$, $R^5 = OAc$	DMF, $POCl_3$	$R^3 = CHO$ (68)	645, 665
C_{14} 	—	 (—)	666

TABLE XIV. INDOLES (*Continued*)

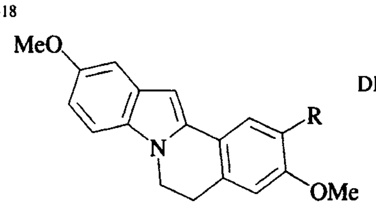
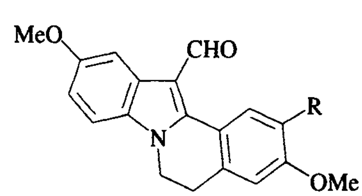
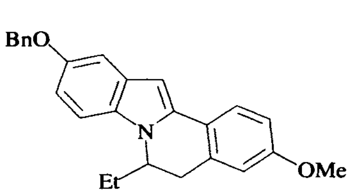
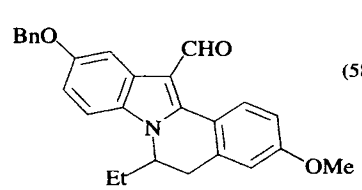
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{15} $R^1 + R^2 = (CH_2)_3CHOAc$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (66)	667
C_{16} $R^1 = Ph$, $R^2 = Me$, $R^5 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (81)	645
C_{17} $R^1 = Ph$, $R^2 = Me$, $R^5 = OAc$	DMF, $POCl_3$	$R^3 = CHO$ (81)	645, 665
C_{17-18} 	DMF, $POCl_3$		668
R: H		(70-90)	
R: OMe		(70-90)	
C_{18} $R^1 + R^2 = (CH_2)_2CO$, $R^5 = OBn$	—	$R^3 = CHO$ (17)	669
$R^1 = Bn$, $R^2 = Me$, $R^5 = OAc$	DMF, $POCl_3$	$R^3 = CHO$ (47)	665
C_{26} 	DMF, $POCl_3$	 (58)	670

TABLE XIV. INDOLES (*Continued*)

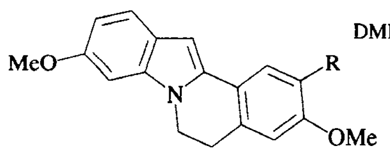
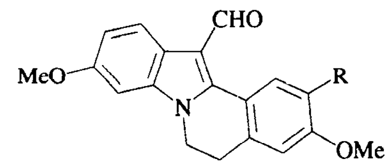
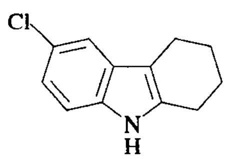
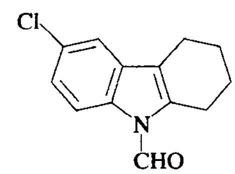
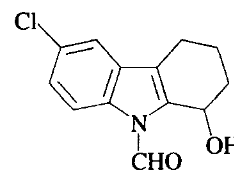
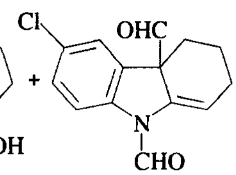
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		D3. R^1, R^2, R^6 Substituents	
$C_{17\text{-}18}$			
	DMF, $POCl_3$		669
R			
H		(70-90)	
OMe		(70-90)	
		D4. R^2, R^3, R^5 Substituents	
C_{12}			
	DMF, $POCl_3$	 (1.5) +  (15) +  (45)	643
C_{13}			
R^2 = Me, R^3 = CO_2Et, R^5 = OMe	DMF, $POCl_3$	R^6 = CHO (34)	645

TABLE XIV. INDOLES (*Continued*)

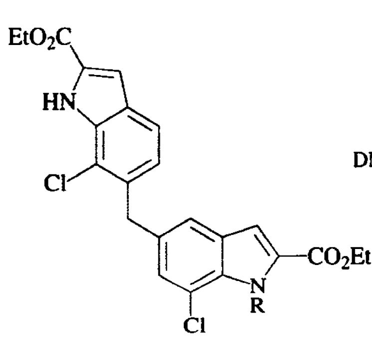
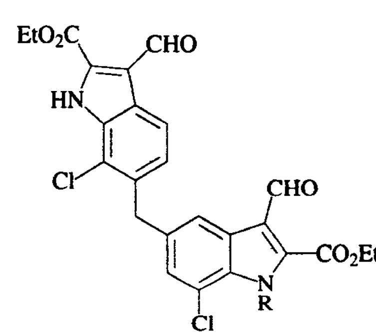
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{14}			
R^2 + R^3 = $C(Me)_2(CH_2)_3$, R^5 = Cl	DMF, $POCl_3$	R^1 = CHO (10) + R^4 = CHO (5) + R^6 = CHO (60)	643
C_{21}			
R^2 = R^3 = Ph, R^5 = Me	DMF, $POCl_3$	R^6 = CHO (90)	671
R^2 = R^3 = Ph, R^5 = OMe	—	R^6 = CHO (—)	672
		D5. R^2, R^4, R^6 Substituents	
$C_{11\text{-}16}$			
R^2 = R, R^4 = R^6 = OMe			
R			
Me	DMF, $POCl_3$	R^3 = CHO (90) + R^7 = CHO (2)	109
4-BrC_6H_4	DMF, $POCl_3$	R^3 = CHO (33) + R^7 = CHO (35)	109
Ph	DMF, $POCl_3$	R^3 = CHO (38) + R^7 = CHO (36)	109
	DMF, $POCl_3$		257
R			
H		(90)	
Et		(40)	

TABLE XIV. INDOLES (*Continued*)

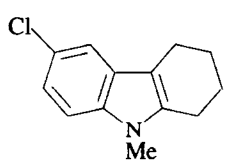
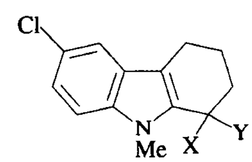
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	D6. R^2, R^5, R^6 Substituents		
C_{11}			
$R^2 = CONHNH_2$, $R^5 = R^6 = OMe$	DMF, $POCl_3$	$R^2 + R^3 = CONHN{=}CH$ (80-85)	673
C_{12}			
$R^2 = CO_2Me$, $R^5 = R^6 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (52)	674
C_{13}			
$R^2 = CO_2Et$, $R^5 = R^6 = OMe$	DMF, $POCl_3$	$R^3 = CHO$ (85)	673
	D7. R^3, R^4, R^5 Substituents		
C_{11}			
$R^3 = Me$, $R^4 = R^5 = OMe$	DMF, $POCl_3$	$R^2 = CHO$ (44) + $R^7 = CHO$ (46)	109
	$Me_2NCO(C_6H_4Cl\text{-}4)$	$R^2 = CO(C_6H_4Cl\text{-}4)$ (—) + $R^7 = CO(C_6H_4Cl\text{-}4)$ (—)	675
	D8. R^4, R^5, R^6 Substituents		
C_8			
$R^4 = R^5 = R^6 = Br$	DMF, $POCl_3$	$R^3 = CHO$ (86)	676
	D9. R^5, R^6, R^7 Substituents		
C_8			
$R^5 = R^6 = R^7 = Br$	DMF, $POCl_3$	$R^3 = CHO$ (87)	676
	E. Tetrasubstituted Indoles		
	E1. R^1, R^2, R^3, R^5 Substituents		
C_{13}			
	DMF, $POCl_3$ (3 eq), 70°	 X, Y = O (10) + X = Y = CHO (65) + X = OH, Y = CHO (12)	661

TABLE XIV. INDOLES (*Continued*)

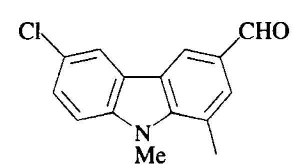
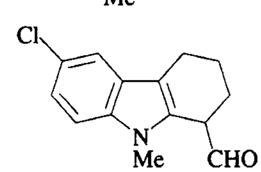
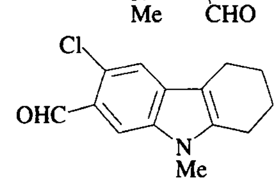
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$ (1.3 eq), 100°	 (2-8) +  (2-21) +  (2)	661
C_{14}			
$R^1 = R^2 = Me$, $R^3 = CO_2Et$, $R^5 = OMe$	DMF, $POCl_3$	$R^6 = CHO$ (34)	645
C_{19}			
$R^1 = Ph$, $R^2 = Me$, $R^3 = CO_2Et$, $R^5 = OMe$	DMF, $POCl_3$	$R^6 = CHO$ (16)	645
C_{20}			
$R^1 = Bn$, $R^2 = Me$, $R^3 = CO_2Et$, $R^5 = OMe$	DMF, $POCl_3$	$R^6 = CHO$ (10)	645

TABLE XIV. INDOLES (*Continued*)

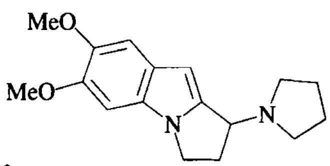
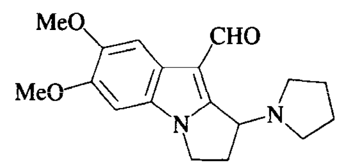
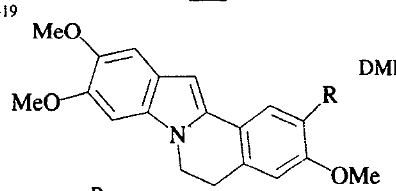
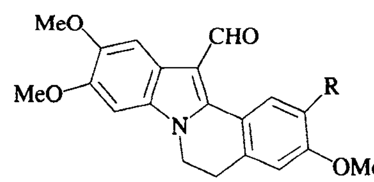
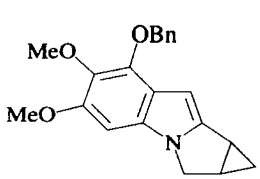
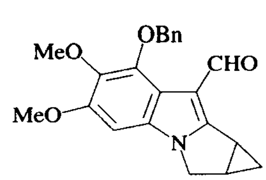
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		E2. R^1, R^2, R^5, R^6 Substituents	
C_{13}			
$R^1 = R^2 = CO(CH_2)_2$, R^5 = OMe, R^6 = Me	DMF, $POCl_3$	R^3 = CHO (96)	677
$R^1 = R^2 = (CH_2)_3$, R^5 = OMe, R^6 = Me	MFA, $POCl_3$	R^3 = CHO (92)	678
R^1 = Me, $R^2 = CH_2OAc$, $R^5 = R^6$ = OMe	DMF, $POCl_3$	R^3 = CHO (66)	679
C_{15}			
$R^1 = (CH_2)_2CN$, $R^2 = CO_2Me$, R^5 = OMe, R^6 = Me	DMF, $POCl_3$	R^3 = CHO (90)	674
$R^1 + R^2 = (CH_2)_2CHOAc$, R^5 = OMe, R^6 = Me	DMF, $POCl_3$	R^3 = CHO (98)	680
$R^1 + R^2 = (CH_2)_2CHOAc$, $R^5 = R^6$ = OMe	—	R^3 = CHO (84)	681
C_{17} 	DMF, $POCl_3$	 (41)	682
C_{18-19} 	DMF, $POCl_3$		669
R			
H		(70-90)	
OMe		(70-90)	

TABLE XIV. INDOLES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		E3. R^2, R^3, R^4, R^6 Substituents	
C_{12}			
$R^2 = R^3 = R^4 = R^6$ = OMe	DMF, $POCl_3$	R^7 = CHO (64)	109
C_{14}			
$R^2 = R^3 = CO_2Me$, $R^4 = R^6$ = OMe	DMF, $POCl_3$	R^7 = CHO (70)	109
C_{20}			
$R^2 = R^3$ = 2-pyridyl, $R^4 = R^6$ = OMe	DMF, $POCl_3$	R^7 = CHO (62)	109
		E4. R^2, R^3, R^5, R^6 Substituents	
C_{12}			
R^2 = Me, $R^3 = CO_2Et$, R^5 = OH, R^6 = Br	DMF, $POCl_3$	R^4 = CHO (70)	155
C_{13}			
R^2 = Me, $R^3 = CO_2Et$, R^5 = OH, R^6 = Me	DMF, $POCl_3$	R^4 = CHO (40)	155
		E5. R^4, R^5, R^6, R^7 Substituents	
C_8			
$R^4 = R^5 = R^6 = R^7$ = F	DMF, $POCl_3$	R^3 = CHO (89)	683
		F. Pentasubstituted Indoles	
		F1. R^1, R^2, R^4, R^5, R^6 Substituents	
C_{20} 	DMF, $POCl_3$	 (63)	684, 685

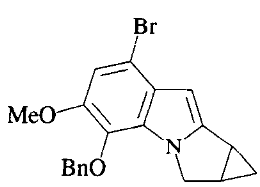
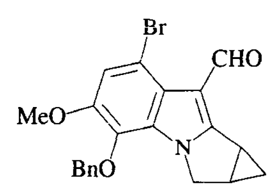
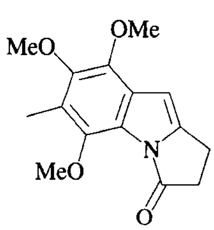
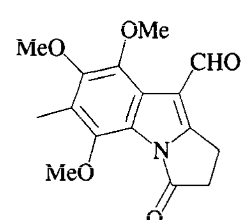
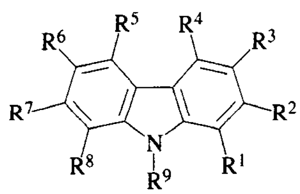
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	F2. R^1, R^2, R^4, R^6, R^7 Substituents		
C_{19} 	DMF, $POCl_3$	 (73)	638, 673
	G. Hexasubstituted Indoles		
	G1. R^1, R^2, R^4, R^5, R^6, R^7 Substituents		
C_{15} 	DMF, $POCl_3$	 (80)	686

TABLE XV. CARBAZOLES



R^1 - R^9 = H except as indicated.

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	A. Carbazole		
C_{12}			
	Me_2NCOPh, $POCl_3$	R^9 = COPh (80)	111
	B. Monosubstituted Carbazoles		
	B1. R^1 Substituents		
C_{12}			
R^1 = Me	MFA, $POCl_3$	R^3 = CHO (33) + R^6 = CHO (36)	112
	B2. R^2 Substituents		
C_{12}			
R^2 = OH	DMF, $POCl_3$	R^1 = R^3 = CHO (30)	687
	B3. R^9 Substituents		
C_{13-19}			
R^9 = Me	MFA, $POCl_3$	R^3 = CHO (81)	112, 113
	DMF, $POCl_3$	R^3 = CHO (60)	688, 689
	MFA, $POCl_3$	R^3 = CHO (87)	690
	MFA, $POCl_3$	R^3 = CHO (—) + R^3 = R^6 = CHO (31)	691
	MFA, $POCl_3$	R^3 = CHO (81)	113
	MFA, $POCl_3$	R^3 = CHO (85)	113
	MFA, $POCl_3$	R^3 = CHO (86)	664
	DMF, $POCl_3$	R^3 = CHO (63)	692
	Et_2NCHO, $POCl_3$	R^3 = CHO (25-32)	664
	i-Pr_2NCHO, $POCl_3$	R^3 = CHO (25-32)	664
	N-Formylpyrrolidine, $POCl_3$	R^3 = CHO (25-32)	664

TABLE XV. CARBAZOLES (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C. Disubstituted Carbazoles		
	C1. R^1, R^4 Substituents		
C_{14}			
$R^1 = R^4 = Me$	MFA, $POCl_3$	$R^3 = CHO$ (44)	112, 693-695
	MFA, $POCl_3$ (xs)	$R^3 = CHO$ (42)	695
	C2. R^1, R^6 Substituents		
C_{13}			
$R^1 = OH$, $R^6 = Me$	MFA, $POCl_3$	$R^2 = CHO$ (12)	114
	C3. R^1, R^7 Substituents		
C_{13}			
$R^1 = OH$, $R^7 = Me$	MFA, $POCl_3$	$R^2 = CHO$ (10)	114
	C4. R^1, R^8 Substituents		
C_{13}			
$R^1 = OH$, $R^8 = Me$	MFA, $POCl_3$	$R^2 = CHO$ (18)	114
	C5. R^1, R^9 Substituents		
C_{14}			
$R^1 = R^9 = Me$	DMF, $POCl_3$	$R^3 = CHO$ (74)	110
C_{20}			
$R^1 = Me$, $R^9 = Bn$	DMF, $POCl_3$	$R^3 = CHO$ (42) + $R^6 = CHO$ (28)	662, 663
	C6. R^2, R^6 Substituents		
C_{13}			
$R^2 = OH$, $R^6 = Me$	MFA, $POCl_3$	$R^3 = CHO$ (18)	114
	C7. R^2, R^7 Substituents		
C_{13}			
$R^2 = OH$, $R^7 = Me$	MFA, $POCl_3$	$R^3 = CHO$ (10) + $R^9 = CHO$ (53)	114

TABLE XV. CARBAZOLES (*Continued*)

Substrate		Reagents	Product(s) and Yield(s) (%)	Refs.
		C8. R^2, R^8 Substituents		
C_{13}				
$R^2 = OH$, $R^8 = Me$		MFA, $POCl_3$	$R^3 = CHO$ (12)	114
		C9. R^3, R^9 Substituents		
C_{14-18}				
R^3	R^9			
Me	Me	MFA, $POCl_3$	$R^6 = CHO$ (—)	113
Me	Et	MFA, $POCl_3$	$R^6 = CHO$ (60)	690
Me	*n*-Bu	MFA, $POCl_3$	$R^6 = CHO$ (85)	113
Me	*i*-C_5H_{11}	MFA, $POCl_3$	$R^6 = CHO$ (—)	113
		D. Trisubstituted Carbazoles		
		D1. R^1, R^4, R^6 Substituents		
C_{15}				
$R^1 = R^4 = R^6 = Me$		MFA, $POCl_3$	$R^3 = CHO$ (29)	695
$R^1 = R^4 = Me$, $R^6 = OMe$		MFA, $POCl_3$	$R^3 = CHO$ (60)	693
C_{17}				
$R^1 = R^4 = Me$, $R^6 = NMe_2$		—	$R^6 = CHO$ (—)	696
		DMF, $POCl_3$, 0°	$R^9 = CHO$ (29)	692
		DMF, $POCl_3$, 100°	$R^3 = CHO$ (9) + $R^5 = CHO$ (3)	692
		D2. R^1, R^4, R^7 Substituents		
C_{15}				
$R^1 = R^4 = R^7 = Me$		MFA, $POCl_3$	$R^3 = CHO$ (71)	693
$R^1 = R^4 = Me$, $R^7 = OMe$		MFA, $POCl_3$	$R^6 = CHO$ (13) + $R^8 = CHO$ (3)	693
		D3. R^1, R^4, R^9 Substituents		
C_{15}				
$R^1 = R^4 = R^9 = Me$		MFA, $POCl_3$	$R^3 = CHO$ (19) + $R^6 = CHO$ (4)	693
C_{21}				
$R^1 = R^4 = Me$, $R^9 = Bn$		DMF, $POCl_3$	$R^3 = CHO$ (66) + $R^6 = CHO$ (14)	662, 692

TABLE XV. CARBAZOLES (*Continued*)

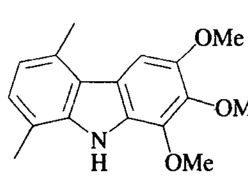
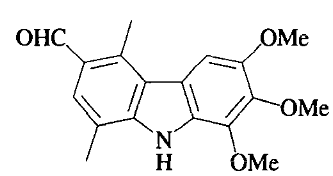
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		E. Tetrasubstituted Carbazoles	
		E1. R^1, R^4, R^6, R^7 Substituents	
C_{15}			
$R^1 = R^4 = Me$, $R^6 + R^7 = OCH_2O$	MFA, $POCl_3$	$R^3 = CHO$ (50)	112
		E2. R^1, R^4, R^6, R^9 Substituents	
C_{16}			
$R^1 = R^4 = R^9 = Me$, $R^6 =$ OMe	MFA, $POCl_3$	$R^3 = CHO$ (68)	693
C_{23} $R^1 = R^4 = Me$, $R^6 = NMe_2$, $R^9 = Bn$	DMF, $POCl_3$	$R^3 = R^5 = CHO$ (3) + $R^5 = CHO$ (7)	692
		F. Pentasubstituted Carbazoles	
		F1. R^1, R^2, R^3, R^5, R^8 Substituents	
C_{17}			
	MFA, $POCl_3$	 (100)	697

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING

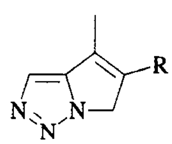
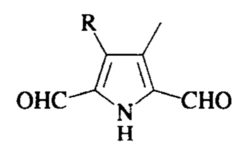
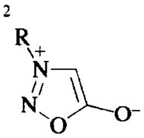
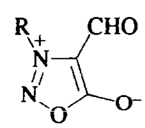
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_2N_3 **1,2,3-Triazoles**		
C_{6-7} 	DMF, $COCl_2$		698
R			
H		(35)	
Me		(30)	
	C_2N_2O **1,2,3-Oxadiazolium-5-olates (Sydnones)**		
C_{3-12} 			
R			
Me	MFA, $POCl_3$	(77)	699
4-ClC_6H_4	DMF, $POCl_3$	(34)	127
	MFA, $POCl_3$	(20)	700
4-BrC_6H_4	DMF, $POCl_3$	(40)	127
Ph	DMF, $POCl_3$	(46)	127
	MFA, $POCl_3$	(55)	701, 700
C_6H_{11}	DMF, $POCl_3$	(69)	702
2-MeC_6H_4	DMF, $POCl_3$	(30)	127
4-MeC_6H_4	DMF, $POCl_3$	(61)	127
4-$MeOC_6H_4$	DMF, $POCl_3$	(76)	127
	MFA, $POCl_3$	(81)	699, 700
Bn	MFA, $POCl_3$	(15)	701
4-$EtOC_6H_4$	MFA, $POCl_3$	(52)	700

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

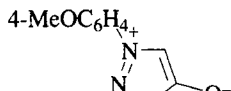
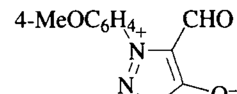
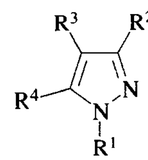
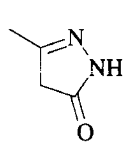
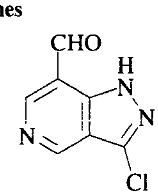
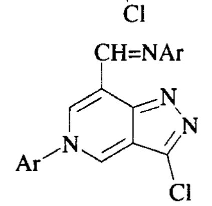
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_2N_2S **1,2,3-Thiadiazolium-5-olates**		
C_9 	DMF, $POCl_3$	 (92)	703
	C_3N_2 **Pyrazoles** 		
R^1 - R^4 = H except as indicated		R^1 - R^4 = as in substrate except as indicated	
C_{5-24}			
$R^1 = R^2$ = Me	DMF, $POCl_3$	R^3 = CHO (58)	115
$R^1 = R^4$ = Me	DMF, $POCl_3$	R^3 = CHO (57)	115
R^1 = 3-$O_2NC_6H_4$	DMF, $POCl_3$	R^3 = CHO (9)	704
R^1 = 4-ClC_6H_4, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (70)	116
	N-Formylpiperidine, $POCl_3$	R^2 = CHO, R^4 = N=CH(*N*-piperidyl) (76)	116
R^1 = 4-$O_2NC_6H_4$, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (92)	116
R^1 = Ph, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (84)	116
	N-Formylpiperidine, $POCl_3$	R^2 = CHO, R^4 = N=CH(*N*-piperidyl) (96)	116
R^1 = 3-$CF_3C_6H_4$	—	R^3 = CHO (—)	705
R^1 = Me, $R^2 = NH_2$, R^4 = 4-FC_6H_4	DMF, $POCl_3$	R^3 = CHO (35)	706
R^1 = Me, $R^2 = NH_2$, R^4 = 4-ClC_6H_4	DMF, $POCl_3$	R^3 = CHO (60)	706
R^1 = 4-ClC_6H_4, R^3 = Me, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (71)	116
R^1 = 4-$O_2NC_6H_4$, R^3 = Me, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (80)	116
R^1 = Ph, R^2 = Me, $R^4 = NH_2$	DMF, $POCl_3$	R^3 = CHO (64)	707
R^1 = Ph, R^3 = Me, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (70)	116

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$R^1 = R^2$ = Me, R^4 = 2-oxypyridyl	—	R^3 = CHO (—)	708
R^1 = 4-ClC_6H_4, R^3 = Ph, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (94)	116
R^1 = 4-$O_2NC_6H_4$, R^3 = Ph, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (99)	116
$R^1 = R^3$ = Ph, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (83)	116
R^1 = 4-MeC_6H_4, R^3 = Ph, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (91)	116
R^1 = 4-$MeOC_6H_4$, R^3 = Ph, $R^4 = NH_2$	DMF, $POCl_3$	R^2 = CHO, R^4 = N=CHNMe$_2$ (74)	116
$R^1 = R^2$ = Ph, R^4 = 4-(1-phenylpyrazolyl)	DMF, $POCl_3$	R^3 = CHO (83)	704
	Pyrazol-5-ones		
C_4 	1. DMF, $POCl_3$ 2. NH_4Cl	 (80)	709
	1. DMF, $POCl_3$ 2. $ArNH_2$		709

Ar	
2-ClC_6H_4	(80)
4-$O_2NC_6H_4$	(83)
Ph	(85)
2-$MeOC_6H_4$	(91)
2,5-$(MeO)_2C_6H_3$	(87)

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

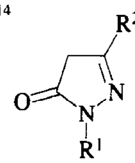
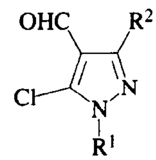
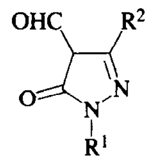
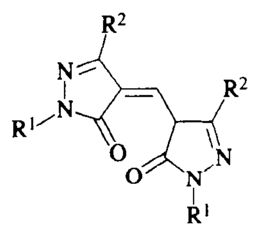
Substrate		Reagents	Product(s) and Yield(s) (%)	Refs.
C_{4-14} 				
R^1	R^2			
Me	H	DMF, $POCl_3$	 **I** (72)	710
Me	Me	DMF, $POCl_3$	**I** (91)	118, 121, 710, 711
		DMF, $POCl_3$, 3 h	 **II** (27)	711
		DMF, $POCl_3$, prolonged standing	 **III** (—)	711

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

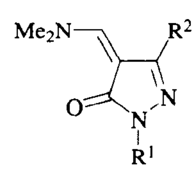
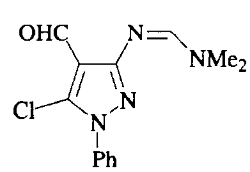
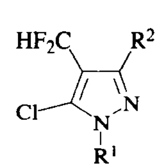
Substrate		Reagents	Product(s) and Yield(s) (%)	R efs.
R^1	R^2			
H	*i*-Pr	DMF, $POCl_3$	**I** (48)	712
Me	*i*-Pr	DMF, $POCl_3$	**I** (87)	710
H	*i*-Bu	DMF, $POCl_3$	**II** (68)	713
H	*t*-Bu	DMF, $POCl_3$	**I** (30)	712
Ph	Cl	DMF, $POCl_3$	 **IV** (76)	711
Ph	H	DMF, $POCl_3$	**IV** (89)	711
H	Ph	DMF, $POCl_3$	**II** (99)	713
Ph	OH	DMF, $POCl_3$	**IV** (82)	711
Ph	NH_2	DMF, $POCl_3$	 (60)	714
2,4-$F_2C_6H_3$	Me	1. — 2. Et_2NSF_3	 (—)	715
2-pyridyl	Me	DMF, $POCl_3$	**I** (77)	121

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

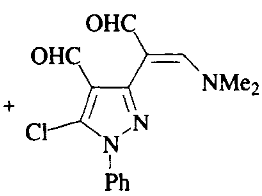
Substrate		Reagents	Product(s) and Yield(s) (%)	Refs.
R^1	R^2			
4-$O_2NC_6H_4$	Me	DMF, $POCl_3$	**I** (30)	121
		DMF, $POCl_3$	**I** (—)	716
Me	4-ClC_6H_4	DMF, $POCl_3$	**I** (77)	710
Me	Ph	DMF, $POCl_3$	**I** (80)	710
		DMF, $POCl_3$	**I** (60)	711
Ph	Me	DMF, $POCl_3$	**I** (94)	121, 716
		DMF, $POCl_3$	**II** (86)	713
		DMF, $POCl_3$	**II** (—) + **III** (—)	717
		DMF, $POCl_3$	**I** (6) + **IV** (22-48)	718
		DMF, $POCl_3$	**I** (—) +  (51)	719
		DMF, $POCl_3$	**IV** (78)	119, 720, 721
4-MeC_6H_4	Me	DMF, $POCl_3$	**IV** (—)	721
Me	4-$MeOC_6H_4$	DMF, $POCl_3$	**I** (82)	710
Ph	NMe_2	DMF, $POCl_3$	**IV** (72)	119
Ph	CO_2Et	DMF, $POCl_3$	**IV** (76)	119, 721
Ph	*i*-Bu	DMF, $POCl_3$	**II** (90)	713
Ph	*t*-Bu	DMF, $POCl_3$	**I** (79)	184
Ph	3-pyridyl	DMF, $POCl_3$	**II** (43)	722, 723
Ph	Ph	DMF, $POCl_3$	**I** (60)	724, 725
		DMF, $POCl_3$	**II** (72)	713
Ph	$NH(C_6H_4Cl$-4)	DMF, $POCl_3$	**IV** (84)	726
Ph	4-$MeOC_6H_4$	DMF, $POCl_3$	**IV** (—)	721

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

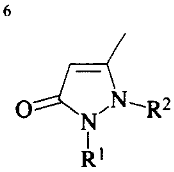
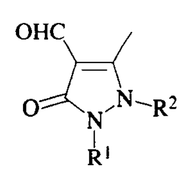
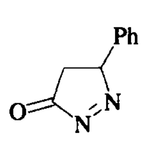
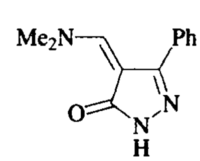
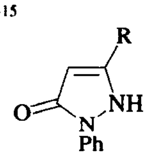
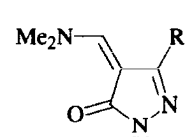
Substrate		Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{6\text{-}16}$ 				
R^1	R^2			
Me	Me	DMF, $POCl_3$	(40)	117
Me	Ph	DMF, $POCl_3$	(52)	727
Ph	Me	DMF, $POCl_3$	(80)	729, 728
		MFA, $POCl_3$	(53)	728
Ph	Ph	DMF, $POCl_3$	(—)	730
C_9 		DMF, $POCl_3$	 (42)	731
$C_{10\text{-}15}$ 		DMF, $POCl_3$		732
R				
Me			(70)	
n-Pr			(60)	
Ph			(80)	

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

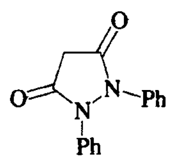
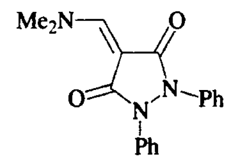
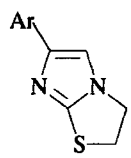
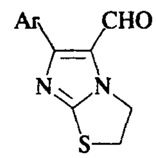
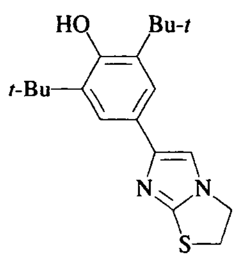
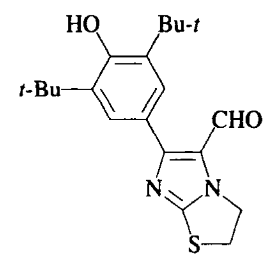
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		Pyrazole-3,5-diones	
C_{15} 	DMF, $POCl_3$	 (—)	731
		Imidazoles	
C_{11-19} 		 I	
Ar			
2,4-$Cl_2C_6H_3$	DMF, $POCl_3$	I (64)	120
4-ClC_6H_4	DMF, $POCl_3$	I (60-80)	733
4-MeC_6H_4	DMF, $POCl_3$	I (60-80)	733
4-PhC_6H_4	DMF, $POCl_3$	I (60-80)	733
	DMF, $POCl_3$	 (62)	733

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

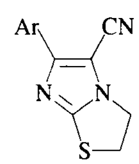
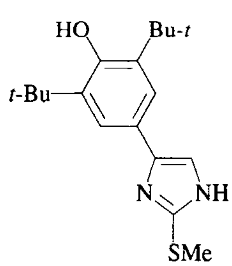
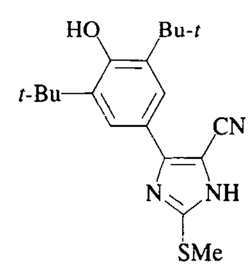
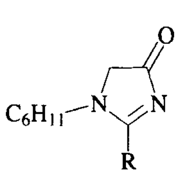
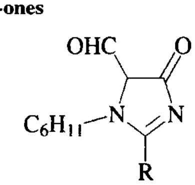
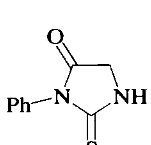
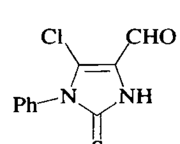
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. NH_2OH 3. Dehydrate	 (15)	734
C_{18} 	1. DMF, $POCl_3$ 2. NH_2OH 3. $SOCl_2$	 (—)	735
		Imidazol-(5*H*)-4-ones	
C_{10-15} 	DMF, $POCl_3$	 R = Me (58) R = Ph (90)	121, 736 121
		Thiohydantoins	
C_9 	DMF, $POCl_3$	 (40)	737

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

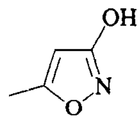
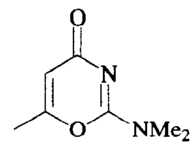
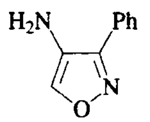
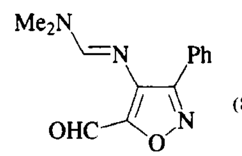
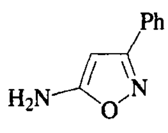
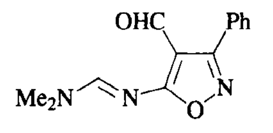
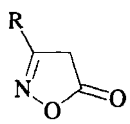
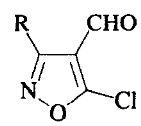
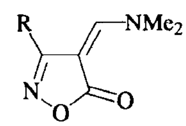
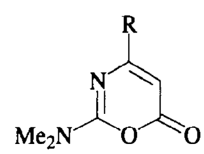
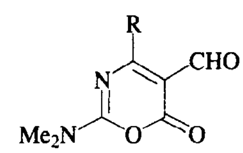
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_3NO **1,2-Oxazoles**	
C_4			
	DMF, $COCl_2$	 (45)	738
C_9			
	DMF, $POCl_3$	 (82)	739
	DMF, $POCl_3$	 (82)	740
		1,2-Oxazol-(4*H*)-5-ones	
C_{4-10}			
		 **I**  **II**  **III**  **IV**	

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

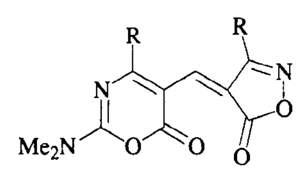
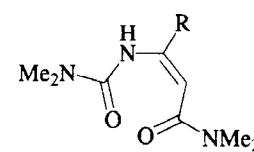
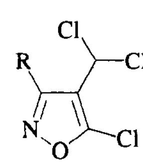
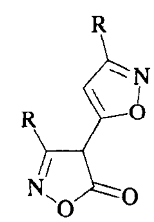
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 **V**  **VI**	
		 **VII**  **VIII**	
R			
Me	DMF, $POCl_3$ (1 eq)	**III** (53) + **IV** (5) + **VI** (9)	122
	DMF, $POCl_3$ (2 eq)	**III** (16) + **IV** (42) + **VI** (6)	122
n-Pr	DMF, $POCl_3$ (1 eq)	**III** (62) + **IV** (6) + **VI** (6)	122
	DMF, $POCl_3$ (2 eq)	**IV** (66) + **V** (11)	122
t-Bu	DMF, $POCl_3$ (1 eq)	**I** (4) + **II** (70)	122
	DMF, $POCl_3$ (2 eq)	**I** (64) + **IV** (17)	122
Ph	DMF, $POCl_3$ (1 eq)	**I** (4) + **II** (50) + **IV** (15)	122
	DMF, $POCl_3$ (1 eq)	**II** (35)	741
	DMF, $POCl_3$ (1 eq)	**VI** (59) + **VIII** (30)	742
	DMF, $POCl_3$ (2 eq)	**I** (15) + **IV** (80)	122
	DMF, $POCl_3$ (12 eq)	**IV** (71)	741
	DMF (8 eq), $POCl_3$ (17 eq)	**I** (46)	741
	DMF, $POCl_3$ (xs)	**VIII** (78)	742

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

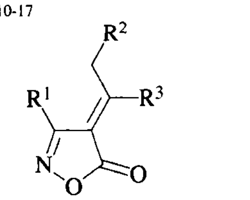
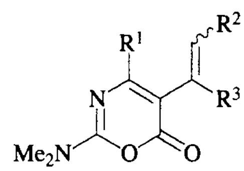
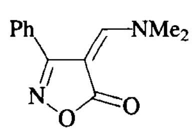
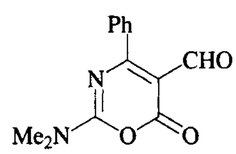
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R			
4-$O_2NC_6H_4$	DMF, $POCl_3$ (1 eq)	**II** (67)	122
	DMF, $POCl_3$ (2 eq)	**I** (11) + **II** (22) + **IV** (54)	122
4-MeC_6H_4	DMF, $POCl_3$ (1 eq)	**VII** (58) + **VIII** (29)	742
	DMF, $POCl_3$ (xs)	**VIII** (79)	742
4-$MeOC_6H_4$	DMF, $POCl_3$ (1 eq)	**VII** (60) + **VIII** (28)	742
	DMF, $POCl_3$ (xs)	**VIII** (78)	742
C_{10-17} 	DMF, $POCl_3$		743
R^1 / R^2 / R^3			
Me / CO_2Me / Me		*E* (82) + *Z* (8)	
n-Pr / CO_2Et / Me		*E* (80) + *Z* (14)	
n-Pr / $(CH_2)_3$		(67)	
Ph / H / Me		(57)	
Ph / $(CH_2)_3$		(74)	
Ph / $(CH_2)_4$		(75)	
Ph / CO_2Et / Me		*E* (51) + *Z* (28)	
Ph / Ph / H		*E* (72)	
C_{12} 	DMF, $POCl_3$	 (—)	741

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

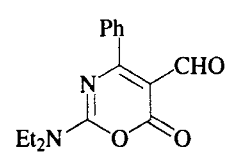
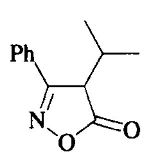
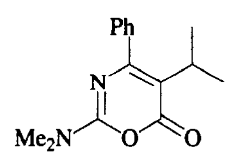
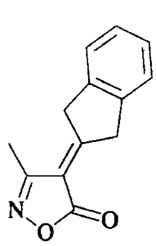
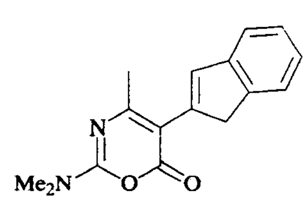
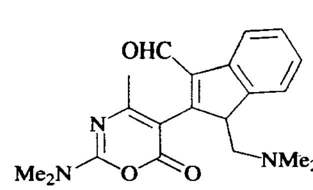
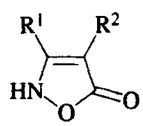
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	Et_2NCHO, $POCl_3$	 (77)	741
	DMF, $POCl_3$	 (61)	743
C_{14} 	DMF, $POCl_3$	 (47) +  (15)	743

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

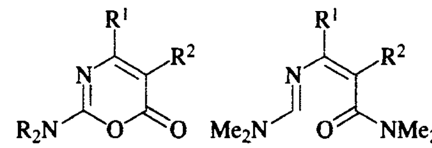
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.

1,2-Oxazol-(2*H*)-5-ones

C_{6-20}



R_2NCHO, $POCl_3$ (n eq)



I   II

R^1	R^2	R	n	Product(s) and Yield(s) (%)	Refs.
H	CO_2Et	Me	1	**I** (69)	122
H	CO_2Et	Me	2	**I** (8) + **II** (76)	122
CO_2Et	Me	Me	1	**I** (70)	122
$(CH_2)_4$		Me	1	**I** (85)	122, 744
$(CH_2)_4$		Et	1	**I** (85)	122
Me	CH_2CO_2Me	Me	1	**I** (62)	122
Ph	H	Me	1	**I** (69)	122
H	Ph	Me	1	**I** (69)	122
H	Ph	Et	1	**I** (93)	122
H	Ph	R_2N = morpholino	1	**I** (60)	122
H	Ph	Me	2	**I** (73) + **II** (11)	122
H	Ph	Et	1	**I** (93)	122
H	Ph	R_2N = morpholino	1	**I** (60)	122
H	4-ClC_6H_4	Me	1	**I** (62)	122
H	4-ClC_6H_4	Me	2	**I** (48) + **II** (49)	122
H	4-MeC_6H_4	Me	1	**I** (87)	122
H	4-MeC_6H_4	Me	2	**I** (28) + **II** (57)	122
H	4-MeC_6H_4	R_2N = morpholino	1	**I** (45)	122
Me	Ph	Me	1	**I** (73)	122, 744
Ph	Me	Me	1	**I** (87)	122, 744
Me	Bn	Me	1	**I** (80)	122, 744
Ph	Et	Me	1	**I** (72)	122, 744
Ph	CO_2Et	Me	1	**I** (74)	122
Me	CH_2Bn	Me	1	**I** (87)	122
Ph	Bn	Me	1	**I** (62)	122
Ph	*n*-C_8H_{17}	Me	1	**I** (90)	122
Me	*n*-$C_{16}H_{33}$	Me	1	**I** (77)	122

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

1,3-Oxazoles

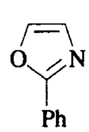
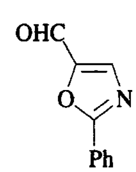
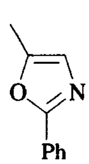
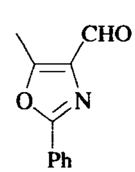
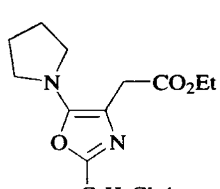
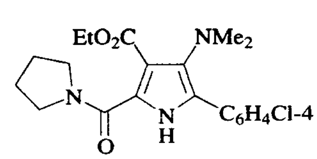
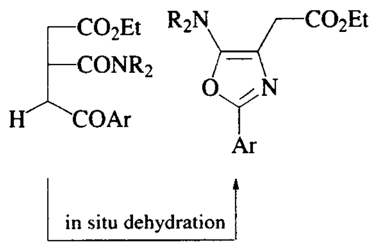
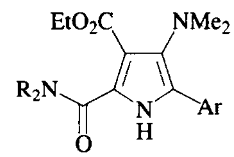
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_9 	DMF, $POCl_3$	 (58)	123
C_{10} 	DMF, $POCl_3$	 (—)	745
C_{17} 	DMF, $POCl_3$	 (71)	124

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{17\text{-}21}$			
	DMF, $POCl_3$		124

R_2	Ar	Yield (%)
$(CH_2)_4$	4-ClC_6H_4	(80)
$(CH_2)_2O(CH_2)_2$	4-ClC_6H_4	(82)
$(CH_2)_2O(CH_2)_2$	4-FC_6H_4	(57)
$(CH_2)_2N(Me)(CH_2)_2$	4-ClC_6H_4	(95)
$N[(CH_2)_2CO_2Me]_2$	Ph	(95)

1,3-Oxazol-(4*H*)-5-ones

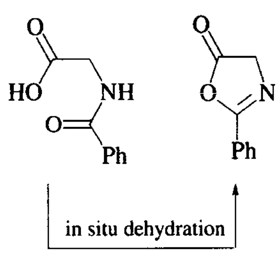
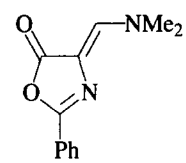
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMF, $POCl_3$	 (93)	746

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

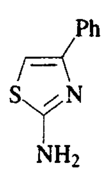
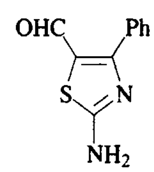
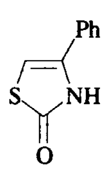
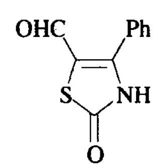
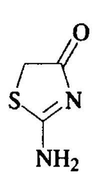
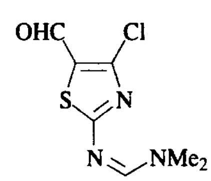
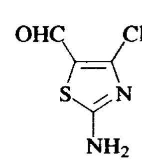
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_3NS		
	1,3-Thiazoles		
C_9			
	DMF, $POCl_3$	 (12)	125
	1,3-Thiazol-(3*H*)-2-ones		
C_9			
	—	 (40)	747
	1,3-Thiazol-(5*H*)-4-ones		
C_3			
	DMF, $POCl_3$	 (—)	748
	—	 (—)	749

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

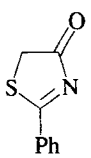
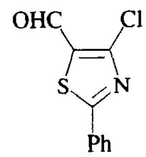
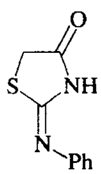
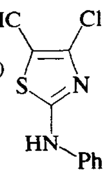
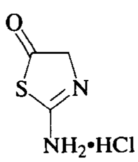
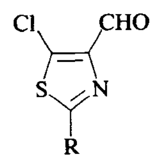
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_9 	DMF, $POCl_3$	 (63)	121
		1,3-Thiazol-(3,5*H*)-4-ones	
	DMF, $POCl_3$	(55) 	750
		1,3-Thiazol-(4*H*)-5-ones	
C_3 			
	DMF, $POCl_3$, 50°	R = NH_2 (—)	751
	DMF, $POCl_3$, 70°	R = $N{=}CHNMe_2$ (—)	751

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

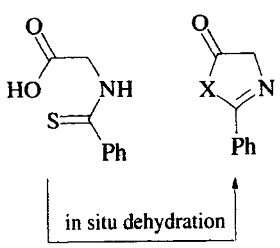
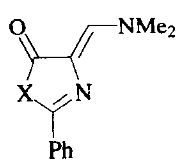
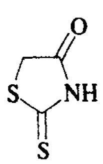
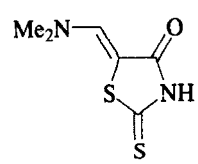
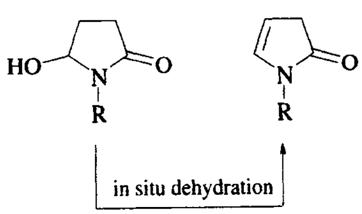
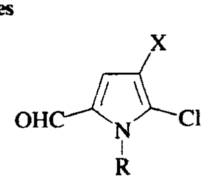
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_9  X = O, S	DMF, $POCl_3$	 X = O (30) + X = S (35)	746
		1,3-Thiazol-(3,5*H*)-2-thion-4-ones	
C_3 	—	 (59)	751
		C_4N **Pyrrol-(3*H*)-2-ones**	
C_{4-11} 		 **I**, X = H **II**, X = CHO	752

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

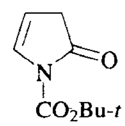
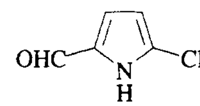
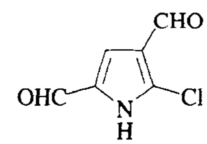
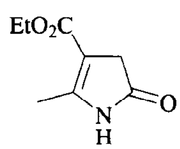
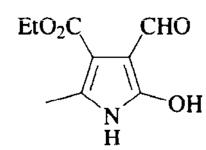
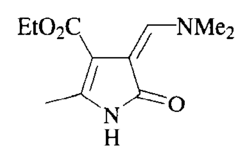
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R			
H	DMF, $POCl_3$ (3:6), 25°	**I** (2)	
	DMF, $POCl_3$ (5:10), 50°	**II** (2)	
Me	DMF, $POCl_3$ (3:6), 25°	**I** (3) + **II** (tr)	
	DMF, $POCl_3$ (5:10), 50°	**I** (5) + **II** (62)	
n-C_5H_{11}	DMF, $POCl_3$ (3:6), 25°	**I** (35) + **II** (tr)	
	DMF, $POCl_3$ (5:10), 50°	**I** (4) + **II** (56)	
Bn	DMF, $POCl_3$ (3:6), 25°	**I** (57) + **II** (tr)	
	DMF, $POCl_3$ (5:10), 50°	**II** (87)	
		 **III**  **IV**	
	DMF, $POCl_3$ (3:3), 25°	**III** (46) + **IV** (9)	
	DMF, $POCl_3$ (5:5), 25°	**III** (25) + **IV** (9)	
C_8			
	DMF, $POCl_3$	 (72)	75 3
	DMF, $POBr_3$	 (75)	754

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

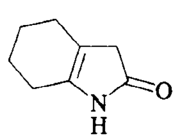
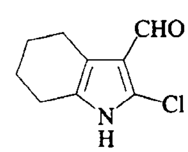
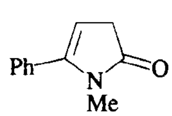
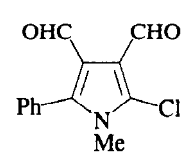
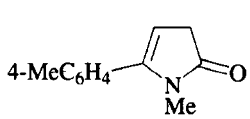
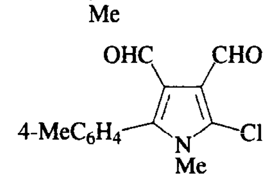
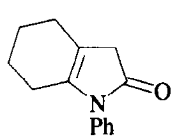
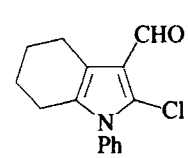
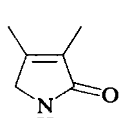
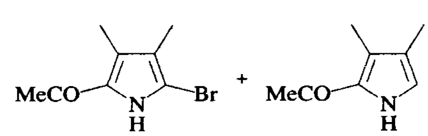
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (50-60)	755
C_{11}			
	DMF, $POCl_3$	 (79)	710
C_{12}			
	DMF, $POCl_3$	 (67)	710
C_{14}			
	DMF, $POCl_3$	 (50-60)	755
	Pyrrol-(5*H*)-2-ones		
C_6			
	DMA, $POBr_3$	 (total 17)	754

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

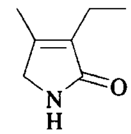
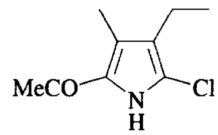
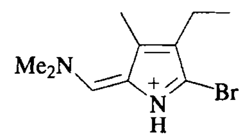
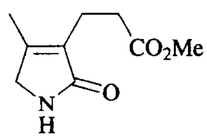
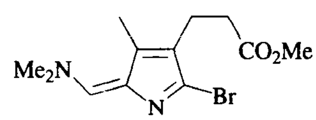
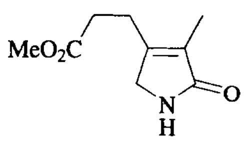
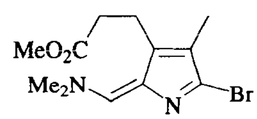
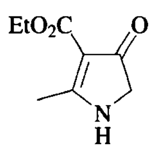
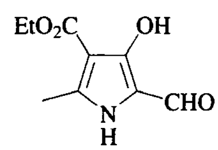
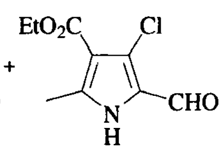
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_7 	DMA, $POCl_3$	 (50)	754
	1. DMF, $POBr_3$ 2. ClO_4^-	 ClO_4^- (50)	756
C_9 	1. DMF, $POBr_3$ 2. ClO_4^- 3. base	 (75)	756
	1. DMF, $POBr_3$ 2. ClO_4^- 3. base	 (80)	756
		Pyrrol-(2*H*)-3-ones	
C_8 	DMF, $POCl_3$	 (3) +  (10)	753

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

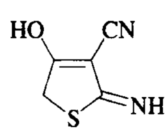
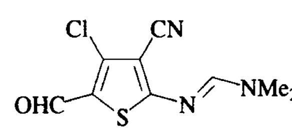
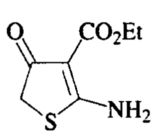
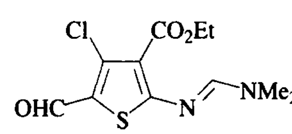
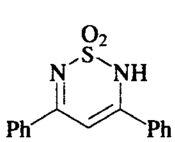
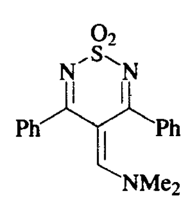
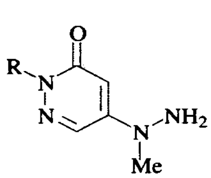
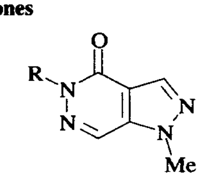
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		Thiophen-(5*H*)-2-imines	
C_5 	DMF, $POCl_3$	 (83)	757
		Thiophen-(5*H*)-4-ones	
C_7 	—	 (—)	758, 759
		C_3N_2S **1,2,6-Thiadiazoles**	
C_{15} 	DMF, $POCl_3$	 (74)	760
		C_4N_2 **Pyridazin-3-ones**	
C_{5-12} 	DMF, $POCl_3$		761

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

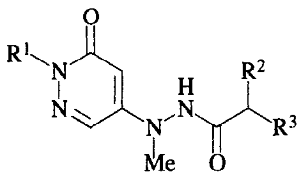
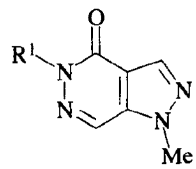
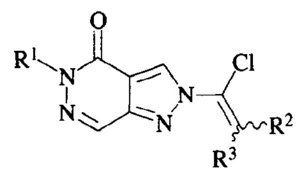
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R: H		(59)	
R: Me		(88)	
R: Ph		(88)	
R: Bn		(71)	
C_{8-14} 	DMF, $POCl_3$	 I +  II	761
R^1 = Me, R^2 = H, R^3 = H		I (48) + II (18)	
R^1 = Me, R^2 = H, R^3 = Me		I (48) + (*E*)-II (15) + (*Z*)-II (4)	
R^1 = Me, R^2 = Me, R^3 = Me		I (51) + II (22)	
R^1 = Ph, R^2 = H, R^3 = H		I (63) + II (15)	
R^1 = Bn, R^2 = H, R^3 = H		I (58) + II (24)	

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

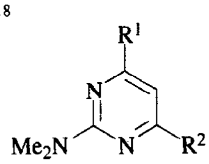
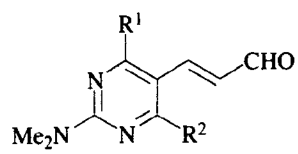
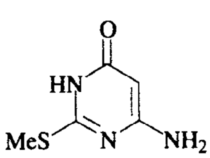
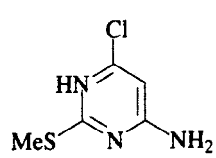
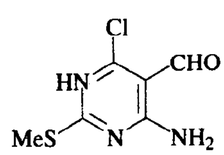
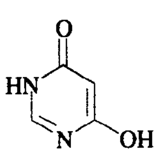
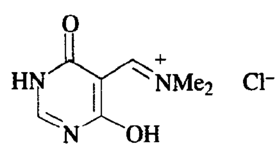
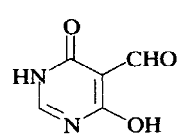
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		Pyrimidines	
C_{16-18} 	PhN(Me)CH=CHCHO, $POCl_3$		641
R^1 = 4-FC_6H_4, R^2 = *i*-Pr		(70)	
R^1 = Ph, R^2 = Ph		(56)	
		Pyrimid-(1*H*)-6-ones	
C_4 	DMF, $POCl_3$	 (26) +  (11)	762
	DMF, $COCl_2$	 (93)	763
	1. DMF, $COCl_2$ 2. H_2O	 (54)	763

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

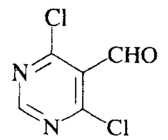
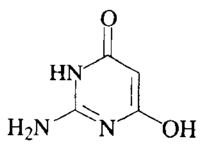
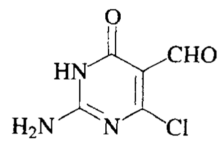
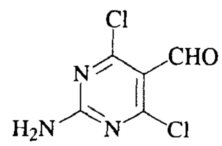
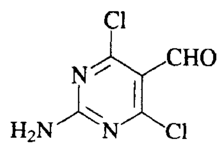
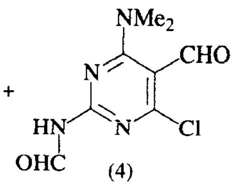
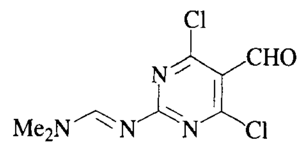
Substrate	Reagents	Product(s) and Yield(s) (%)	Re fs.
		 (48)	762
	DMF, $POCl_3$	 (28)	764
	DMF, $POCl_3$	 (28)	129, 762, 765
	DMF, $POCl_3$	 (51) +  (4)	766
	DMF, $POCl_3$	 (65)	765, 129

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

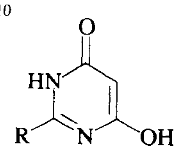
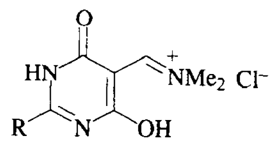
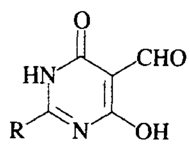
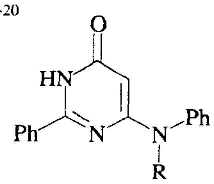
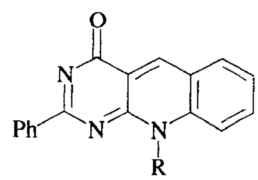
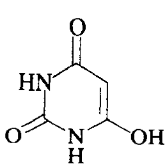
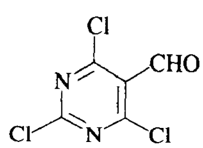
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{5-10} 	DMF, $COCl_2$	 R = Me (98) R = Ph (93)	763
	1. DMF, $COCl_2$ 2. H_2O	 R = Me (78) R = Ph (60)	763
C_{17-20}  R Me Et *n*-Pr *n*-Bu	DMF, $POCl_3$	 (96) (98) (93) (99)	130
	Pyrimi-(1,3*H*)-2,6-diones		
C_4 	DMF, $POCl_3$	 (—)	767, 768

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

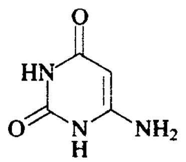
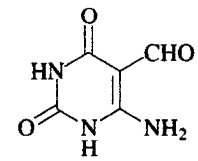
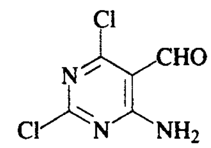
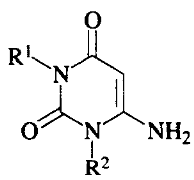
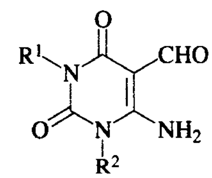
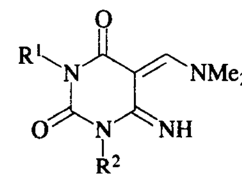
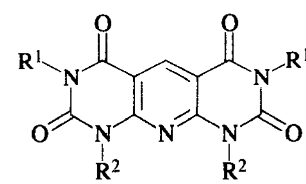
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (82)	769
	DMF, $POCl_3$	 (24)	762
C_{5-11} 		 I  II  III	

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

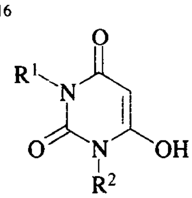
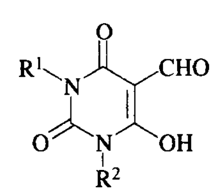
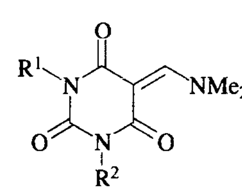
Substrate		Reagents	Product(s) and Yield(s) (%)	Refs.
R^1	R^2			
Me	H	DMF, $POCl_3$	**I** (82)	769
H	Me	DMF, $POCl_3$	**I** (81)	769
Me	Me	DMF, $POCl_3$	**I** (85) + **III** (6)	769
		DMF, —	**II** (95)	770
		DMF, $POCl_3$	**II** (95)	771
		DMF, $COCl_2$	**II** (95)	771
		DMF, $SOCl_2$	**II** (60)	771
		DMF, PhCOCl	**II** (80)	771
		DMF, Me_2SO_4	**III** (20-26)	771
Me	Ph	DMF, $POCl_3$	**I** (86) + **III** (7)	769
C_{5-16} 			 I  II	
R^1	R^2			
Me	H	DMF, $POCl_3$	**I** (68)	772
Me	Me	DMF, $POCl_3$ (xs)	**I** (30)	773
Me	Me	DMF, $POCl_3$	**II** (50)	773
H	*n*-Bu	DMF, $POCl_3$ (xs)	**I** (12)	773
H	Ph	DMF, $POCl_3$ (xs)	**I** (88)	773
H	C_6H_{11}	DMF, $POCl_3$ (xs)	**I** (45)	773
H	C_6H_{11}	DMF, $POCl_3$	**II** (45)	773
CH(Me)Ph	H	DMF, $POCl_3$	**I** (—) (*R*) and (*S*)	774
Ph	Ph	DMF, $POCl_3$ (xs)	**I** (45)	773
Ph	Ph	DMF, $POCl_3$	**II** (40)	773
C_6H_{11}	C_6H_{11}	DMF, $POCl_3$ (xs)	**I** (56)	773
C_6H_{11}	C_6H_{11}	DMF, $POCl_3$	**II** (73)	773

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

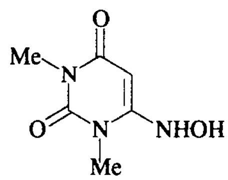
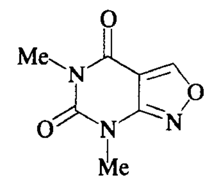
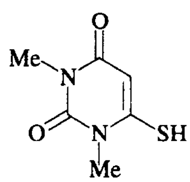
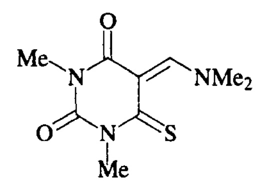
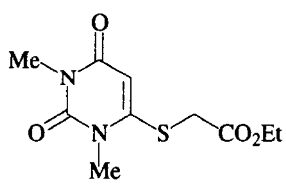
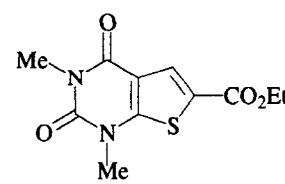
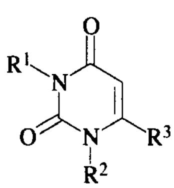
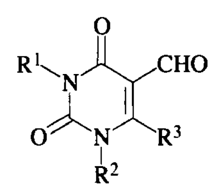
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_6			
	DMF, $POCl_3$	 (59)	775
	DMF, $POCl_3$	 (40)	776
C_{10}			
	DMF, $POCl_3$	 (67)	429
C_{6-12}			
			

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

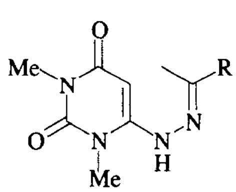
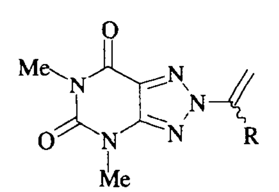
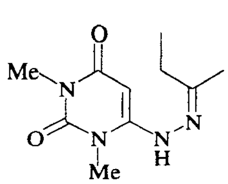
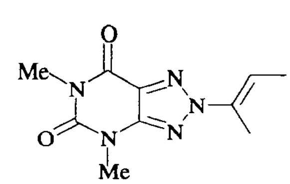
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^1 / R^2 / R^3			
Me / Me / H	DMF, $POCl_3$	(93)	777
Me / Me / Me	DMF, $POCl_3$ (xs)	(44)	773
Me / C_6H_{11} / H	DMF, $POCl_3$ (xs)	(60)	773
Me / Ph / Me	DMF, $POCl_3$ (xs)	(70)	773
C_6H_{11} / Me / Me	DMF, $POCl_3$ (xs)	(65)	773
	Me_2NNO, $POCl_3$	 (57)	778
R			
Me		(57)	
4-ClC_6H_4		(31)	
Ph		(65)	
4-MeC_6H_4		(52)	
C_8			
	Me_2NNO, $POCl_3$	 (44)	778

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

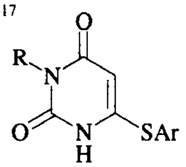
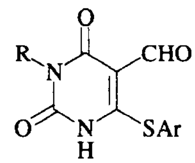
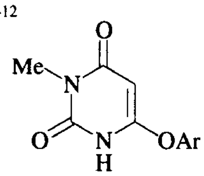
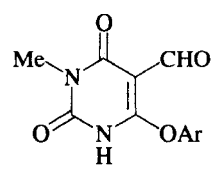
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{10-17} 	DMF, $POCl_3$		779
R, Ar			
H, 4-ClC_6H_4		(96)	
H, Ph		(86)	
H, 4-MeC_6H_4		(94)	
Me, 4-ClC_6H_4		(94)	
Me, Ph		(93)	
Me, 2-MeC_6H_4		(75)	
Me, 3-MeC_6H_4		(70)	
Me, 4-MeC_6H_4		(92)	
Ph, 4-ClC_6H_4		(99)	
Ph, Ph		(67)	
Ph, 4-MeC_6H_4		(76)	
C_{11-12} 	DMF, $POCl_3$		780
Ar			
3-ClC_6H_4		(79)	
4-ClC_6H_4		(90)	
Ph		(84)	
3-MeC_6H_4		(89)	
4-MeC_6H_4		(81)	

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

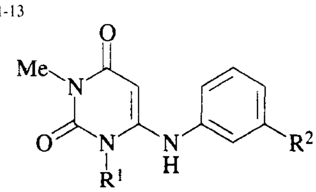
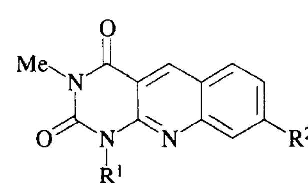
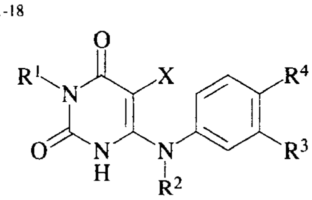
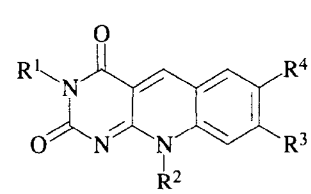
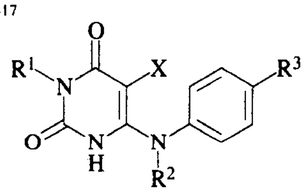
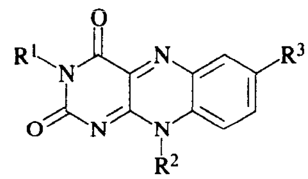
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{11-13} 	DMF, $POCl_3$		781
R^1, R^2			
H, OH		(96)	
H, Me		(88)	
H, OMe		(90)	
Me, OH		(78)	
Me, OMe		(66)	
C_{11-18} 			
R^1, R^2, R^3, R^4, X			
H, Me, H, H, H	DMF, $POCl_3$	(95)	772
H, H, Me, Me, H	DMF, $POCl_3$	(85)	782
H, Et, H, H, H	DMF, $POCl_3$	(87)	772
H, Me, Me, Me, H	DMF, $POCl_3$	(80)	782
H, *n*-Pr, H, H, H	DMF, $POCl_3$	(90)	772
H, *n*-Bu, H, H, H	DMF, $POCl_3$	(92)	772
Me, Me, H, H, H	DMF, $POCl_3$	(96)	772
Me, Et, H, H, H	DMF, $POCl_3$	(88)	772

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

R^1	R^2	R^3	R^4	X	Reagents	Product(s) and Yield(s) (%)	Refs.
Me	Et	H	H	NO_2	DMF, $POCl_3$, 130°	(63)	783
Me	Me	Me	Me	H	DMF, $POCl_3$	(89)	784
Me	*n*-Pr	H	H	H	DMF, $POCl_3$	(86)	772
Me	*n*-Pr	H	H	NO_2	DMF, $POBr_3$, 130°	(81)	783
Me	*n*-Bu	H	H	H	DMF, $POCl_3$	(89)	772
Me	*n*-Bu	H	H	NO_2	DMF, $POBr_3$, 130°	(72)	783
H	ribityl	Me	Me	H	1. Ac_2O 2. DMF, $POCl_3$	R^2 = tetraacetylribityl (91)	785

C_{12-17}



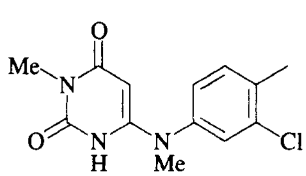


R^1	R^2	R^3	X	Reagents	Product(s) and Yield(s) (%)	Refs.
H	Et	H	H	Me_2NNO, $POCl_3$	(70)	786
Me	Me	Br	H	Me_2NNO, $POCl_3$	(60)	786
Me	Me	H	H	Me_2NNO, $POCl_3$	(68)	786
Me	Et	H	H	Me_2NNO, $POCl_3$	(65)	786
Me	Et	Br	H	Me_2NNO, $POCl_3$	(67)	786
Me	Et	Me	H	Me_2NNO, $POCl_3$	(70)	786
Me	Me	H	NO_2	DMF, $POCl_3$	(73)	787
Me	Me	H	NO_2	DMF, $POBr_3$, 80°	(87)	783
Me	Et	H	NO_2	DMF, $POCl_3$	(71)	787
Me	Et	H	NO_2	DMF, $POBr_3$, 80°	(73)	783
Me	*n*-Pr	H	NO_2	DMF, $POCl_3$	(72)	787
Me	*n*-Pr	H	NO_2	DMF, $POBr_3$, 80°	(55)	783

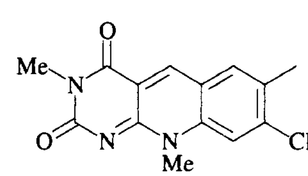
TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

R^1	R^2	R^3	X	Reagents	Product(s) and Yield(s) (%)	Refs.
Me	*n*-Bu	H	NO_2	DMF, $POCl_3$	(65)	787
Me	*n*-Bu	H	NO_2	DMF, $POBr_3$, 80°	(68)	783
Me	Et	Me	NO_2	DMF, $POCl_3$	(82)	787
Me	Ph	H	NO_2	DMF, $POCl_3$	(88)	787

C_{13}

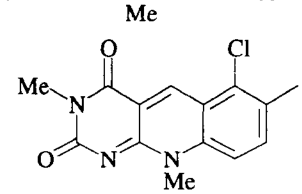


DMF, $POCl_3$

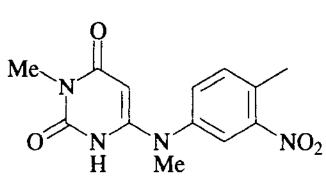


(48) +

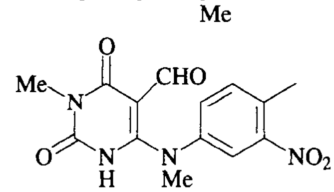
784



(29)



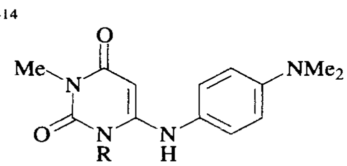
DMF, $POCl_3$



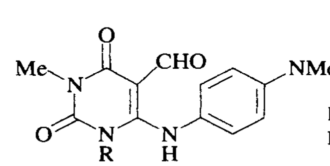
(83)

784

C_{13-14}



DMF, $POCl_3$



R = H (82)
R = Me (56)

781

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

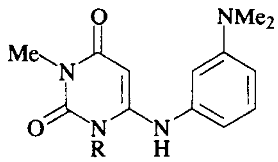
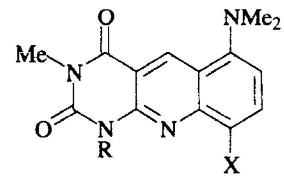
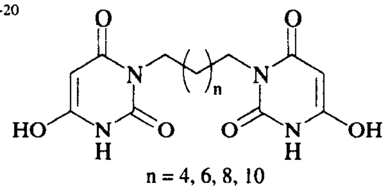
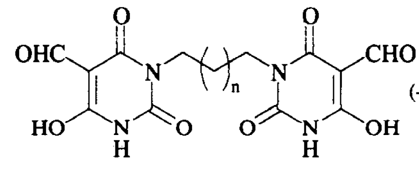
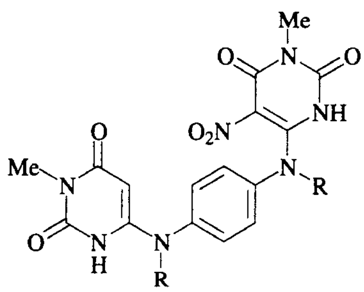
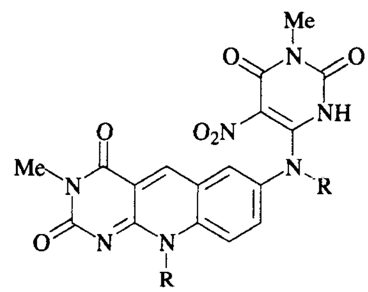
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 I, X = H; II, X = CHO	781
R			
H		I (74) + II (11)	
Me		I (77) + II (14)	
C_{14-20}  n = 4, 6, 8, 10	DMF, $POCl_3$	 (—)	788
C_{20-40} 		 I +	789

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

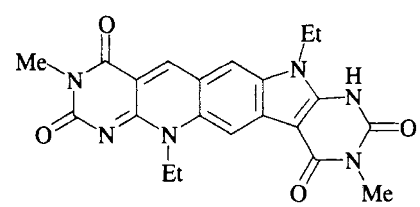
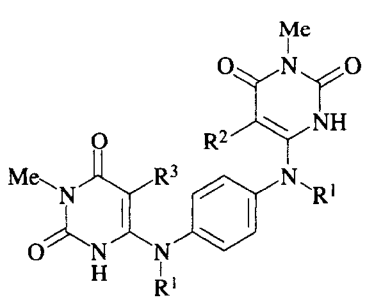
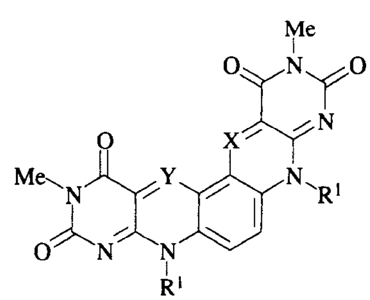
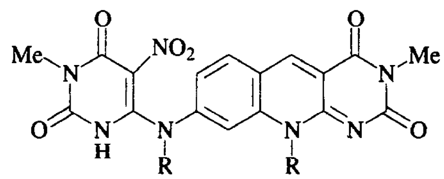
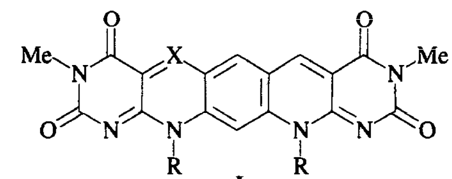
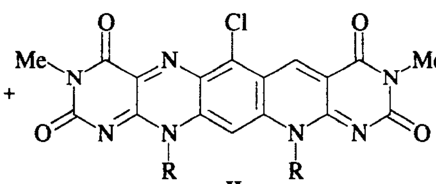
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 II	
R			
Et	DMF, $POCl_3$ (7:1)	I (10)	
Et	DMF, $POCl_3$ (1:12)	I (14) + II (7)	
n-C_8H_{17}	DMF, $POCl_3$ (7:1)	I (20)	
n-$C_{12}H_{25}$	DMF, $POCl_3$ (7:1)	I (28)	
		 I, X = Y = CH; II, X = Y = N; III, X = CH, Y = N	
R^1 / R^2 / R^3			
Et / H / H	DMF, $POCl_3$	I (34)	790, 791
Et / NO_2 / NO_2	DMF, $POCl_3$ (1:1)	II (7) + III (2)	789
Et / NO_2 / H	DMF, $POCl_3$ (5:1)	II (31) + III (3)	789
n-C_8H_{17} / NO_2 / H	DMF, $POCl_3$ (5:1)	II (6) + III (2)	789
n-C_8H_{17} / H / H	DMF, $POCl_3$	I (36)	790, 791
n-$C_{12}H_{25}$ / NO_2 / H	DMF, $POCl_3$ (5:1)	II (4) + III (1)	789
n-$C_{12}H_{25}$ / H / H	DMF, $POCl_3$	I (35)	790, 791

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{31-50}			
		 I	792
		+  II	
R			
n-C_8H_{17}	DMF, $POCl_3$ (5:1)	I, X = N (7) + I, X = CH (2-3)	
n-$C_{12}H_{25}$	DMF, $POCl_3$ (5:1)	I, X = N (12) + I, X = CH (2-3)	
	DMF, $POCl_3$ (1:1)	I, X = CH (3) + II (15)	
n-$C_{18}H_{37}$	DMF, $POCl_3$ (5:1)	I, X = N (12) + I, X = CH (2-3)	

C_4NS

1,3-Thiazin-5-ones

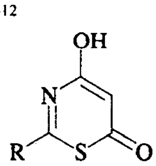
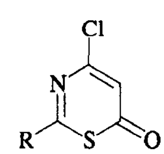
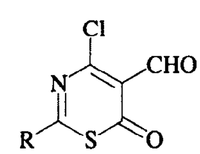
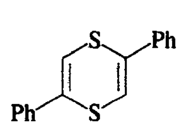
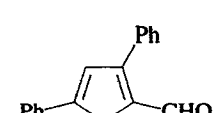
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{10-12}			
	DMF, $POCl_3$	 I +  II	793

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R		I II	
4-BrC_6H_4		(56) (32)	
4-$O_2NC_6H_4$		(62) (16)	
4-$MeOC_6H_4$		(64) (5)	
3,4-$(MeO)_2C_6H_4$		(21) (59)	
4-$Me_2NC_6H_4$		(10) (73)	

C_4S_2

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMF, $POCl_3$	 (32)	443

C_5B

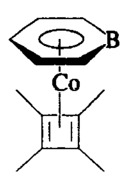
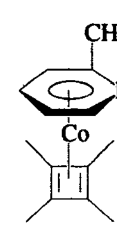
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	MFA, $POCl_3$	 (65)	794

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

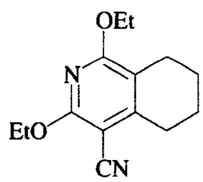
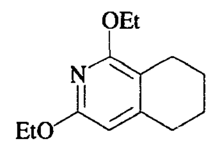
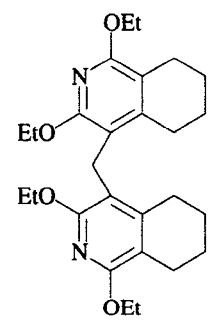
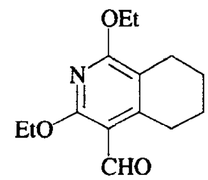
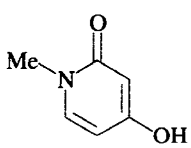
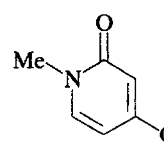
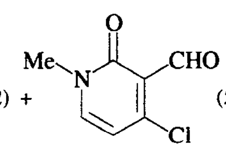
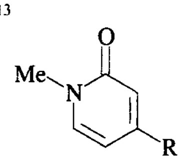
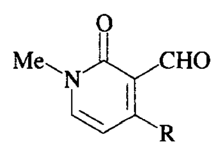
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		Pyridines	
C_{14} 	DMF, $POCl_3$	 (0-80)  (0-86)  (5-82)	795
		Pyrid-2-ones	
C_6 	DMF, $POCl_3$	 (22) +  (5)	128
C_{7-13} 	DMF, $POCl_3$		

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

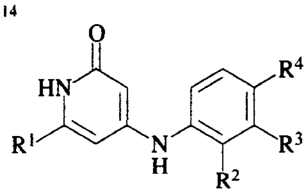
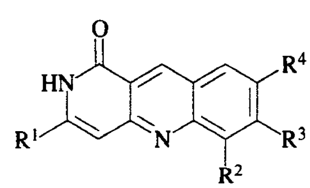
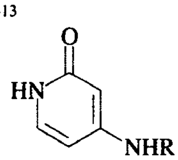
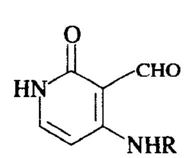
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R			
OMe		(73)	128, 796
OEt		(73)	128
OBn		(67)	128
C_{11-14} 	DMF, $POCl_3$, 90°		797
R^1 R^2 R^3 R^4			
H H H H		(80)	
Me Cl H H		(69)	
Me H OMe H		(66)	
Me Me H Me		(83)	
C_{12-13} 	DMF, $POCl_3$		797
R			
Bn		(29)	
2,5-$Me_2C_6H_3$		(31)	

TABLE XVI. OTHER HETEROCYCLES WITH ONE FULLY CONJUGATED RING (*Continued*)

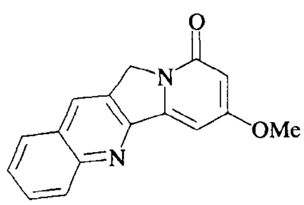
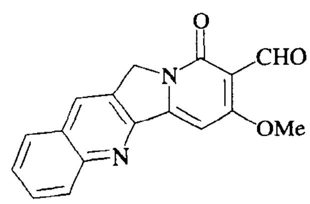
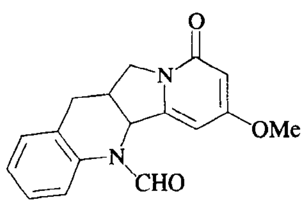
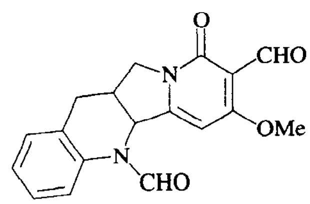
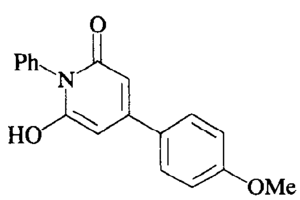
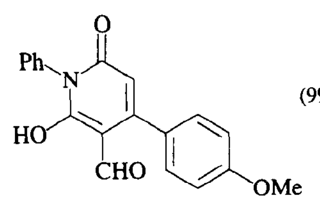
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMF, $POCl_3$	 (82)	798
C_{17}			
	DMF, $POCl_3$	 (75)	796, 798
C_{18}			
	DMF, $POCl_3$	 (99)	799

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS

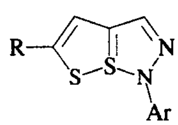
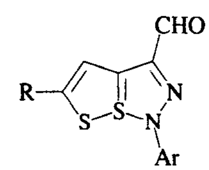
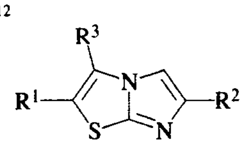
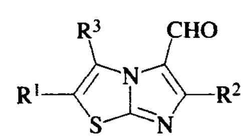
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_2N_2S/C_3S_2	
C_{10-14} 	DMF, $POCl_3$		800
R / Ar			
H / Ph		(15)	
t-Bu / 4-$O_2NC_6H_4$		(18)	
t-Bu / Ph		(57)	
		C_3N_2/C_3NS	
C_{5-12} 			
R^1 / R^2 / R^3			
H / Br / H	DMF, $POBr_3$	(73)	800
H / Cl / H	DMF, $POCl_3$	(57)	802, 801
Me / Cl / H	DMF, $POCl_3$	(60)	803
H / Me / H	DMF, $POCl_3$	(60)	137
Me / Me / H	DMF, $POCl_3$	(65)	805, 804
H / 4-ClC_6H_4 / H	DMF, $POCl_3$	(60)	803
H / Ph / H	DMF, $POCl_3$	(81)	137, 805
H / Ph / Me	DMF, $POCl_3$	(65)	209

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

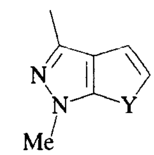
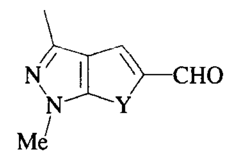
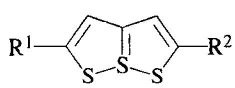
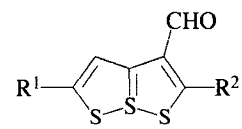
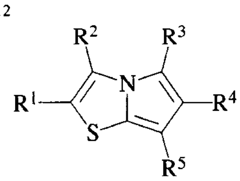
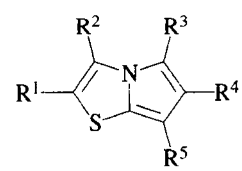
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_3N_2/C_4S, Se	
C_7 	DMF, $POCl_3$	 Y = S (86) Y = Se (88)	806
		C_3S_2/C_3S_2	
$C_{5\text{-}18}$ 			
R^1 R^2			
H H	Me_2NCHS, $POCl_3$	(21)	138
D D	Me_2NCHS, $POCl_3$	(21)	138
t-Bu H	Me_2NCHS, $POCl_3$	(77)	138
t-Bu D	Me_2NCHS, $POCl_3$	(77)	138
Ph 4-$MeOC_6H_4$	DMF, $POCl_3$	(50)	807
		C_3NS/C_4N	
$C_{5\text{-}12}$ 			

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

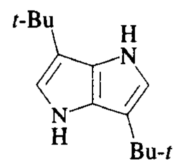
R^1	R^2	R^3	R^4	R^5	Reagents	Product(s) and Yield(s) (%)	Refs.
						R^1 - R^5 as in substrate except as indicated	
H	H	H	Me	H	DMF, $POCl_3$	R^3 = CHO (88)	136, 143
					DMF, $POCl_3$ (2.7 eq)	R^3 = CHO (95) + R^5 = CHO (5)	136
					DMF, $POCl_3$ (6 eq)	R^3 = CHO (70) + R^5 = CHO (30)	136
					1. DMF, $POCl_3$ 2. H_2S or NaSH, H_2O	R^3 = CHS (89)	632, 808
					1. Me_2NCDO, $POCl_3$ 2. H_2S, H_2O	R^3 = CDS (89)	808
Me	H	H	Me	H	DMF, $POCl_3$	R^3 = CHO (43)	143
					1. DMF, $POCl_3$ 2. H_2S, H_2O	R^3 = CHS (89)	808
H	Me	H	Me	H	DMF, $POCl_3$	R^3 = CHO (80)	809
					1. DMF, $POCl_3$ 2. H_2S, H_2O	R^3 = CHS (49) + R^5 = CHS (5)	808
H	H	Me	Me	H	DMF, $POCl_3$	R^3 = CHO (54)	136, 143
					1 . DMF, $POCl_3$ 2. H_2S, H_2O	R^3 = CHS (65)	808
H	H	H	Me	Me	DMF, $POCl_3$	R^3 = CHO (84)	136, 143
					1. DMF, $POCl_3$ 2. H_2S, H_2O	R^3 = CHS (71)	808
Me	Me	H	Me	H	1. DMF, $POCl_3$ 2. H_2S, H_2O	R^3 = CHS (77)	808
					1. Me_2NCDO, $POCl_3$ 2. H_2S, H_2O	R^3 = CDS (83)	808
H	Me	Me	Me	H	1. DMF, $POCl_3$ 2. H_2S, H_2O	R^5 = CHS (92)	808
Me	Me	Me	Me	H	1. DMF, $POCl_3$ 2. H_2S, H_2O	R^5 = CHS (75)	808

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

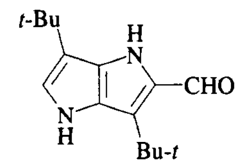
Substrate					Reagents	Product(s) and Yield(s) (%)	Refs.
R^1	R^2	R^3	R^4	R^5			
H	Me	H	*t*-Bu	H	1. DMF, $POCl_3$ 2. H_2S, H_2O	R^3 = CHS (12) + R^5 = CHS (17)	808
H	Me	H	4-BrC_6H_4	H	DMF, $POCl_3$	R^3 = CHO (78)	809
H	4-ClC_6H_4	H	Me	H	DMF, $POCl_3$	R^3 = CHO (78) + R^5 = CHO (12)	809

C_4N/C_4N

C_{14}



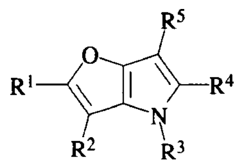
DMF, $POCl_3$



(90) — 810

C_4N/C_4O

C_{9-16}



DMF, $POCl_3$ — 135

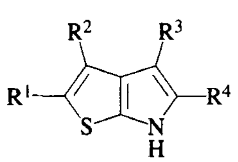
R^1	R^2	R^3	R^4	R^5	Reagents	R^1 - R^5 as in substrate except as indicated
H	H	H	H	CO_2Et		R^2 = CHO (58)
H	H	Me	H	CO_2Et		R^2 = CHO (71)
Ph	H	COMe	H	H		R^4 = CHO (71)
Ph	H	H	H	CO_2Et	8 h	R^3 = CHO (44)
					60 h	R^5 = CHO (43)
Ph	H	Me	H	CO_2Et		R^5 = CHO (67)
4-MeC_6H_4	H	COMe	H	H		R^4 = CHO (72)
4-MeC_6H_4	H	H	H	CO_2Et		R^3 = CHO (54)
4-MeC_6H_4	H	Me	H	CO_2Et		R^5 = CHO (62)

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.

C_4N/C_4S

C_{6-9}

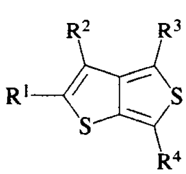


DMF, $POCl_3$ — 134

R^1	R^2	R^3	R^4	R^1 - R^4 as in substrate except as indicated
H	H	H	H	R^1 = CHO (1) + R^3 = CHO (3) + R^4 = CHO (51)
H	H	H	CO_2Et	R^1 = CHO (78) + R^3 = CHO (3)

C_4S/C_4S

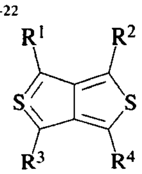
C_{6-8}



DMF, $POCl_3$ — 131

R^1	R^2	R^3	R^4	R^1 - R^4 as in substrate except as indicated
H	H	H	H	R^3 = CHO (39) + R^4 = CHO (17)
CO_2Me	H	H	H	R^3 = CHO (20) + R^4 = CHO (20)

C_{18-22}



R^1	R^2	R^3	R^4	Reagents	R^1 - R^4 as in substrate except as indicated	Refs.
i-PrS	*i*-PrS	*i*-PrS	*i*-PrS	DMF, $POCl_3$	R^1 = CHO (33) + R^1 = R^2 = CHO (14)	811, 812
				DMF, $POCl_3$ (xs)	R^1 = R^2 = CHO (51)	811
t-BuS	*t*-BuS	*t*-BuS	*t*-BuS	DMF, $POCl_3$	R^1 = CHO (40)	812

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

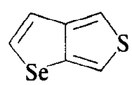
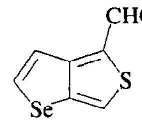
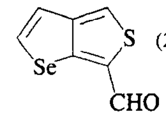
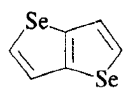
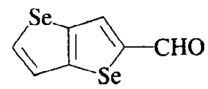
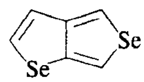
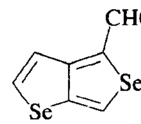
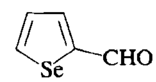
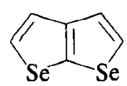
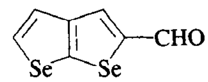
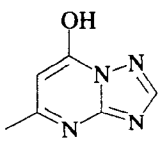
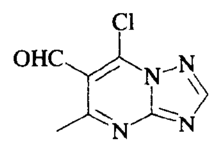
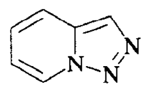
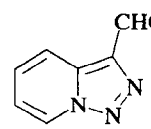
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_4S/C_4Se		
C_6 	MFA, $POCl_3$	 (42) +  (28)	133
	C_4Se/C_4Se		
C_6 	DMF, $POCl_3$	 (77)	132
	DMF, $POCl_3$	 (37) +  (31)	132
	DMF, $POCl_3$	 (96)	132
	C_2N_3/C_4N_2		
C_6 	—	 (85)	813
	C_2N_3/C_5N		
C_7 	DMF, $POCl_3$	 (8)	146

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

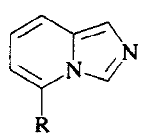
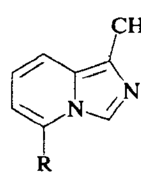
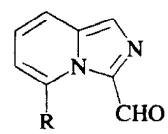
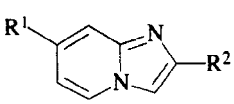
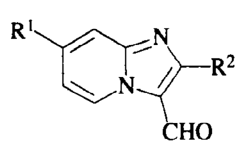
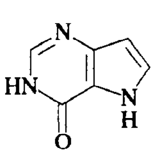
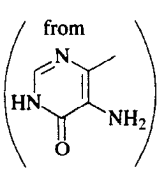
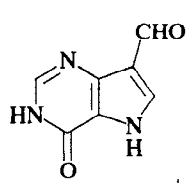
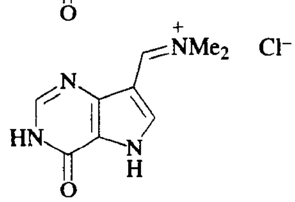
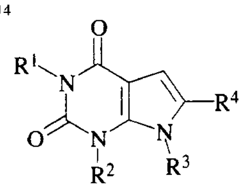
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_3N_2/C_5N		
C_{6-7} 	DMF, $POCl_3$	 **I** +  **II**	144
R = H		**I** (20) + **II** (8)	
R = Me		**II** (68)	
C_{13-14} 	DMF, $POCl_3$		
R^1 = H, R^2 = Ph		(—)	814
R^1 = Me, R^2 = 2-$O_2NC_6H_4$		(80)	815
	C_4N/C_4N_2		
C_6  (from )	1. DMF, $POCl_3$ 2. $NaHCO_3$	 (70)	816, 817
	DMF, $POCl_3$		816

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

Substrate				Reagents	Product(s) and Yield(s) (%)	Refs.
C_{8-14}						

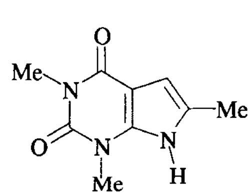
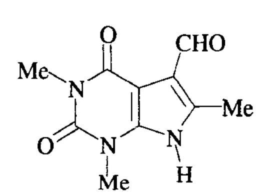


R^1	R^2	R^3	R^4	Reagents	R^1 - R^4 as in substrate except as indicated	Refs.
Me	Me	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (90)	818, 819
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (95)	818
H	Et	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (74)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (85)	818
Me	Et	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (95)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (92)	818
H	*n*-Pr	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (94)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (95)	818
Me	Me	Me	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (90)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (73)	818
H	$CH_2CH{=}CH_2$	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (87)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (89)	818
Me	$CH_2CH{=}CH_2$	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (83)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (98)	818

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

R^1	R^2	R^3	R^4	Reagents	R^1 - R^4 as in substrate except as indicated	Refs.
Et	Et	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (33)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (76)	818
Me	$CH_2CH{=}CH_2$	Me	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (78)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (87)	818
Me	*n*-Bu	H	H	DMF, $POCl_3$	R^4 = $CH{=}NMe_2^+$ Cl^- (87)	818
				1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (90)	818
Me	Ph	H	H	1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (63)	818
Me	Ph	Me	H	1. DMF, $POCl_3$ 2. NaOH	R^4 = CHO (85)	818

C_9

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (51)	818

C_{9-14}

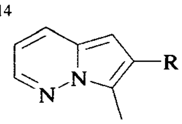
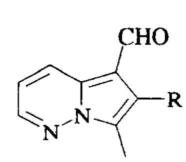
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$		820
R = Me		(72)	
R = Ph		(88)	

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

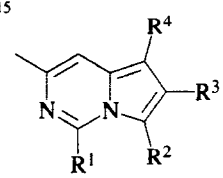
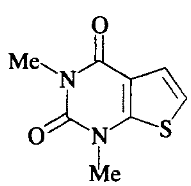
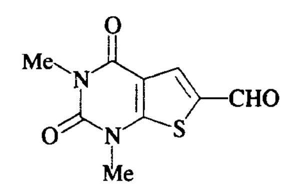
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{9-15} 			145
R^1 R^2 R^3 R^4		R^1 - R^4 as in substrate except as indicated	
Me H H H	DMF, $POCl_3$	R^2 = CHO (62)	
	1. DMF, $POCl_3$ 2. NaSH	R^2 = CHS (58)	
H Me Me H	DMF, $POCl_3$	R^4 = CHO (68)	
Me H Me H	DMF, $POCl_3$	R^2 = CHO (20) + R^3 = CHO (2)	
Me Me Me H	DMF, $POCl_3$	R^4 = CHO (5)	
Me H Ph H	DMF, $POCl_3$	R^4 = CHO (5)	
	C_4S/C_4N_2		
C_8 	DMF, $POCl_3$	 (92)	821

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

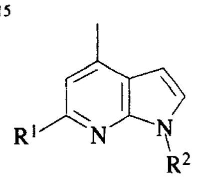
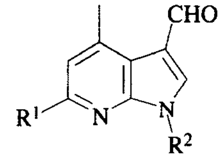
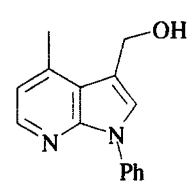
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	C_4N/C_5N (No bridgehead nitrogen)		
C_{8-15} 			
R^1 R^2			
H H	DMF, $POCl_3$	 **I** (25)	139
Cl H	DMF, $POCl_3$	**I** (25)	139
H Me	DMF, $POCl_3$	**I** (17)	139
H *n*-Bu	DMF, $POCl_3$	**I** (48)	139
H Ph	1. DMF, $POCl_3$ 2. $NaBH_4$	 (76)	822
H Bn	DMF, $POCl_3$	**I** (38)	139
H 4-$MeOC_6H_4$	DMF, $POCl_3$	**I** (71)	139

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

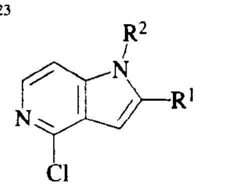
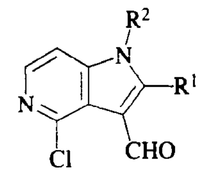
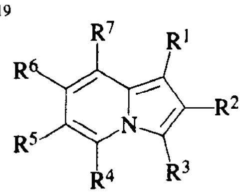
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{8-23} 	DMF, $POCl_3$		
R^1 / R^2			
H / Me		(94)	823
CH(Me)Ph / Me		(16)	824
$CH(Me)C_6H_4Me$-4 / Me		(39)	824
$CH(Me)C_6H_4Me$-4 / Bn		(32)	824
		C_4N/C_5N, Bridgehead nitrogen	
C_{7-19} 			
R^1 - R^7 = H except as indicated		R^1 - R^7 as in substrate except as indicated	
	DMF, $POCl_3$	R^1 = CHO (tr) + R^3 = CHO (44)	144
	1. DMF, $POCl_3$ 2. NaSH	R^3 = CHS (77)	141, 142
R^2 = Me	MFA, $POCl_3$	R^3 = CHO (8)	825
	DMF, $POCl_3$, 70°	R^1 = R^3 = CHO (96)	141, 142
	1. DMF, $POCl_3$ 2. NaSH	R^3 = CHS (86)	141, 142 632

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^1 - R^7 = H except as indicated		R^1 - R^7 as in substrate except as indicated	
	1. DMF, $POCl_3$ 2. NaSeH	R^3 = CHSe (3)	143
R^1 = R^2 = Me	DMF, $POCl_3$	R^3 = CHO (84)	141, 142
	1. DMF, $POCl_3$ 2. NaSH	R^3 = CHS (81)	141, 142
	1. DMA, $POCl_3$ 2. NaSH	R^3 = C(S)Me (66)	632
	1. DMF, $POCl_3$ 2. NaSeH	R^3 = CHSe (43)	143
R^2 = R^3 = Me	DMF, $POCl_3$	R^1 = CHO (62)	141, 142
	MFA, $POCl_3$	R^1 = CHO (36)	825
	1. DMF, $POCl_3$ 2. NaSH	R^1 = CHS (76)	141, 142
	1. DMF, $POCl_3$ 2. NaSeH	R^1 = CHSe (12)	143
R^2 = R^5 = Me	1. DMF, $POCl_3$ 2. NaSH	R^3 = CHS (86)	141, 142
R^2 = R^6 = Me	1. DMF, $POCl_3$ 2. NaSH	R^3 = CHS (83)	141, 142
	1. DMF, $POCl_3$ 2. NaSeH	R^3 = CHSe (46)	143
R^2 = R^7 = Me	1. DMF, $POCl_3$ 2. NaSH	R^3 = CHS (82)	141, 142
	1. DMF, $POCl_3$ 2. NaSeH	R^3 = CHSe (46)	143
R^2 = R^3 = Me, R^5 = Et	DMF, $POCl_3$	R^1 = CHO (77)	826
R^2 = *t*-Bu	1. DMF, $POCl_3$ 2. NaSH	R^1 = CHS (5) + R^3 = CHS (90)	141, 142

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

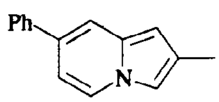
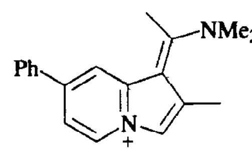
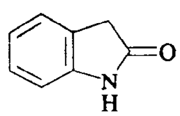
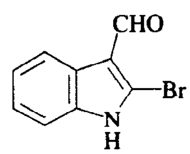
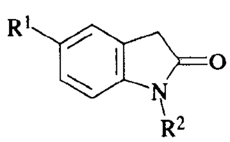
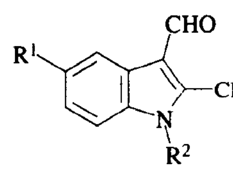
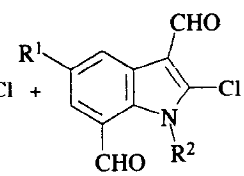
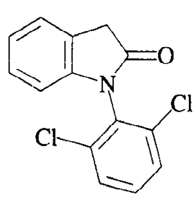
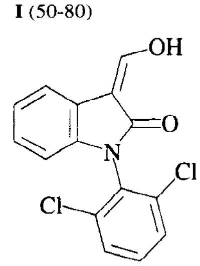
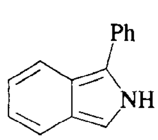
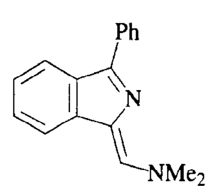
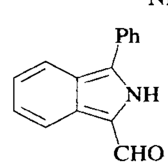
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^1 - R^7 = H except as indicated		R^1 - R^7 as in substrate except as indicated	
R^1 = Me, R^2 = *t*-Bu	1. DMF, $POCl_3$ 2. NaSeH	R^3 = CHSe (40)	143
R^2 = *t*-Bu, R^6 = Me	1. DMF, $POCl_3$ 2. NaSeH	R^3 = CHSe (37)	143
R^2 = R^6 = Ph, R^4 = Me	DMF, $POCl_3$	R^1 = R^3 = CHO (50)	827
C_{15}			
	1. DMA, $POCl_3$ 2. $HClO_4$	 ClO_4^- (—)	828
	C_4N/C_6		
C_8			
	—	 (48)	829
C_{8-15}			
	DMF, $POCl_3$	 I +  II	
R^1 R^2			
H H		I (50-80)	830, 753, 755
H Me		I (50-80) + II (10-15)	830
OMe H		I (77)	753
H Ph		I (75)	753
		I (50-80) + II (10-15)	830
H 4-ClC_6H_4CO		I (50-80)	830
H COPh		I (50-80)	830
C_{14}			
	DMF, $POCl_3$	 (—)	831
	DMF, $POCl_3$	 (68)	185
	1. DMF, $POCl_3$ 2. H_2O, OH^-	 (33)	185

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

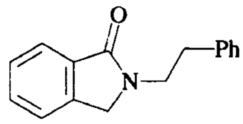
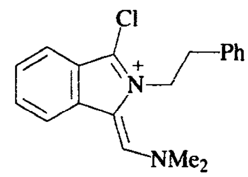
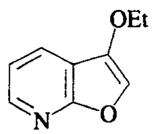
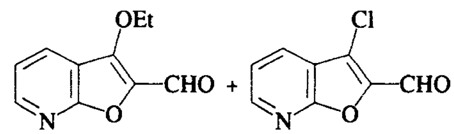
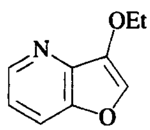
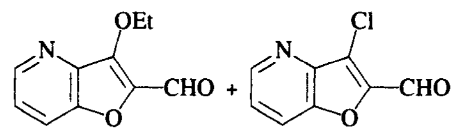
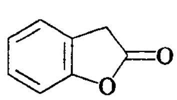
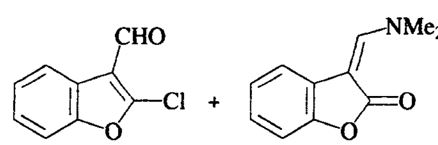
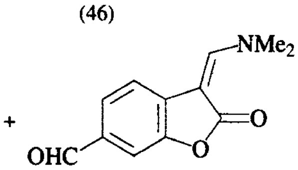
	Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{16}		1. DMF, $POCl_3$ 2. ClO_4^-	 ClO_4^- (80)	756
		C_4O/C_5N		
C_9		DMF, $POCl_3$	 (22) + (43)	140
		DMF, $POCl_3$	 (30) + (35)	140
		C_4O/C_6		
C_8		DMF, $POCl_3$	 (46) + (10) +  (24)	832

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

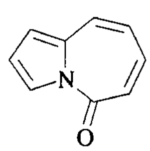
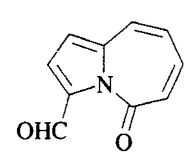
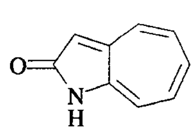
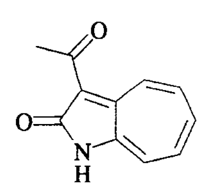
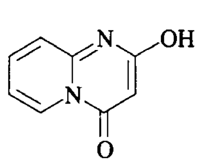
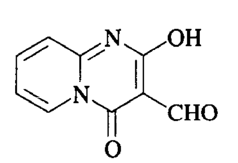
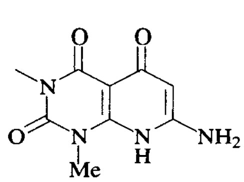
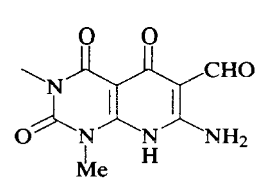
	Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_4N/C_6N		
C_9		DMF, $POCl_3$	 (73)	147
		DMA, $POCl_3$	 (43)	833
		C_4N_2/C_5N		
C_8		DMF, $POCl_3$	 (50)	151
C_9		—	 (—)	834

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

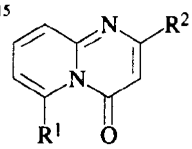
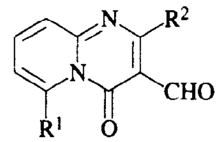
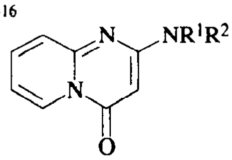
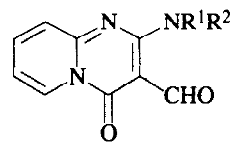
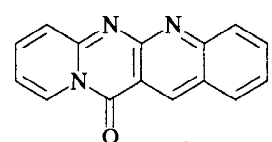
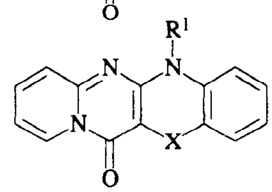
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{8-15} 	DMF, $POCl_3$		835
R¹ H, R² Cl		(94)	
R¹ Me, R² Cl		(93)	
R¹ H, R² OMe		(79-95)	
R¹ H, R² NHBu		(90)	
R¹ H, R² *N*-piperidyl		(89)	
R¹ Me, R² NHBu		(89)	
R¹ Me, R² *N*-piperidyl		(93)	
C_{10-16} 		 **I** +  **II** +  **III**, X = CH_2 **IV**, X = CO	152

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

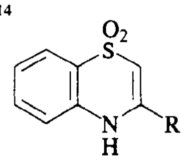
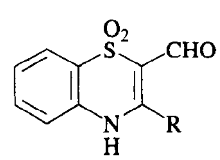
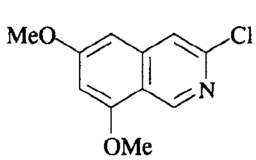
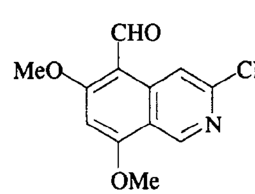
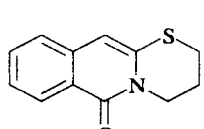
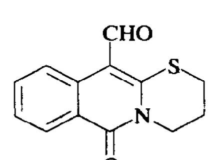
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R¹ Me, R² Me	DMF, $POCl_3$	**I** (92)	
R¹ Et, R² Et	DMF, $POCl_3$	**I** (87)	
$(CH_2)_4$	DMF, $POCl_3$	**I** (83)	
R¹ H, R² Ph	DMF, $POCl_3$, 45°	**I** (77) + **II** (8)	
	DMF, $POCl_3$, 90°	**I** (11) + **II** (57)	
R¹ Me, R² Ph	DMF, $POCl_3$	**III** (37) + **IV** (41)	
R¹ Et, R² Ph	DMF, $POCl_3$	**III** (23) + **IV** (22)	
		C_4NS/C_6	
C_{8-14} 	—	 R = H (—) R = Ph (—)	836
		C_5N/C_6	
C_{11} 	DMF, $POCl_3$	 (40)	837
C_{12} 	DMF, $POCl_3$	 (71)	838

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

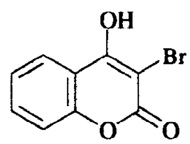
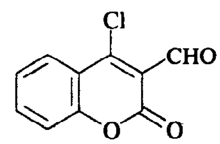
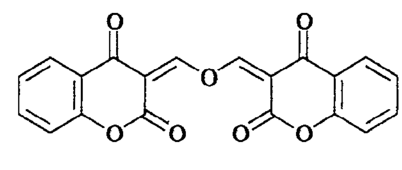
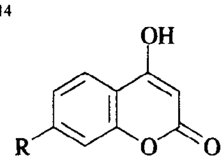
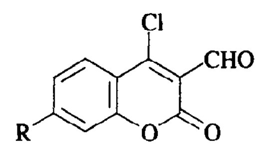
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		C_5O/C_6	
C_9 	DMF, $POCl_3$	 (54) +	839
		 (40)	
$C_{9\text{-}14}$ 	DMF, $POCl_3$		
R			
H		(96)	840, 841
OMe		(70)	841
NMe_2		(75-80)	841
N-piperidyl		(75)	841

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

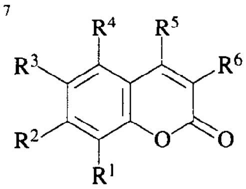
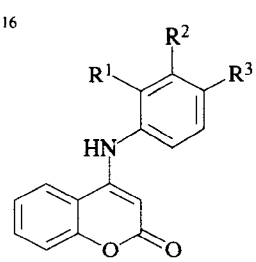
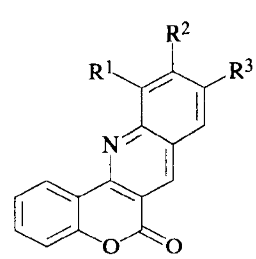
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$C_{9\text{-}17}$ 			
R^1 - R^6 = H except as indicated		R^1 - R^6 as in substrate except as indicated	
$R^3 = R^6 = NO_2$, R^5 = Cl	DMF, $POCl_3$	R^6 = Cl (—) + R^6 = CHO (—)	48
$R^3 = R^6 = NO_2$, R^5 = OH	DMF, $POCl_3$	R^6 = Cl, R^6 = CHO (—) + $R^5 = R^6$ = Cl (—)	48
R^4 = OH, R^5 = Me	MFA, $POCl_3$	R^3 = CHO (9)	842
$R^2 = R^4$ = OH, R^5 = Me	MFA, $POCl_3$	R^1 = CHO (54)	842
$R^2 = R^5$ = Me, R^4 = OH	MFA, $POCl_3$	R^1 = CHO (7) + R^3 = CHO (—)	842
$R^2 = R^4$ = OMe	DMF, $POCl_3$	R^1 = CHO (76)	149
$R^2 = R^4$ = OMe, R^5 = Me	MFA, $POCl_3$	R^1 = CHO (—) + R^3 = CHO (32)	842
$R^2 = R^3 = R^4$ = OMe, R^5 = Me	MFA, $POCl_3$	R^1 = CHO (—)	842
R^5 = NH(C_5H_{11}-*n*)	DMF, $POCl_3$	R^6 = CHO (88)	843
R^5 = NHBn	DMF, $POCl_3$	R^6 = CHO (80)	843, 844
R^5 = $NHCH_2Bn$	DMF, $POCl_3$	R^6 = CHO (81)	843
R^5 = NH($C_6H_3Me_2$-2,4)	DMF, $POCl_3$	R^6 = CHO (67)	843
$C_{14\text{-}16}$ 	DMF, $POCl_3$		

TABLE XVII. OTHER HETEROCYCLES WITH TWO FULLY CONJUGATED RINGS (*Continued*)

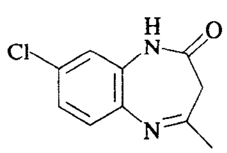
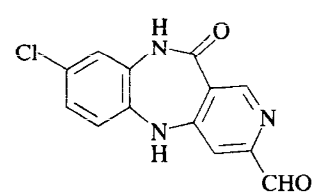
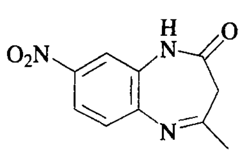
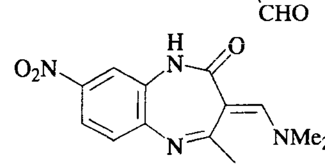
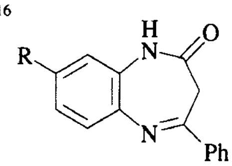
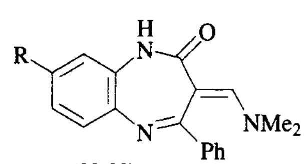
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R^1 R^2 R^3			
H H Cl		(69)	843
H H H		(89)	150, 843
Me H H		(98)	843
OMe H H		(96)	843
H Me H		(86)	150
H H Me		(78)	843
H H OMe		(86)	843
H H OEt		(88)	843
		C_6/C_5N_2	
C_{11} 	DMF, $POCl_3$	 (—)	845
	DMF, $POCl_3$	 (—)	845
$C_{15\text{-}16}$ 	DMF, $POCl_3$		
R = Cl		(20-80)	846
R = H		(52)	847
R = OMe		(30)	846

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS

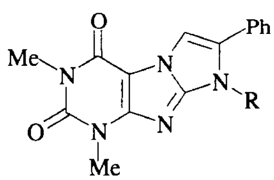
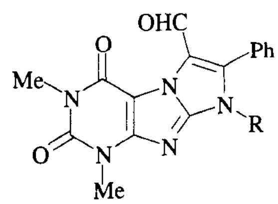
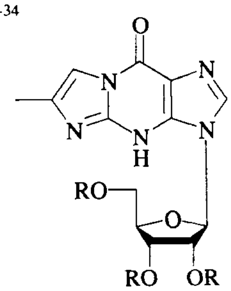
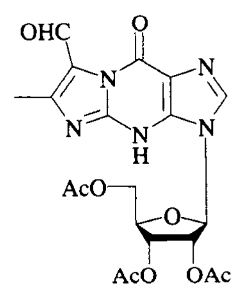
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_3N_2/C_3N_2/C_4N_2$	
C_{16-21}  R = Me, Bu, Ph	DMF, $POCl_3$	 (77-95)	848
		$C_3N_2/C_4N_2/C_5N$	
C_{13-34}  R = H	1. Ac_2O, Py 2. DMF, $POCl_3$	 **I** (92)	170
R = COMe	DMF, $POCl_3$, -25°	**I** (92)	171

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

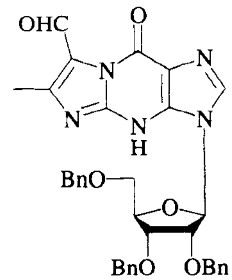
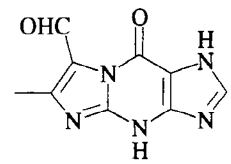
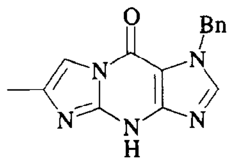
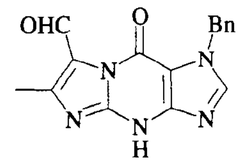
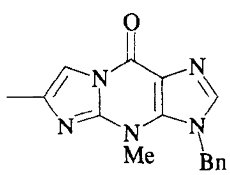
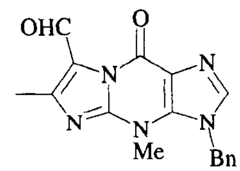
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
R = Bn	DMF, $POCl_3$, -30°	 (63)	171
	DMF, $POCl_3$, rt	 (—)	171
C_{15} 	DMF, $POCl_3$	 (65)	171
C_{16} 	DMF, $POCl_3$	 (100)	849, 850

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

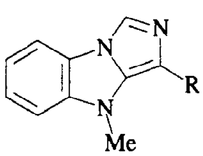
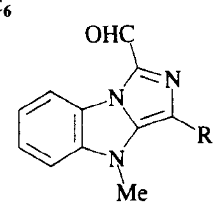
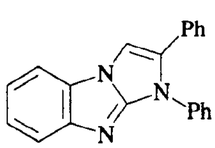
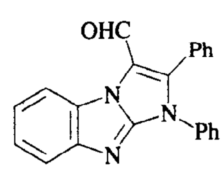
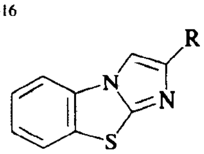
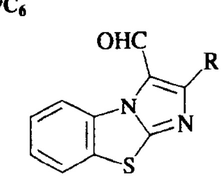
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_3N_2/C_3N_2/C_6$	
C_{11-16}  R = Me, Ph	DMF, $POCl_3$	 (72)	164
C_{21} 	DMF, $POCl_3$	 (88)	165
		$C_3N_2/C_3NS/C_6$	
C_{15-16} 	DMF, $POCl_3$		
R			
Cl		(—)	801
4-ClC_6H_4		(91)	166
4-BrC_6H_4		(62)	166
Ph		(89)	166
4-MeC_6H_4		(92)	166
4-$MeOC_6H_4$		(91)	166

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

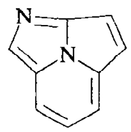
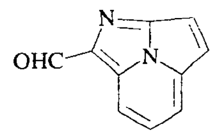
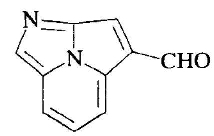
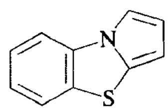
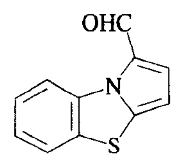
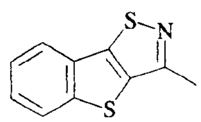
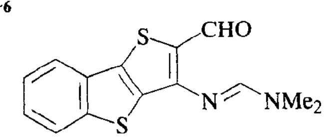
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_3N_2/C_4N/C_5N$	
C_9 	DMF, $POCl_3$	 (37) +  (25)	167
		$C_3NS/C_4N/C_6$	
C_{10} 	DMF, $POCl_3$	 (62)	484
		$C_3NS/C_4S/C_6$	
C_{10} 	—	 (—)	163

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

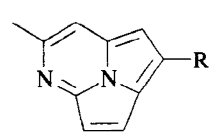
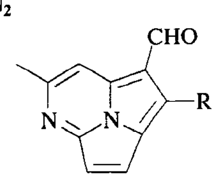
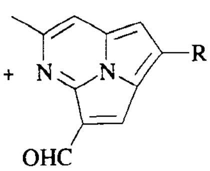
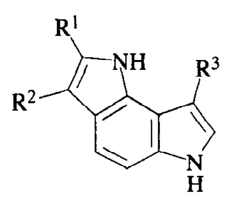
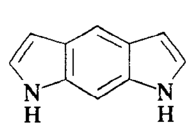
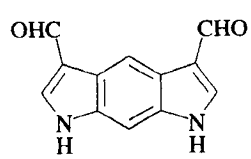
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_4N/C_4N/C_4N_2$	
C_{11-16} 	DMF, $POCl_3$	 **I** +  **II**	145
R = Me		**I** (20) + **II** (27)	
R = Ph		**I** (28) + **II** (28)	
		$C_4N/C_4N/C_6$	
C_{10} 			
$R^1 = R^2 = R^3 = H$		R^1 - R^3 as in substrate except as indicated	
	DMF, $POCl_3$, 1:1	R^1 = CHO (2) + R^3 = CHO (27)	851
	DMF, $POCl_3$, 3:1	$R^1 = R^3$ = CHO (4) + $R^2 = R^3$ = CHO (81)	851
	DMA, $POCl_3$	R^1 = COMe (9) + R^2 = COMe (20) + R^3 = COMe (34) + $R^2 = R^3$ = COMe (6)	852
	DMF, $POCl_3$	 (74)	853

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

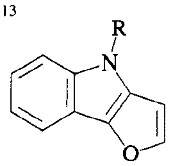
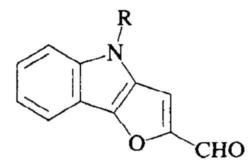
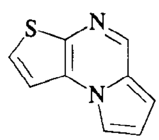
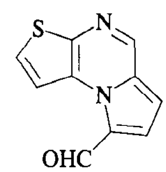
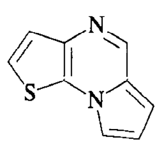
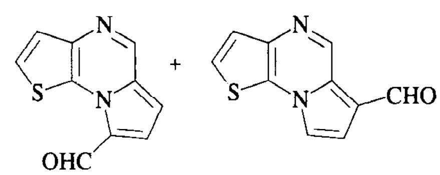
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_4N/C_4O/C_6$	
C_{10-13} 	DMF, $POCl_3$		162
R			
H		(81)	
Me		(82)	
Et		(85)	
n-Pr		(72)	
		$C_4N/C_4S/C_4N_2$	
C_9 	DMF, $POCl_3$	 (82)	168
	DMF, $POCl_3$	 (28) + (9)	169

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

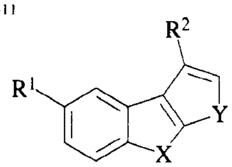
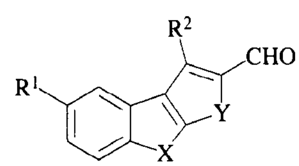
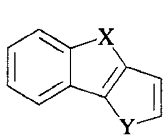
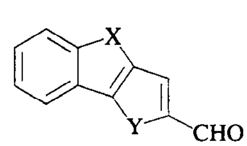
Substrate				Reagents	Product(s) and Yield(s) (%)	Refs.
					$C_4S/C_4S/C_6$ and $C_4S/C_4Se/C_6$	
C_{10-11} 						
R^1	R^2	X	Y			
H	H	S	S	MFA, $POCl_3$	(83)	161
H	Br	S	S	MFA, $POCl_3$	(95)	854
Me	H	S	S	MFA, $POCl_3$	(91)	854
H	H	S	Se	—	(—)	708
H	H	Se	S	—	(—)	708
H	H	Se	Se	—	(—)	708
						
X	Y					
S	S			MFA, $POCl_3$	(84)	161
S	Se			—	(—)	708
Se	S			—	(—)	708
Se	Se			—	(—)	708

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

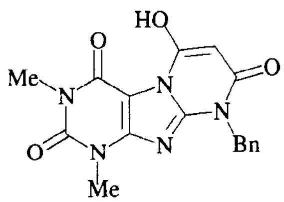
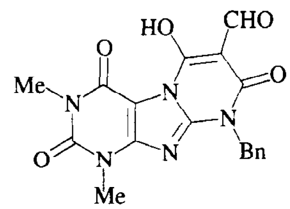
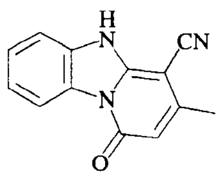
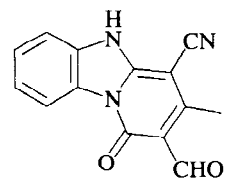
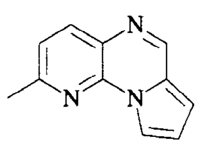
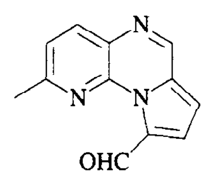
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_3N_2/C_4N_2/C_4N_2$	
C_{17} 	DMF, $POCl_3$	 (82)	855
		$C_3N_2/C_5N/C_6$	
C_{13} 	DMF, $POCl_3$	 (84)	856
		$C_4N/C_4N_2/C_5N$	
C_{11} 	DMF, $POCl_3$	 (47)	857

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

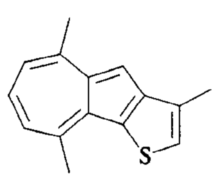
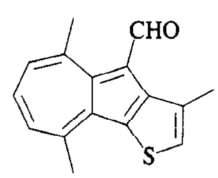
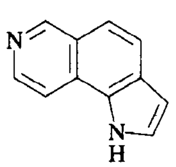
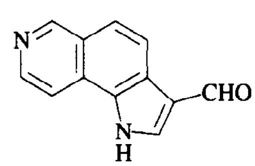
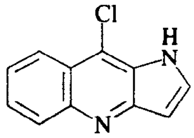
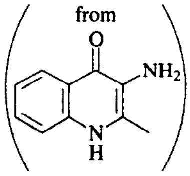
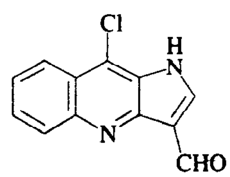
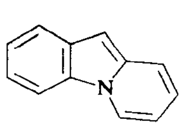
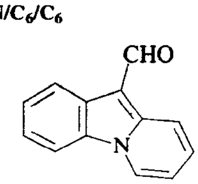
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_4S/C_5/C_7$	
C_{15} 	DMF, $POCl_3$	 (100)	858
		$C_4N/C_5N/C_6$	
C_{11} 	DMF, $POCl_3$	 (41)	859
	(from ) DMF, $POCl_3$	 (97)	860
		$C_4N/C_6/C_6$	
C_{12} 	DMF, $POCl_3$	 (94)	153

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

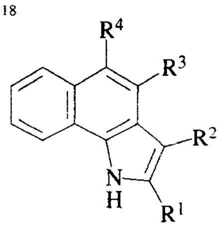
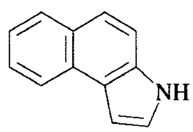
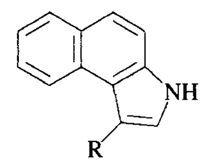
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{12-18} 			
R^1 / R^2 / R^3 / R^4		R^1 - R^4 as in substrate except as indicated	
H / H / H / H	DMF, $POCl_3$	R^2 = CHO (50)	154
	—	R^2 = CHO (6-8) + R^3 = CHO (78-80)	861
CO_2Et / H / H / H	DMF, $POCl_3$	R^2 = CHO (69)	154
CO_2Et / Me / H / H	DMF, $POCl_3$	R^4 = CHO (82)	154
Me / CO_2Et / H / OH	DMF, $POCl_3$	R^3 = CHO (80)	155
Ph / H / H / H	DMF, $POCl_3$	R^2 = CHO (75)	154
		 R	
	DMF, $POCl_3$	CHO (72)	154
	Me_2NCOMe, $POCl_3$	COMe (—)	862
	Et_2NCOMe, $POCl_3$	COMe (—)	862
	Me_2NCOCH_2Cl, $POCl_3$	$COCH_2Cl$ (—)	862
	Et_2NCOCH_2Cl, $POCl_3$	$COCH_2Cl$ (—)	862
	Me_2NCOPh, $POCl_3$	COPh (—)	862
	Et_2NCOPh, $POCl_3$	COPh (—)	862

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

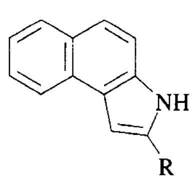
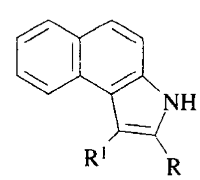
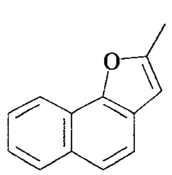
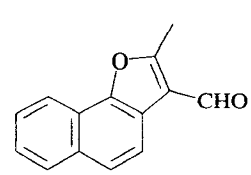
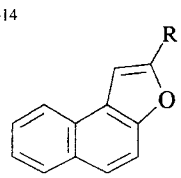
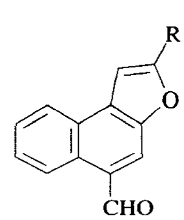
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
 R		 R^1	
CO_2Et	DMF, $POCl_3$	CHO (65)	154
Ph	DMF, $POCl_3$	CHO (74)	154
	$C_4O/C_6/C_6$		
C_{13} 	DMF, $POCl_3$	 (—)	157
C_{13-14} 		 **I**	
R = Me	DMF, $POCl_3$	**I** (—)	157
R = Et	DMF, $POCl_3$	**I** (—)	157

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

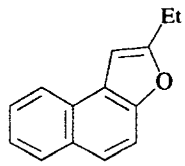
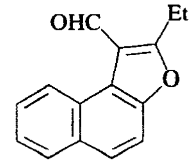
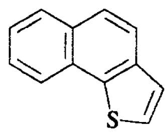
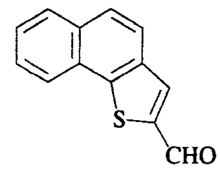
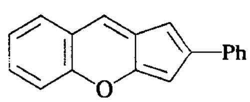
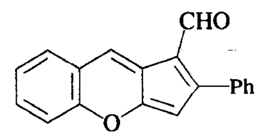
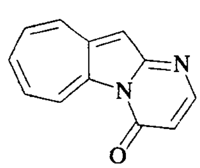
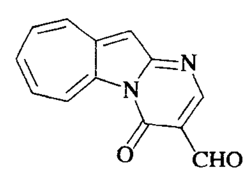
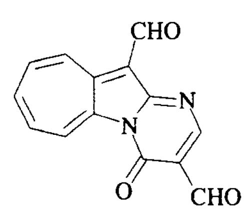
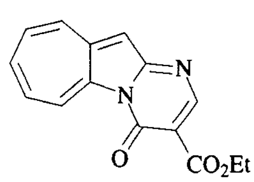
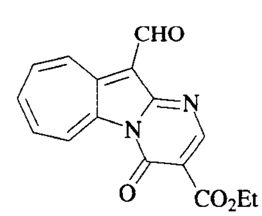
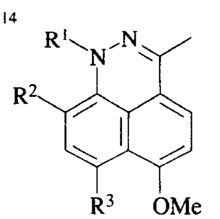
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (50)	156
		$C_4S/C_6/C_6$	
C_{12} 	DMF, $POCl_3$	 (69)	863
		$C_5/C_5O/C_6$	
C_{17} 	DMF, $POCl_3$	 (92)	864
		$C_4N/C_4N_2/C_7$	
	DMF, $POCl_3$	 (24) +	865

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		 (18)	
	DMF, $POCl_3$	 (44)	865
		$C_4N_2/C_6/C_6$, $C_4NO/C_6/C_6$, and $C_4NS/C_6/C_6$	
C_{13-14} 			866

R^1	R^2	R^3	Reagents	R^1 - R^3 as in substrate except as indicated
H	H	H	DMF, $POCl_3$	R^1 = CHO (5) + R^2 = CHO (33) + R^3 = CHO (3) + R^1 = R^3 = CHO (30)
			DMA, $POCl_3$	R^2 = COMe (75)
Me	H	H	DMF, $POCl_3$	R^3 = CHO (87)
			1. DMF, $POCl_3$ 2. $HClO_4$	R^3 = $CH{=}NMe_2^+ ClO_4^-$ (66)

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

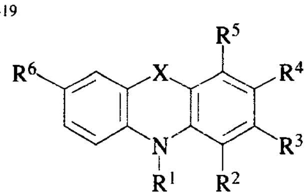
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{13-19} 			
R^1 R^2 R^3 R^4 R^5 R^6 X		X, R^1 - R^3 as in substrate except as indicated	
Me H H H H H O	DMF, $POCl_3$	R^4 = CHO (—)	867
Me H H H H H S	DMF, $POCl_3$	R^4 = CHO (—), R^2 = H or CHO (—)	202
	MFA, $POCl_3$	R^4 = CHO (83)	869, 868
Me H H Cl H H S	DMF, $POCl_3$	R^6 = CHO (—)	202
Me H H H H H NMe	DMF, $POCl_3$	R^4 = CHO (63)	872, 871, 870
Me Me H H H H S	DMF, $POCl_3$	R^6 = CHO (67)	873
Me H Me H H H S	DMF, $POCl_3$	R^4 = CHO (82)	873
Me H H Me H H S	DMF, $POCl_3$	R^4 = CHO (55)	873
Me H H H H Me S	MFA, $POCl_3$	R^4 = CHO (48)	869
Et H H H H H S	MFA, $POCl_3$	R^4 = CHO (84)	874, 869
Et H OMe H H H S	DMF, $POCl_3$	R^4 = CHO (87)	875
Me H Me H Me H S	DMF, $POCl_3$	R^6 = CHO (67)	873
Me H Me H H Me S	DMF, $POCl_3$	R^4 = CHO (85)	873
Et H H H H Me S	MFA, $POCl_3$	R^4 = CHO (72)	869
Ph H H H H H S	MFA, $POCl_3$	R^4 = CHO (63)	869
Ph H H H H Me S	MFA, $POCl_3$	R^4 = CHO (49)	869

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

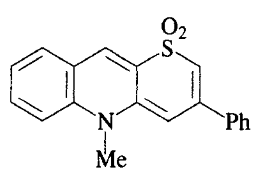
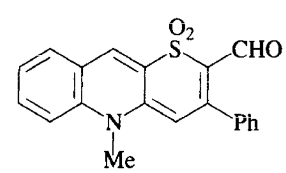
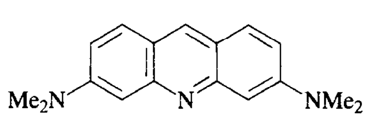
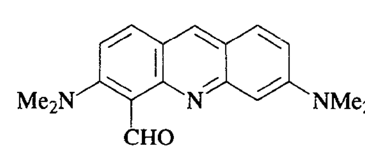
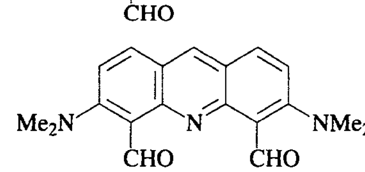
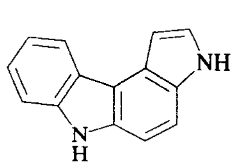
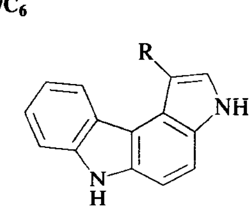
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_5N/C_5S/C_6$	
C_{19} 	1. DMF, $POCl_3$ 2. HBF_4 3. OH^-	 (17)	173
		$C_5N/C_6/C_6$	
C_{17} 	DMF, $POCl_3$	 (28)	172
	DMF, $POCl_3$ (xs)	 (62)	172
		$C_4N/C_4N/C_6/C_6$	
C_{14} 			
	DMA, $POCl_3$	R = COMe (10)	159
	Me_2NCOCH_2Cl, $POCl_3$	R = $COCH_2Cl$ (40)	159

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

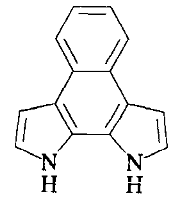
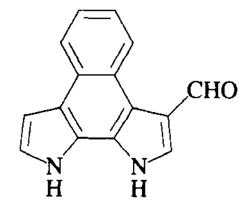
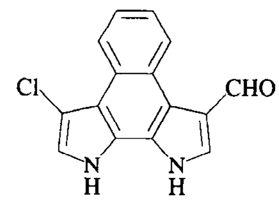
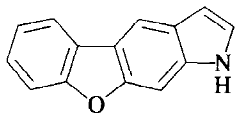
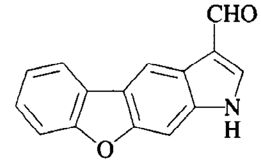
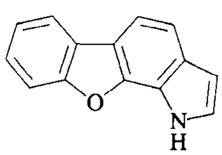
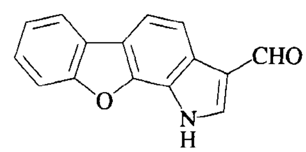
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$, 1:3	 (50)	160
	DMF, $POCl_3$, 1:15	 (64)	160
	$C_4N/C_4O/C_6/C_6$		
C_{14} 	DMF, $POCl_3$	 (88)	876
	DMF, $POCl_3$	 (100)	876

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

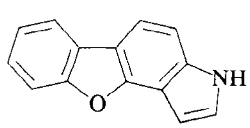
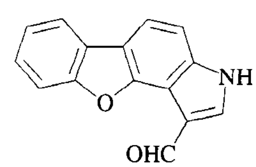
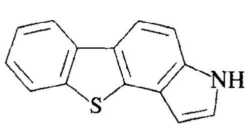
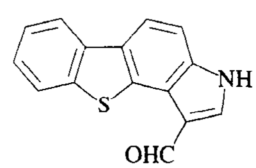
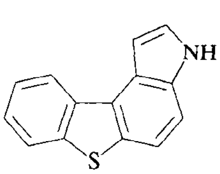
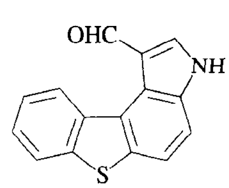
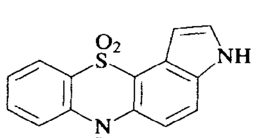
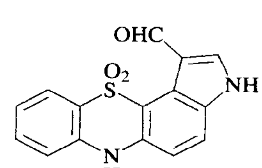
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (100)	876
	$C_4N/C_4S/C_6/C_6$		
C_{14} 	—	 (—)	877
	—	 (—)	878
	$C_4N/C_4NS/C_6/C_6$		
C_{14} 	MFA, $POCl_3$	 (59)	879

TABLE XVIII. OTHER HETEROCYCLES WITH THREE OR MORE FULLY CONJUGATED RINGS (*Continued*)

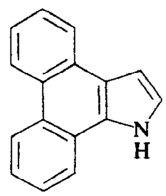
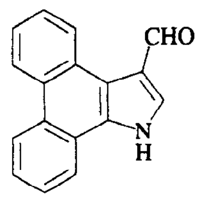
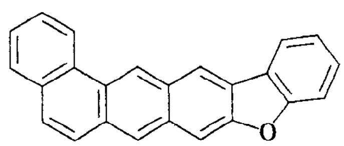
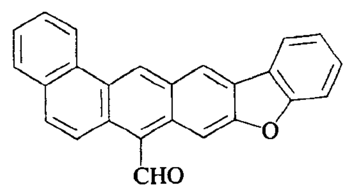
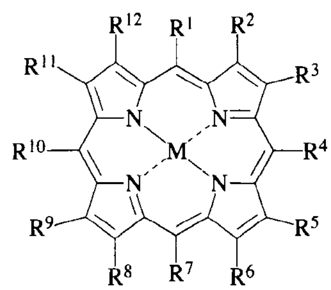
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
		$C_4N/C_6/C_6/C_6$	
C_{16} 	—	 (85)	158
		$C_4O/C_6/C_6/C_6/C_6$	
C_{24} 	MFA, $POCl_3$	 (2)	880

TABLE XIX. PORPHYRINS



R^1 - R^{12} = H except as indicated.
M = H_2 in substrate except as indicated, and is unchanged in the product unless indicated otherwise.

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{20}			
M = Cu	DMF, $POCl_3$	R^4 = CHO (—)	881
C_{28}			
$R^1 = R^4 = R^7 = R^{10} = CO_2Me$	DMF, $POCl_3$	R^3 = CHO (70)	882
C_{32}			
$R^2 = R^5 = R^8 = R^{11}$ = Me, $R^3 = R^6 = R^9 = R^{12}$ = Et, M = Ni	DMF, $POCl_3$	R^1 = CHO (95)	174, 175
$R^2 = R^5 = R^8 = R^{11}$ = Me, $R^3 = R^6 = R^9 = R^{12}$ = Et, M = Cu	DMF, $POCl_3$	R^1 = CHO, M = H_2 (24) + $R^1 = R^7$ = CHO (43) + $R^1 = R^4 = R^7$ = CHO (5)	883
	DMF, $POCl_3$	$R^1 = R^4$ = CHO (16) + $R^1 = R^7$ = CHO (13) + $R^1 = R^4 = R^7$ = CHO (16) + $R^1 = R^4 = R^7 = R^{10}$ = CHO (<1)	884, 885
$R^3 = R^5 = R^9 = R^{11}$ = Me, $R^2 = R^6 = R^8 = R^{12}$ = Et, M = Ni	1. DMF, $POCl_3$ 2. $NaBH_4$	$R^1 = CH_2NMe_2$ (26) + $R^4 = CH_2NMe_2$ (65)	886
$R^3 = R^5 = R^9 = R^{11}$ = Me, $R^2 = R^6 = R^8 = R^{12}$ = Et, M = Cu	DMF, $POCl_3$	R^1 = CHO + R^4 = CHO (95)	886
	1. DMF, $POCl_3$ 2. $NaBH_4$	$R^1 = CH_2NMe_2$ + $R^4 = CH_2NMe_2$ (80-90), 1:2	886

TABLE XIX. PORPHYRINS (*Continued*)

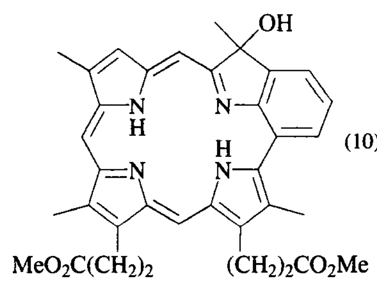
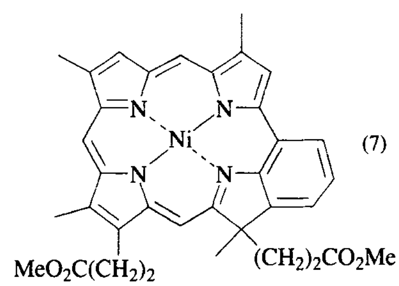
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$R^2 + R^3 = R^5 + R^6 = R^{11} + R^{12} = (CH_2)_4$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	$R^4 = CH{=}CHO$ (65)	176
$R^2 = R^5 = R^9 = R^{11} = Me$, $R^6 = R^8 = (CH_2)_2CO_2Me$, M = Fe	DMF, $POCl_3$	$R^4 = CHO$ (13) + $R^4 = R^{12} = CHO$ (17)	887
$R^2 = R^5 = R^9 = R^{11} = Me$, $R^6 = R^8 = (CH_2)_2CO_2Me$, M = Cu	*i*-Pr_2NCHO, $POCl_3$	$R^1 = CHO$ (13) + $R^3 = CHO$ (28) + $R^4 = CHO$ (5) + $R^{12} = CHO$ (28)	888
	DMF, $POCl_3$	$R^1 = CHO$, $M = H_2$ + $R^3 = CHO$, $M = H_2$ (16) + $R^4 = CHO$, $M = H_2$ (2) + $R^{12} = CHO$, $M = H_2$ (0.5) + $R^3 = R^{12} = CHO$, $M = H_2$ (6) + $R^4 = R^{12} = CHO$, $M = H_2$ (1)	889
$R^2 = R^5 = R^9 = R^{11} = Me$, $R^6 = R^8 = (CH_2)_2CO_2Me$, M = Ni	1. $Me_2NCH{=}CHCHO$, $POCl_3$ 2. H_2SO_4 (conc.)	 (10) +  (7)	176

TABLE XIX. PORPHYRINS (*Continued*)

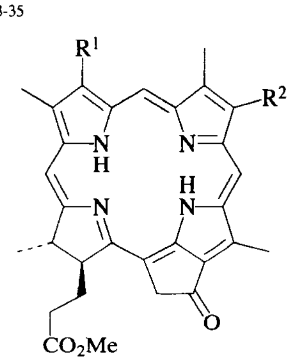
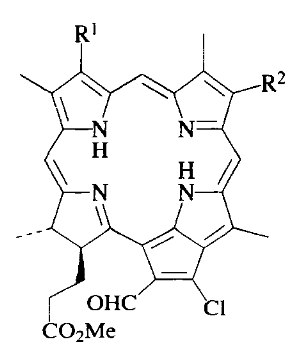
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{33}			
$R^1 = R^3 = R^5 = R^9 = R^{11} = Me$, $R^2 = R^6 = R^8 = R^{12} = Et$, M = Ni	1. DMF, $POCl_3$ 2. $MeNH_2$	$R^4 = CH{=}NMe$ + $R^7 = CH{=}NMe$ (—), 9:1	890
$R^1 = R^2 = R^6 = R^8 = R^{12} = Me$, $R^3 = R^5 = R^9 = R^{11} = Et$, M = Ni	1. DMF, $POCl_3$ 2. $MeNH_2$	$R^4 = CH{=}NMe$ (46) + $R^7 = CH{=}NMe$ (46)	890
$R^1 + R^{12} = (CH_2)_2$, $R^2 = R^6 = R^8 = Me$, $R^3 = R^5 = R^9 = R^{11} = Et$, M = Ni	1. DMF, $POCl_3$ 2. $MeNH_2$	$R^4 = CH{=}NMe$ (14) + $R^7 = CH{=}NMe$ (57) + $R^{10} = CH{=}NMe$ (tr)	890
$R^2 + R^3 = (CH_2)_5$, $R^5 + R^6 = R^{11} + R^{12} = (CH_2)_4$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	$R^4 = CH{=}CHCHO$ (72)	176
	$Me_2NCH{=}CHCHO$, $POCl_3$, (xs)	$R^1 = R^4 = CH{=}CHCHO$ (44)	176
$C_{33\text{-}35}$  R^1 = CHOHMe or Et R^2 = Et, *n*-Pr, *i*-Bu	DMF, $POCl_3$	 (—)	891

TABLE XIX. PORPHYRINS (*Continued*)

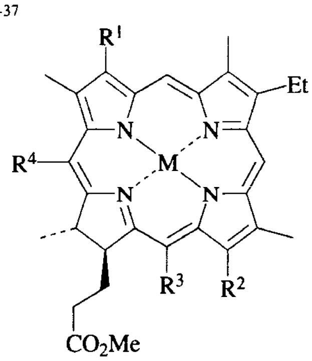
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{34}			
$R^2 = R^5 = R^6 = R^{11} = Me$, $R^3 = (CH_2)_2OH$, $R^6 = R^8 = (CH_2)_2CO_2Me$, M = Cu	$i\text{-}Bu_2NCHO$, $POCl_3$	$R^3 = (CH_2)_2Cl$, $R^{12} = CHO$ (44) + $R^3 = (CH_2)_2Cl$ (10) + *meso*-CHO (20)	177
$R^2 = R^5 = R^9 = R^{11} = Me$, $R^3 = R^{12} = Et$, $R^6 = R^8 = n\text{-}Pr$, M = Cu	DMF, $POCl_3$	$R^7 = CHO$ (75)	892
$C_{34\text{-}37}$  I			
I, $R^1 = Et$, $R^2 + R^3 = COCH_2$, $R^4 = H$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	**I**, $R^1 = Et$, $R^2 + R^3 = COCH_2$, $R^4 = CH{=}CHCHO$ (83)	176
I, $R^1 = CH{=}CH_2$, $R^2 + R^3 = COCH_2$, $R^4 = H$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	**I**, $R^1 = CH{=}CH_2$, $R^2 + R^3 = COCH_2$, $R^4 = CH{=}CHCHO$ (63)	176
I, $R^1 = CH{=}CH_2$, $R^2 = R^4 = H$, $R^3 = CH_2CO_2Me$, M = Fe	DMF, $POCl_3$	**I**, $R^1 = CH{=}CHCHO$, $R^2 = R^4 = H$, $R^3 = CH_2CO_2Me$ (40)	887
I, $R^1 = CH{=}CH_2$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = H$, M = Cu	DMF, $POCl_3$	**I**, $R^1 = CH{=}CHCHO$, $R^2 = CO_2Me$, $R^3 = CH_2COMe$, $R^4 = H$ (35)	893
I, $R^1 = (CH_2)_2OH$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = H$, M = Cu	DMF, $POCl_3$	**I**, $R^1 = (CH_2)_2Cl$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = CHO$ (65)	894
I, $R^1 = CH{=}CH_2$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = H$, M = Fe	DMF, $POCl_3$	**I**, $R^1 = CH{=}CHCHO$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = H$ (7) + **I**, $R^1 = CH{=}CHCHO$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = CHO$ (28)	887
I, $R^1 = Et$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = H$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	**I**, $R^1 = Et$, $R^2 = CO_2Me$, $R^3 = CH_2CO_2Me$, $R^4 = CH{=}CHCHO$ (89)	176
C_{36}			
$R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	$R^4 = CH{=}CHCHO$ (85)	176
	$Me_2NCH{=}CHCHO$, $POCl_3$ (xs)	$R^1 = R^4 = CH{=}CHCHO$ (55)	176
$R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$, M = Cu	DMF, $POCl_3$	$R^1 = CHO$ (20) + $R^1 = R^4 = CHO$ (11) + $R^1 = R^7 = CHO$ (10) + $R^1 = R^4 = R^7 = CHO$ (9) + $R^1 = R^4 = R^7 = R^{10} = CHO$ (1)	885
	DMF, $POCl_3$	$R^1 = CHO$ (72)	892
	$Me_2NCH{=}CHCHO$, $POCl_3$	$R^1 = CH{=}CHCHO$ (57)	176
$R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$, M = Cu	DMF, $POCl_3$	$R^1 = R^7 = CHO$ + $R^1 = R^4 = CHO$ (23) + $R^1 = R^4 = R^7 = CHO$ (9) + $R^1 = R^4 = R^7 = R^{10} = CHO$ (<1)	884

TABLE XIX. PORPHYRINS (*Continued*)

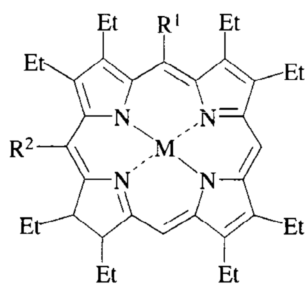
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$R^2 = R^5 = R^9 = R^{11} = Me$, $R^3 = R^{12} = Et$, $R^6 = R^8 = (CH_2)_2CO_2Me$, M = Cu, Ni, Fe, Co	DMF, $POCl_3$	various *meso*-CHO	895
$R^2 = R^5 = R^9 = R^{11} = Me$, $R^3 = R^{12} = CH{=}CH_2$, $R^6 = R^8 = (CH_2)_2CO_2Me$, M = Fe	DMF, $POCl_3$	$R^{12} = CH{=}CHCHO$ (5) + $R^3 = R^{12} = CH{=}CHCHO$ (15)	887
 I			
I, $R^1 = R^2 = H$, M = Cu	DMF, $POCl_3$	**I**, $R^1 = H$, $R^2 = CHO$ (—) + $R^1 = R^2 = CHO$ (—)	896
I, $R^1 = R^2 = H$, M = Ni	$Me_2NCH{=}CHCHO$, $POCl_3$	**I**, $R^1 = H$, $R^2 = CH{=}CHCHO$ (81)	176
C_{38}			
$R^1 = CH{=}CH_2$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$, M = Co	DMF, $POCl_3$, 20°	$R^1 = CH{=}CHCHO$, $R^7 = Cl$ (4) + $R^1 = CH{=}CHCHO$ (85)	897
	DMF, $POCl_3$, 50°	$R^1 = R^7 = CH{=}CHCHO$ (20)	897
$R^1 = CH{=}CH_2$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$, M = Ni	—	$R^1 = CH{=}CHCHO$ (—)	898

TABLE XIX. PORPHYRINS (*Continued*)

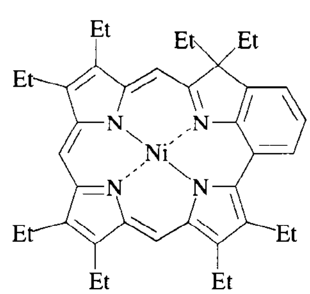
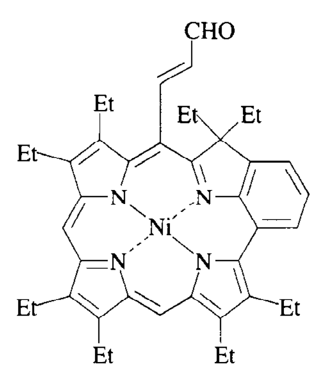
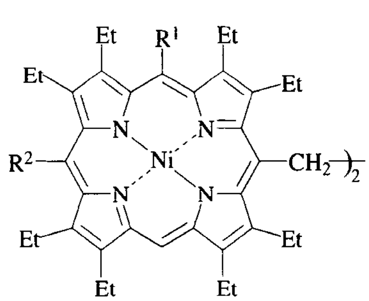
Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{39}			
	$Me_2NCH{=}CHCHO$, $POCl_3$	 (90)	176
C_{40}			
$R^2 = R^5 = R^8 = R^{11} = Me$, $R^3 = R^6 = R^9 = R^{12} = (CH_2)_2CO_2Me$, M = Ni	DMF, $POCl_3$	$R^1 = CHO$ (83)	174
C_{44}			
$R^3 = R^5 = R^9 = R^{11} = Me$, $R^4 = R^{10} = 4\text{-}O_2NC_6H_4$, $R^2 = R^6 = R^8 = R^{12} = Et$, M = Ni	DMF, $POCl_3$	$R^1 = CHO$ (44)	899
$R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Pr$, M = Ni	1. DMF, $POCl_3$ 2. $MeNH_2$ 3. H_2SO_4	$R^4 = CH{=}NMe$, $M = H_2$ (83)	900
$C_{44\text{-}58}$			901
$R^1 = R^4 = R^7 = R^{10} = Ph$, M = Cu	DMF, $POCl_3$	$R^3 = CHO$ (99)	901
$R^1 = R^4 = R^7 = R^{10} = Ph$, M = Co	DMF, $POCl_3$	$R^4 = CH{=}NMe_2^+\ {}^-OPOCl_2$ (97)	901
	1. DMF, $POCl_3$ 2. H_2SO_4 (conc) 3. NaOAc	$R^3 = CHO$, $M = H_2$ (65)	

TABLE XIX. PORPHYRINS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
$R^1 = R^4 = R^7 = R^{10}$ = 4-MeC_6H_4, $M = H_2$	DMF, $POCl_3$	R^3 = CHO (50) + dialdehyde (2)	902
M = Cu	DMF, $POCl_3$	R^3 = CHO (58)	902
M = Co	1. DMF, $POCl_3$ 2. Py	R^3 = CHO, M = $Co(Py)_2$ (71)	902
M = Ni	DMF, $POCl_3$	R^3 = CHO (81)	902
M = Pd	DMF, $POCl_3$	R^3 = CHO (87)	902
M = Pt	DMF, $POCl_3$	R^3 = CHO (84)	902
M = $FeCl_2$	DMF, $POCl_3$	R^3 = CHO (16)	902
M = $Al(OH)_2$	DMF, $POCl_3$	R^3 = CHO (59)	902
M = $Cr(OH)_2$	1. DMF, $POCl_3$ 2. Py	R^3 = CHO, M = $Cr(Py)_2$ (63)	902
M = CoClPy	DMF, $POCl_3$	R^3 = CHO (65)	902
M = MnOMe	DMF, $POCl_3$	R^3 = CHO, M = H_2 (14)	902
C_{46}			
$R^3 = R^5 = R^9 = R^{11}$ = Me, $R^4 = R^{10}$ = 4-MeC_6H_4, $R^2 = R^6 = R^8 = R^{12}$ = Et, M = Ni	DMF, $POCl_3$	R^1 = CHO (90)	899
$R^3 = R^5 = R^9 = R^{11}$ = Me, $R^4 = R^{10}$ = Ts, $R^2 = R^6 = R^8 = R^{12}$ = Et, M = Ni	DMF, $POCl_3$	R^1 = CHO (90)	899
C_{48}			
$R^3 = R^5 = R^9 = R^{11}$ = Me, $R^4 = R^{10}$ = 4-$Me_2NC_6H_4$, $R^2 = R^6 = R^8 = R^{12}$ = Et, M = Ni	DMF, $POCl_3$	R^1 = CHO (60)	899

TABLE XIX. PORPHYRINS (*Continued*)

Substrate	Reagents	Product(s) and Yield(s) (%)	Refs.
C_{56}			
$R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12}$ = Et, $R^4 = R^{10}$ = 1-(2-naphtholyl), M = Ni + $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12}$ = Et, $R^7 = R^{10}$ = 1-(2-naphtholyl), M = Ni	DMF, $POCl_3$	R^1 = CHO (65)	903
C_{64}			
$R^1 = R^4 = R^7 = R^{10}$ = $C_6H_4NHCOBu$-*t*, M = Cu	1. DMF, $POCl_3$ 2. $NaBH_4$	R^1 = CH_2OH (—)	904
	DMF, $POCl_3$	R^1 = CHO (66)	905
C_{73}			
	DMF, $POCl_3$	R^2 = CHO (17) + $R^1 = R^{1'}$ = CHO (2) + $R^2 = R^{2'}$ = CHO (33) + $R^2 = R^{1'}$ = CHO (16)	906

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[6 + 4] Cycloaddition Reactions

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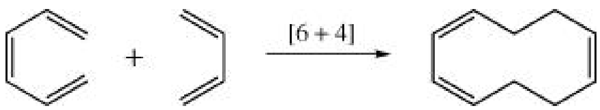
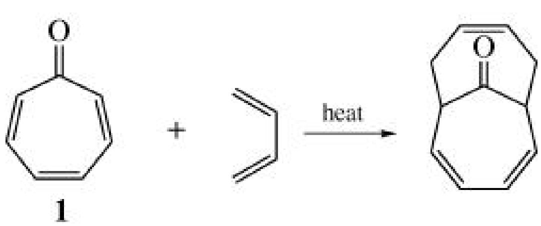
1. Introduction

Higher-order cycloaddition reactions possess many of the attributes that have made the Diels–Alder reaction so useful in synthesis, including high stereoselectivity, rapid increase in molecular complexity, and the ability to accommodate substantial functionalization in both reaction partners. The limiting feature of many higher-order processes, however, is a lack of periselectivity that translates directly into relatively low chemical yields of the desired cycloadducts.



[6 π + 4 π] Cycloaddition reactions are typical higher-order transformations in that they exhibit many of the attractive features delineated above, but afford only modest yields of adducts in many instances. The engagement of the 6 π and 4 π components in these reactions often results in multiple, competitive pericyclic events that yield numerous cycloaddition products. The obvious synthetic potential offered by this class of reactions has prompted recent developments, such as metal mediation, that have successfully addressed the periselectivity issue and, as a result, have considerably broadened the synthetic scope and utility of the reaction. (1)

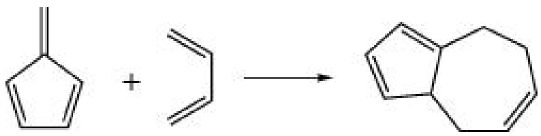
The thermally allowed [6 + 4] cycloaddition of 2,4,6-cycloheptatrien-1-one (tropone) **(1)** has been well studied and offers substantial opportunities for assembling functionally rich and stereochemically homogeneous bicyclic systems (Eq. 1). Typically, the triene partner is heated at 80–140° in the presence of excess



(1)

diene (trienophile) to afford a bicyclo[4.4.1]undecene ring system that is sufficiently functionalized to permit subsequent manipulations. The scope of this transformation for preparative purposes is somewhat restricted, however, since only a limited set of diene partners will effectively participate. For example, electron-rich dienes constitute the majority of reactants that afford meaningful yields of bicyclo[4.4.1]undecane products upon reaction with **1**.

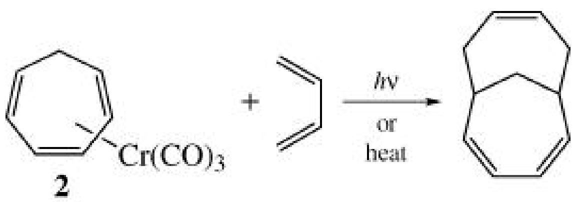
A variety of substituted fulvene species also participate as effective 6 π partners in a closely related set of [6 + 4] cycloaddition reactions (Eq. 2). The range of



(2)

useful 4 π partners is reasonably broad and rapid access to functionalized polycycles of considerable synthetic interest can be achieved with these transformations.

More recently, transition metal promoted versions of the [6 + 4] cycloaddition have been developed. (2, 3) Group VI metals (Cr and Mo) have been identified as capable promoters for this transformation, with chromium(0) emerging as the metal of choice for most applications (Eq. 3). The ring-forming event in this case can



(3)

be achieved through either thermal or photochemical activation, and the metal-promoted process has proven to accommodate a much wider range of triene and trienophilic participants than the thermal metal-free reaction. Unlike the cycloaddition reactions of tropone, the metal-mediated reactions are relatively insensitive to the electronic nature of the diene partner, and high chemical yields of stereochemically homogeneous products are typical for these reactions. It is noteworthy that, in certain instances, reactions employing sub-stoichiometric quantities of metal have been reported. (4)

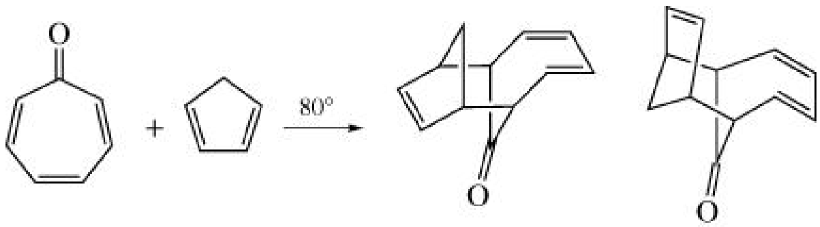
This chapter covers the thermal, metal-free [6 + 4] cycloaddition chemistry of tropone and related trienes, fulvenes, and metal-promoted reactions through mid-1995. Aspects of both the metal-mediated and metal-free versions of the

[6 + 4] cycloaddition reaction have been reviewed. (1-3)

2. Mechanism and Stereochemistry

2.1. Tropone–Diene Cycloadditions

2,4,6-Cycloheptatrien-1-one (tropone) (**1**) reacts with cyclopentadiene at 80° to form a single 1:1 adduct **3**, displaying *exo* stereochemistry (Eq. 4). (5, 6) No evidence



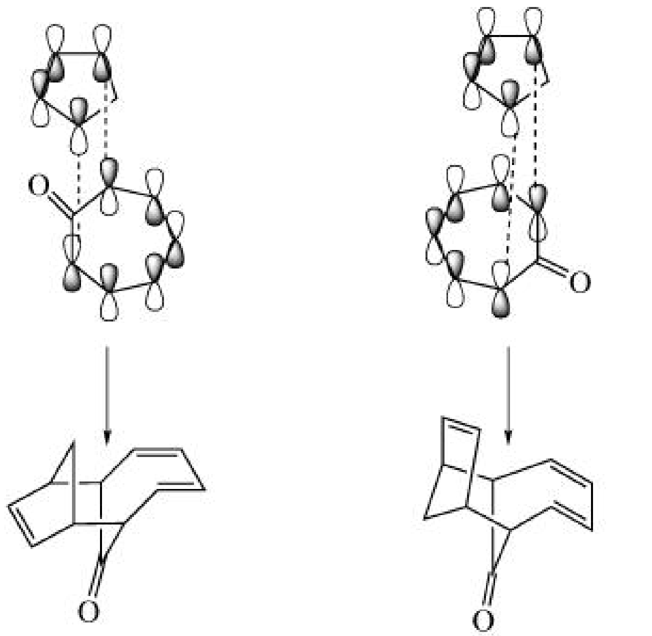
3 (100%) 4 (0%)

(4)

for the alternative *endo* product **4** is observed. It is noteworthy that the *exo* stereochemical preference in the [6 + 4] cycloaddition had been predicted, employing Woodward–Hoffmann orbital symmetry selection rules, a year before it was observed experimentally. (7) Subsequently, it has been found that virtually all metal-free [6 + 4] cycloadditions of cyclic trienes afford *exo* products.

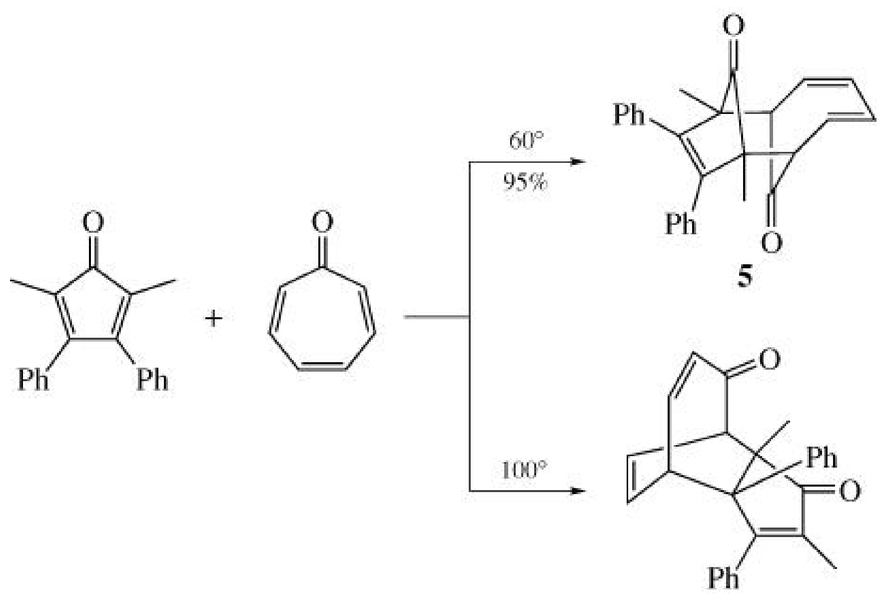
The stereochemical preferences as well as the periselectivity of the [6 + 4] cycloaddition can be rationalized by consideration of the HOMO and LUMO interactions of the diene and triene participants, respectively. (8) Orbital combinations for the *exo* and *endo* transition states are presented in Figure 1. (9) An unfavorable repulsive secondary orbital interaction develops during an *endo* approach of the diene to the 6 π partner, which is avoided in the *exo* transition state. Studies of this reaction at high pressure suggest that favorable secondary orbital interactions in the *exo* transition state may be involved (activation volume, – 7.5 cm^3mol^{-1}). (10) However, other work appears to be more consistent with only a minimal attractive secondary orbital interaction in these processes. (11-13)

Figure 1. Frontier molecular orbitals for the cycloaddition of cyclopentadiene to tropone.



Exo transition state *Endo* transition state

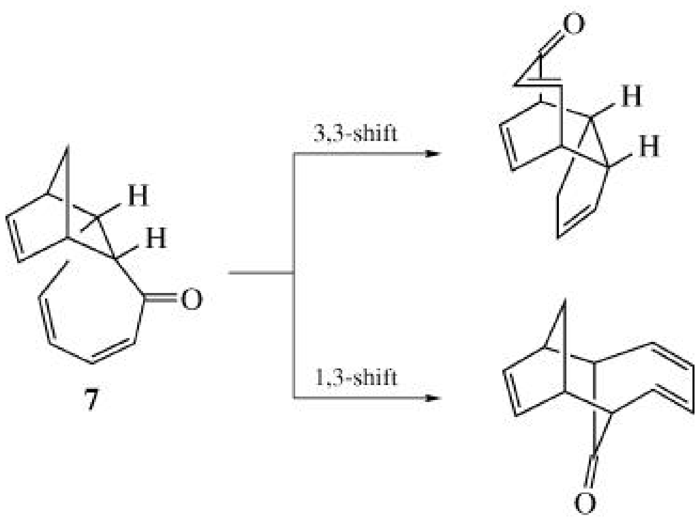
From the earliest investigations on the [6 + 4] tropone–diene cycloaddition, it was noted that the periselectivity of the reaction varied as a function of reaction temperature. (14-16) For example, heating tropone **(1)** and 2,5-dimethyl-3,4-diphenylcyclopentadienone at 60° affords a high yield of the *exo*-[6 + 4] adduct **5.** In contrast, the same combination heated at 100° provides primarily the *endo* [4 + 2] adduct **6** (Eq. 5). (15) Furthermore, heating [6 + 4] adducts at elevated temperatures can often effect cycloreversion to the component reactants. (5)



(5)

These and related observations are attributed to the operation of a concerted, kinetic *exo* [6 + 4] pathway and a thermodynamic *endo*-[4 + 2] pathway in these reactions. Additionally, other kinetic studies on the [6 + 4] tropone–diene cycloaddition ($\triangle H^{\ddagger}$ = 15.3 kcal mol^{-1}; $\triangle S^{\ddagger}$ = –35 eu at 100°) conclude that the higher-order reaction channel possesses a late transition state, consistent with a concerted process, and mechanistically resembles the Diels–Alder reaction. (10-13)

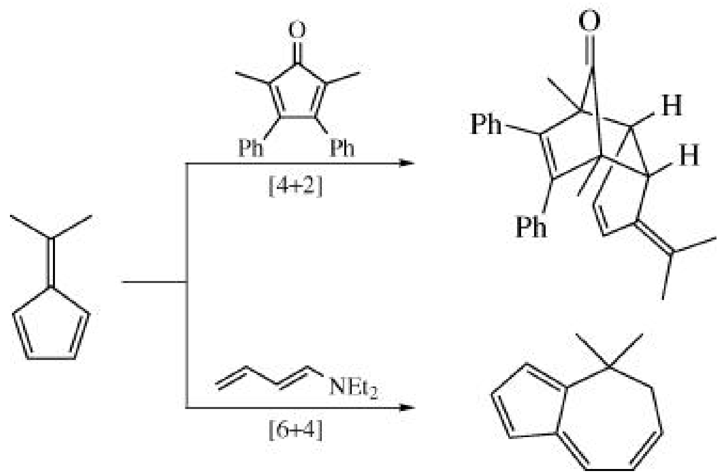
An alternative reaction pathway, outlined in Eq. 6, has been proposed to explain the observed stereo- and periselectivity profiles of the tropone–diene cycloaddition, but direct experimental support for this mechanism is currently lacking. (17)



(6)

2.2. Fulvene–Diene Cycloadditions

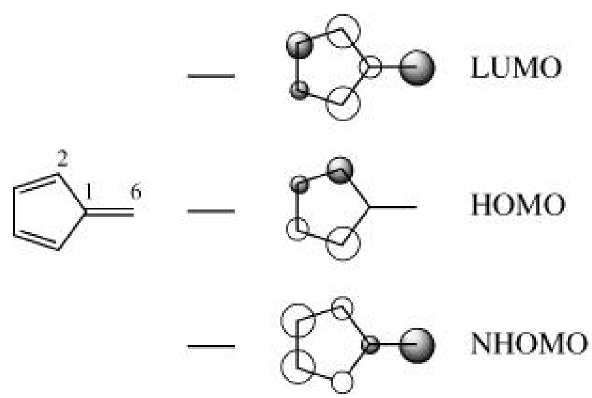
Fulvenes, like their troponoid counterparts, engage dienes in multiple pericyclic reactions, and Eq. 7 reveals typical examples of two of these reaction channels. (18, 19)



(7)

Fulvenes can participate as either 6 π or 2 π reactants in these transformations, and the factors governing which reactivity is expressed in a particular case have been elucidated, employing frontier molecular orbital considerations. The relevant fulvene orbitals are displayed in Figure 2. (20, 21)

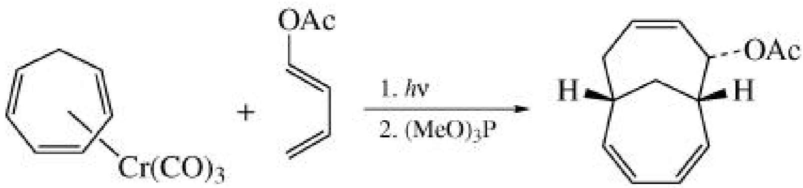
Figure 2. The frontier molecular orbitals of fulvene.



The controlling orbitals in the reaction of a fulvene with an electron-deficient diene are the fulvene HOMO and the diene LUMO. The large coefficients at C-2 and C-3, as well as the node through C-1 and C-6, dictate that the fulvene will participate as a 2 π partner in this situation (see Eq. 7). On the other hand, LUMO-controlled reactions with electron-rich diene partners should react at C-6 and C-2, affording [6 + 4] adducts. Occasionally, products derived from reaction at C-1 and C-6 under these circumstances are also observed. Furthermore, strongly electron-donating substituents located at the C-6 position of fulvene elevate the next highest occupied molecular orbital (NHOMO) sufficiently to permit the [6 + 4] mode of cycloaddition to prevail with electron-deficient 4 π systems. Examples of this type of reaction are presented subsequently.

2.3. Metal-Promoted Cycloadditions

In contrast to thermal, metal-free [6 + 4] cycloadditions, reactions of metal-complexed trienes are known to furnish exclusively *endo* products, rendering the two pathways stereocomplementary. A typical example of this transformation is depicted in Eq. 8, in which photoactivated cycloaddition initially affords the



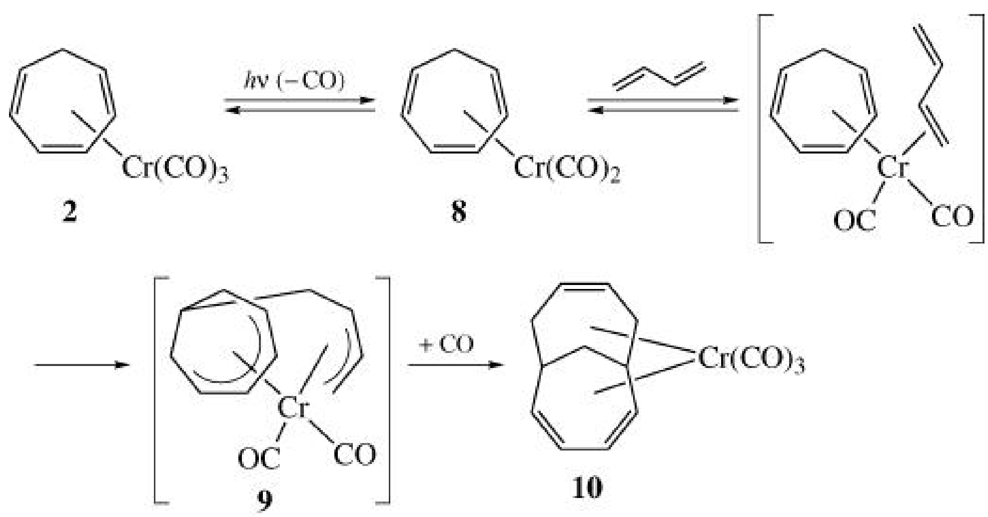
(8)

cycloadduct– $Cr(CO)_3$ complex, and subsequent treatment with trimethyl phosphite provides the metal-free organic product. (22)

Two mechanistic pathways are proposed for the metal-promoted [6 + 4] cycloaddition that differ primarily in the way in which the initial coordinatively unsaturated intermediates are generated. (23-25)

Scheme 1 depicts the carbon monoxide extrusion based mechanism in which the coordinatively unsaturated species **8** is produced by light-induced dissociation of one CO ligand from complex **2**. (25) The resultant 16-electron intermediate then coordinates with the diene, and bond reorganization affords the Cr(II) complex **9**. At this juncture, recapture of the previously dissociated CO ligand produces the observed [6 + 4] cycloadduct–chromium tricarbonyl complex **10**. Support for this pathway comes from matrix-isolation studies in which species related to **8** were observed to lead to bicyclo[4.4.1]undecane products. (25)

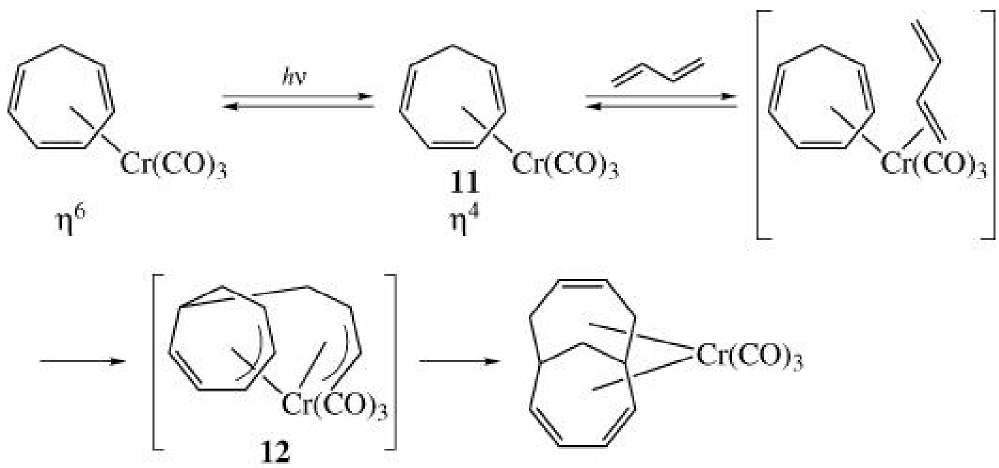
Scheme 1.



An alternative pathway has also been suggested that does not rely on an initial

CO dissociation, but involves a ring "slippage" process to generate the crucial coordinatively unsaturated intermediate. (23, 24) In this instance a reversible, light-induced hapticity change (η^6 ® η^4) occurs to afford 16-electron complex **11**, which then coordinates to the diene. Next, a bond-reorganization event similar to that proposed in Scheme 1 occurs to produce a bis(allyl) intermediate which collapses to the observed cycloadduct complex. This pathway is presented in Scheme 2. The absence of any detectable CO evolution has been cited as evidence in support of this pathway. (24) In addition, the observation that purging the reaction mixture with an inert gas during photolysis results in enhanced yields of cycloadducts is also more consistent with the mechanism presented in Scheme 2. (23) Diminished yields of product would be anticipated under these conditions if the pathway in Scheme 1 were operational in these reactions. (25)

Scheme 2.



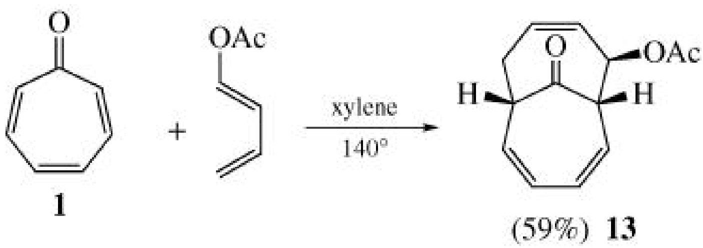
Both mechanistic pathways are consistent with the *endo* nature of the resultant cycloadducts because neither species **9** nor **12** is geometrically capable of accommodating an *exo*-oriented diene component.

3. Scope and Limitations

3.1. Tropone–Diene Cycloadditions

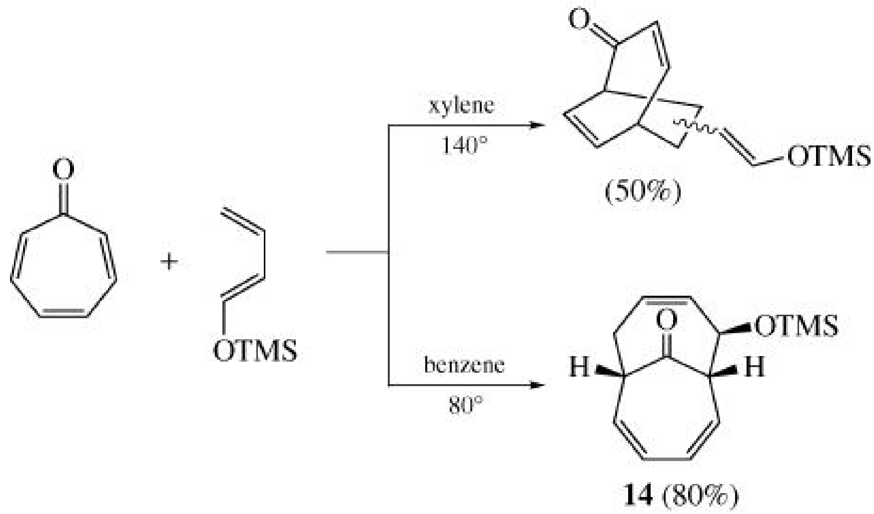
The thermally allowed cycloaddition of tropone and related cyclic trienes with appropriate 4 π reaction partners can offer the opportunity for rapid access to functionalized bicyclic products that are often difficult or impossible to make in other ways. In contrast, most other cyclic triene substrates such as 1,3,5-cycloheptatriene (15) and azepine (26) are frequently poor 6π partners in thermal, metal-free [6 + 4] cycloaddition reactions and offer little synthetic advantage.

The thermally induced cycloaddition between tropone (**1**) and (*E*)-1-acetoxy-1,3-butadiene illustrates many of the salient features of the metal-free [6 π + 4 π] process. (16, 27) Typically, chemical yields are in the range of 60% (occasionally as high as 80%), and the bicyclo[4.4.1]undecatrienone products **13** are isolated in diastereomerically homogeneous form.



(9)

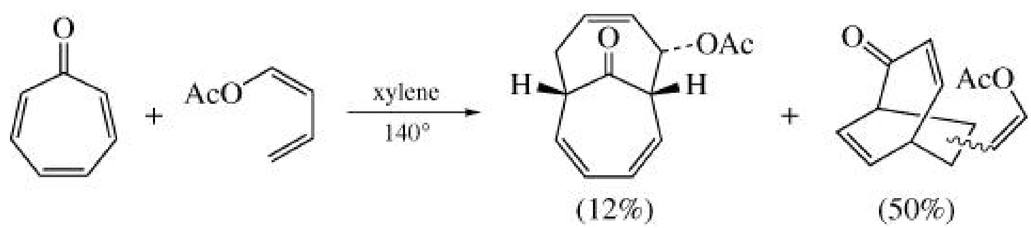
The *exo* isomer is formed to the complete exclusion of the corresponding *endo* species in virtually every known example. Extended reaction times or higher reaction temperatures tend to enhance the yield of other pericyclic products at the expense of higher-order adducts, and an alternative [4 π + 2 π] pathway often prevails under harsher conditions. A good illustration of this phenomenon is the reaction of tropone with (*E*)-1-trimethylsilyloxy-1,3-butadiene at various temperatures (Eq. 10). (16) In benzene at reflux, the electron-rich diene affords an excellent



(10)

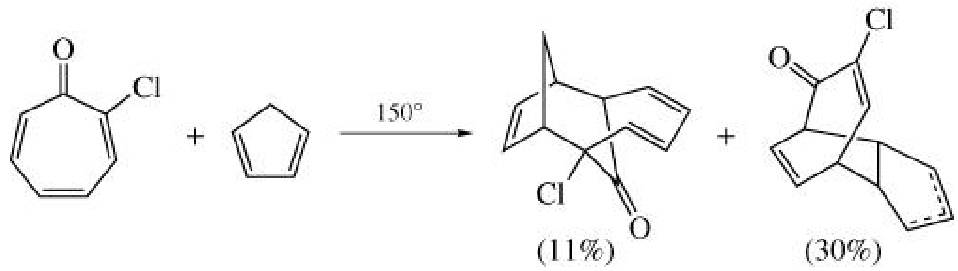
yield of the [6 + 4] cycloadduct, but higher reaction temperature leads to the [4 + 2] adduct nearly exclusively.

Furthermore, only minor structural changes on either reaction partner can have a profound impact on the periselectivity of these transformations. For example, (*Z*)-1-acetoxy-1,3-butadiene affords only a small quantity of [6 + 4] cycloadduct accompanied by a much larger amount of a mixture of isomeric products arising from a [4 π + 2 π] cycloaddition between tropone, participating as the 4 π component, and the diene (Eq. 11a). (16) Other important factors that



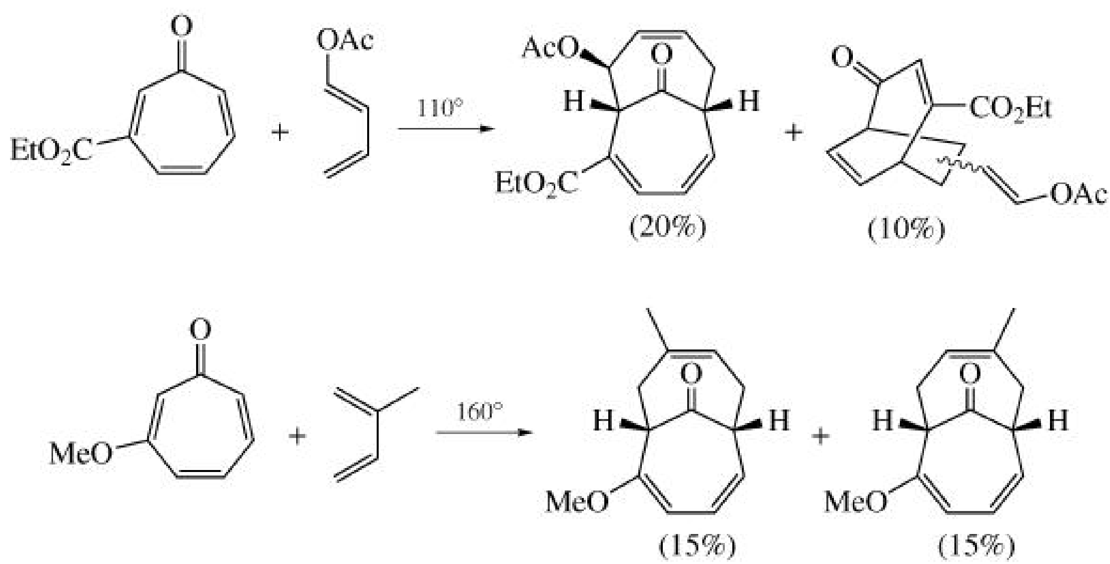
(11a)

affect these reactions include the electronic nature of the diene and the steric environment at the bond-forming centers in the triene. For instance, electron-deficient dienes are normally poor participants in these reactions, and substituents at the 2 position of the tropone partner are known to suppress the higher-order cycloaddition pathway (Eq. 11b). (27, 28)



(11b)

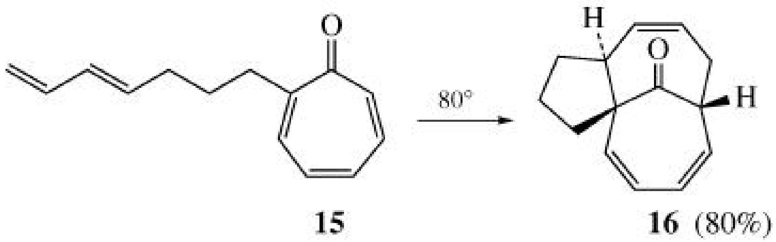
Electronically biased substituents located at sites on the tropone nucleus remote from those participating in bond formation can strongly influence the regiochemical course of the cycloaddition event, although chemical yields tend to be modest in most cases (Eq. 12). (29) It is noteworthy that the regioselectivities exhibited



(12)

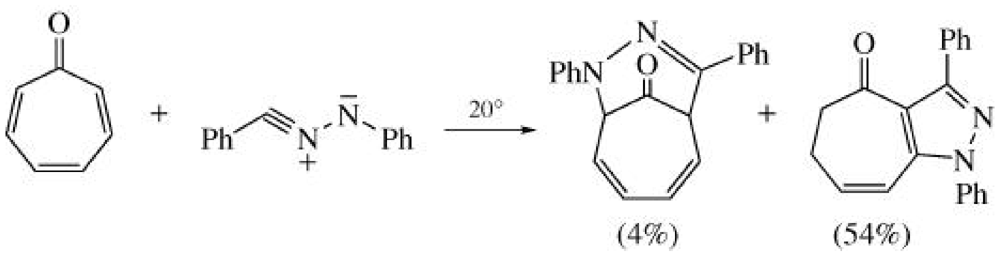
by tropones bearing electron-withdrawing groups in [6 + 4] cycloaddition qualitatively parallel those observed in the Diels–Alder [4 + 2] reaction, whereas 3- and 4-methoxytropone exhibit both low regioselectivity and poor chemical yields, again stressing the crucial role played by the electronic nature of the reactants.

Tethering the diene and triene components together has been an effective ploy for circumventing some of the difficulties encountered with the presence of substituents at the 2-position of tropone. (27, 30) For example, employing a three-carbon spacer permits rapid entry into the ABC tricyclic system of the ingenane diterpenes (Eq. 13). As in the intermolecular version, *exo* stereoselectivity prevails in these transformations.



(13)

1,3-Dipoles have also been examined as 4 π partners in [6 + 4] cycloadditions with tropone; however, only small quantities of higher-order adducts have been isolated in these reactions. (8)

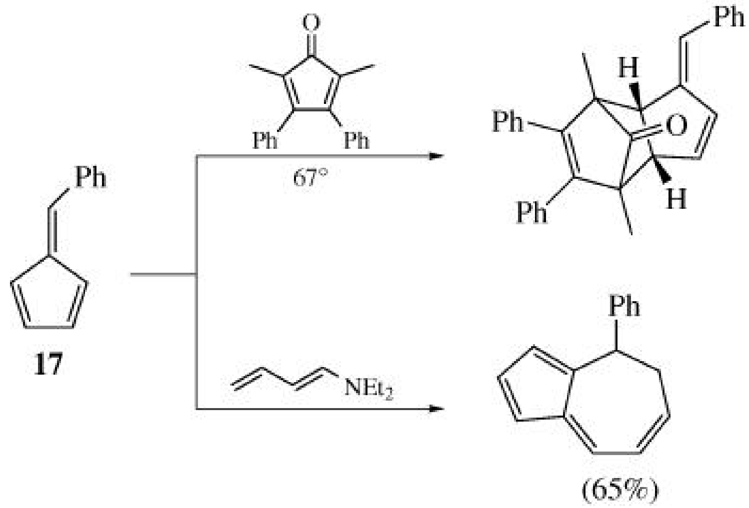


(14)

3.2. Fulvene–Diene Cycloadditions

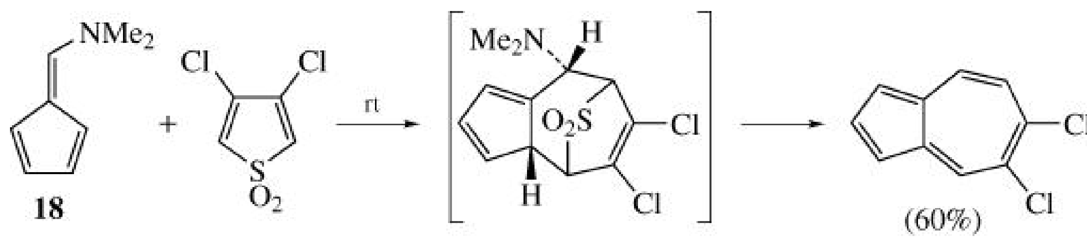
Fulvenes, like the cyclic trienes considered previously, are capable of undergoing multiple, competitive pericyclic reactions with dienes and other 4 π reactants. To a large extent, fulvenes participate in these transformations as either a 6 π or 2 π component, and the factors governing which of these reactivities is expressed in a particular situation have been defined by employing frontier molecular orbital theory (see Fig. 2). (20)

Electron-deficient dienes normally engage fulvenes in a [4 π + 2π] cycloaddition at one of the endocyclic double bonds, (18) while electron-rich dienes react as 4 π components in a [6 π + 4 π] process. (19) An illustration of each of these modes of reaction is given for 6-phenylfulvene (**17**) in Eq. 15. Electron-rich fulvenes



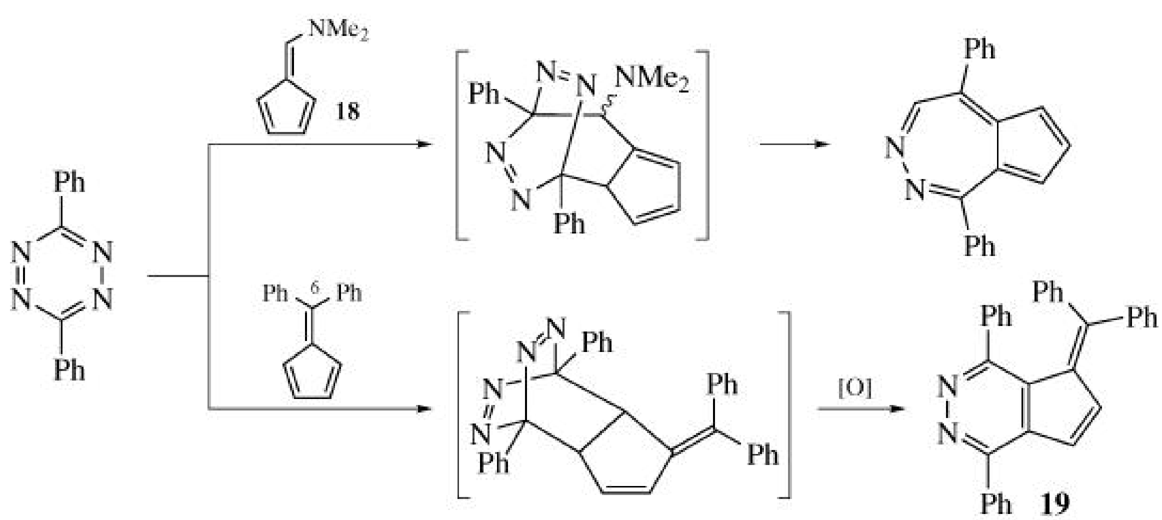
(15)

such as **18** are also known to react with electron-deficient diene partners primarily in the [6 π + 4 π] mode (Eq. 16). (31)



(16)

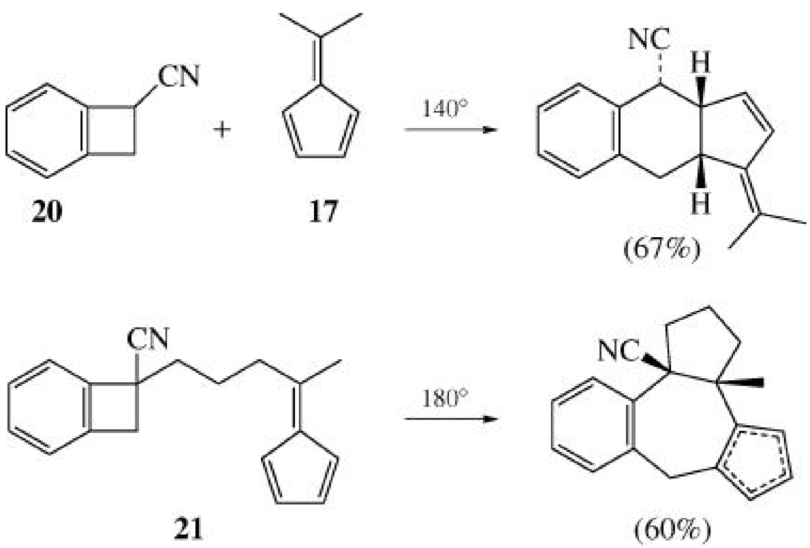
Steric hindrance at the fulvene C-6 position can also influence cycloaddition regiochemistry, as illustrated in Eq. 17. (32) For example, 6-dimethylaminofulvene



(17)

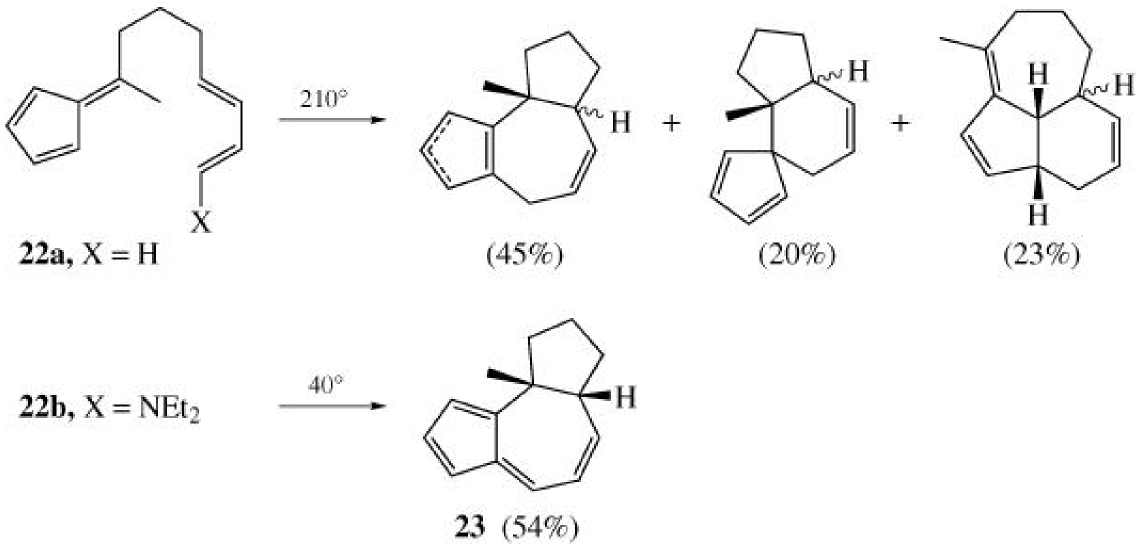
(**18**) reacts with the electron-deficient heterodiene 3,6-diphenyltetrazine in the expected [6 + 4] fashion to afford a diazaazulene product after spontaneous loss of the elements of nitrogen and dimethylamine, whereas 6,6-diphenylfulvene yields compound **19** via an endocyclic [4 + 2] cycloaddition. (33)

The influence of intramolecularity on the periselectivity of fulvene–diene cycloaddition is quite intriguing. Reaction of the quinodimethane precursor **20** with 6,6-dimethylfulvene affords only the product of a [4 + 2] cycloaddition at an endocyclic double bond. (34) When these same reactants are tethered, as in compound **21**, only the [6 + 4] adduct is formed as a mixture of cyclopentadiene isomers. The dramatic change in periselectivity in this case has been ascribed to conformational restrictions imposed on the reactant by the carbon chain connecting the fulvene moiety and the benzocyclobutane unit. (35)



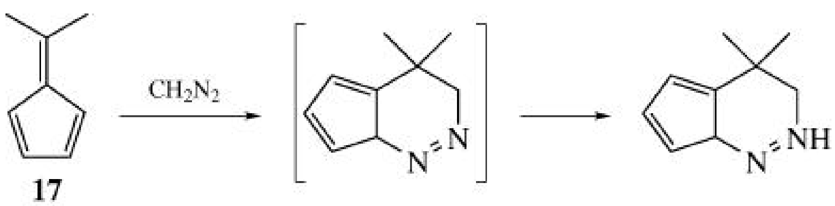
(18)

Electron-donor substituents on the diene moiety exhibit a profound influence on the regiochemical course of the intramolecular cycloaddition in the fulvene series, as depicted in Eq. 19. With X = H in fulvene **22a**, three cycloadducts are produced at elevated temperature; however, when X = NEt_2, only the [6 + 4] adduct **23** is isolated, even at moderate reaction temperatures. (36)



(19)

Cycloadditions involving 1,3-dipoles have received some attention in the fulvene series, and the reactivity patterns observed in the fulvene–diene transformations are repeated. For example, diazomethane, a 1,3-dipole with well-established nucleophilic character, adds exclusively in [6 + 4] fashion to 6,6-dimethylfulvene (**17**), as expected based on FMO considerations. (21, 37) Tropone also can be a serviceable diene partner in combination with 6,6-dimethylfulvene. (38)



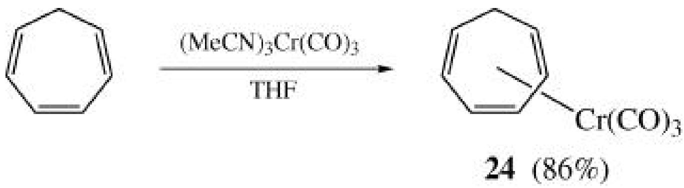
(20)

3.3. Metal-Promoted Cycloadditions

Transition metal promoted [6 π + 4 π] cycloadditions of cyclic trienes offer numerous advantages over the thermal, metal-free versions described above. The inevitable problem of regioselectivity that is a prominent feature of the latter set of transformations does not play a significant role in the course of the metal-promoted process.

The requisite triene–chromium(0) complexes, such as **24**, employed in these reactions are quite stable and can be prepared in a number of ways; the most versatile method employs tris(acetonitrile)tricarbonylchromium(0) (39) as the

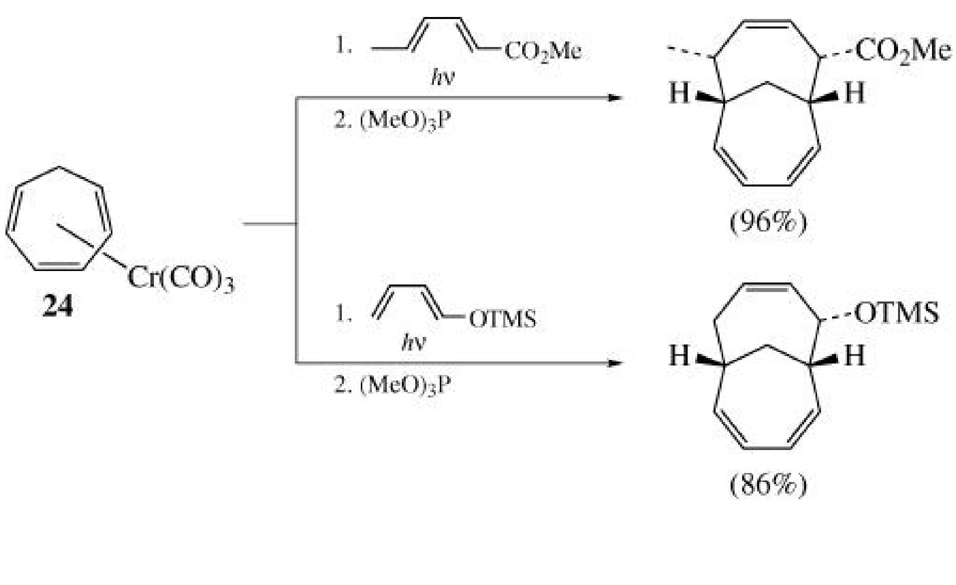
" $Cr(CO)_3$" source (Eq. 21). Group VI metals (Cr, Mo, W) have been examined as



(21)

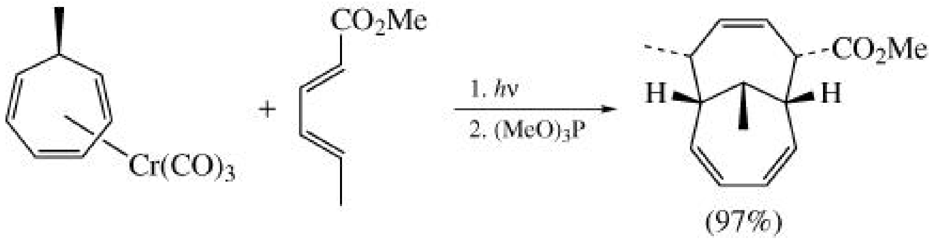
promoters for the [6 + 4] reaction, with chromium(0) emerging as the metal of choice. It is noteworthy that tungsten does not appear to promote cycloaddition. (23)

Equation 22 depicts many of the salient features of the photoinitiated, metal-promoted [6 + 4] cycloaddition. In concurrence with the thermal, metal-free version, diastereoselection is virtually complete; however, the metal-mediated process affords *endo* products exclusively. It is particularly significant that the efficiency of these transformations is relatively insensitive to the electronic nature of the reactants. Both electron-rich and electron-poor dienes afford high yields of cycloadducts. Indeed, little rate difference has been noted in competitive studies between electron-rich and electron-poor dienes in their reaction with complex **24**. In most cases, the initially formed cycloadduct–metal complex is demetalated with trimethyl phosphite prior to isolation, and all yields reported in this review are for isolated, metal-free cycloadducts. Trimethylphosphine or air/diethyl ether (see *Caution*, p. 351) have also been effective for demetalating cycloadduct–metal complexes.

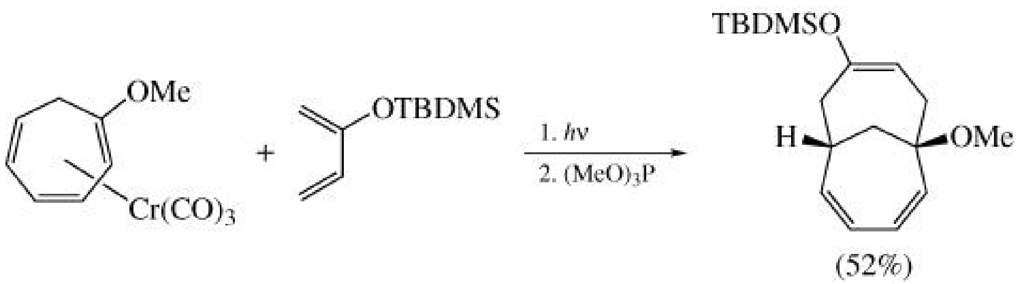


(22)

Considerable stereochemical information can be generated during these cycloadditions. Readily available 7-*exo*- or 7-*endo*-substituted complexes (40, 41) afford adducts possessing as many as five contiguous stereogenic centers. (23) In stark contrast to the thermal, metal-free reactions which, in most instances, cannot tolerate substituents at triene bond-forming centers, the metal-promoted version provides adducts from substituted triene complexes in good to moderate yields and with high levels of regiocontrol (Eq. 24). (23)

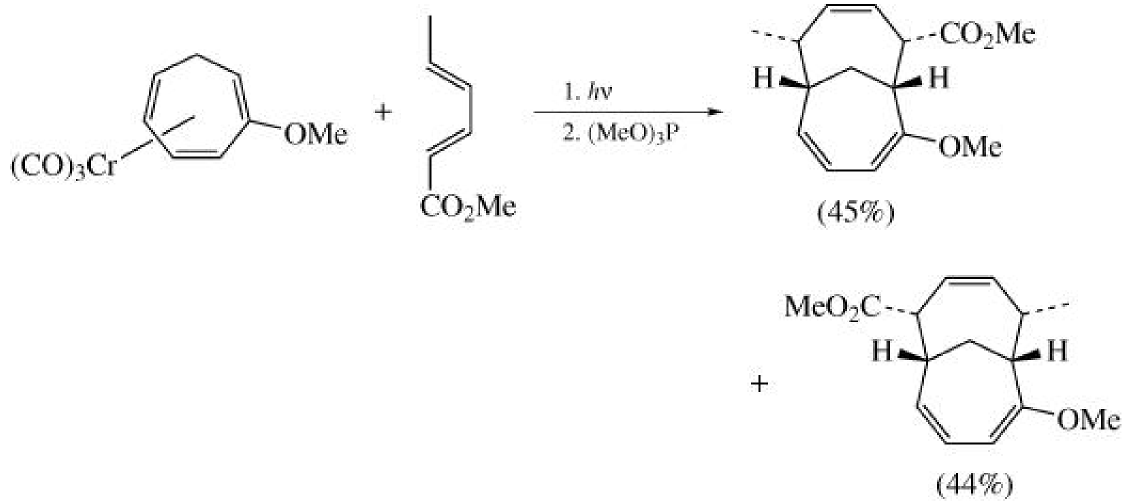


(23)



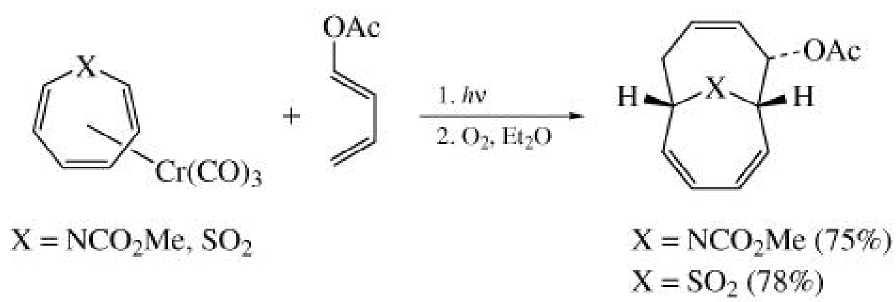
(24)

Substituents at either the 2 or 3 positions of the triene ligand tend not to have much impact on the regiochemical course of cycloaddition (Eq. 25), but chemical yields remain quite high, and good to excellent levels of asymmetric induction can be achieved during cycloaddition by incorporating a chiral auxiliary onto either the diene or triene moiety.



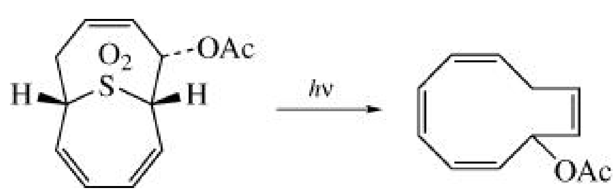
(25)

Metal-promoted cycloadditions can also be effected with heterocyclic triene complexes (Eq. 26); this example also illustrates an alternative method for



(26)

demetalation by passing air through an ether solution of the complex. (42) The resultant cycloadducts are amenable to conversion into 10-membered carbocycles by heteroatom extrusion, as depicted in Eq. 27. In this case, the cycloaddition is best



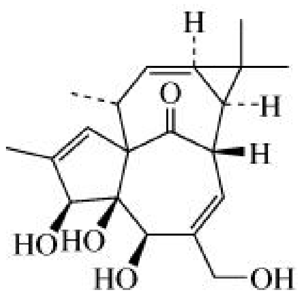
(27)

achieved using a uranium glass filter (350 nm), while the extrusion proceeds only with quartz-filtered light.

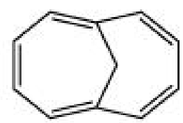
It is noteworthy that the metal-promoted [6 + 4] cycloaddition can be effected thermally as well as photochemically. In a typical example, heating a mixture of complex **24** with methyl sorbate at 140° in di-*n*-butyl ether affords a cycloadduct that is identical in all ways to the product obtained from the corresponding photochemical reaction (Eq. 22). (23) Efforts to carry out catalytic [6 + 4] reactions have met with limited success, but the related [6 + 2] reaction works well with substoichiometric quantities of metal. (43)

4. Comparison with Other Methods

The majority of methods for the construction of the bicyclo[4.4.1]undecane ring system have focused on the synthesis of 1,6-methano[10]annulenes (44) and the potent tumor-promoting diterpene, ingenol. (45) Most of these reports involve multi-step procedures for the assembly of the bicyclic architecture; however, the [6 π + 4 π] cycloaddition method has the distinct advantage of affording the target ring system in only one operation.

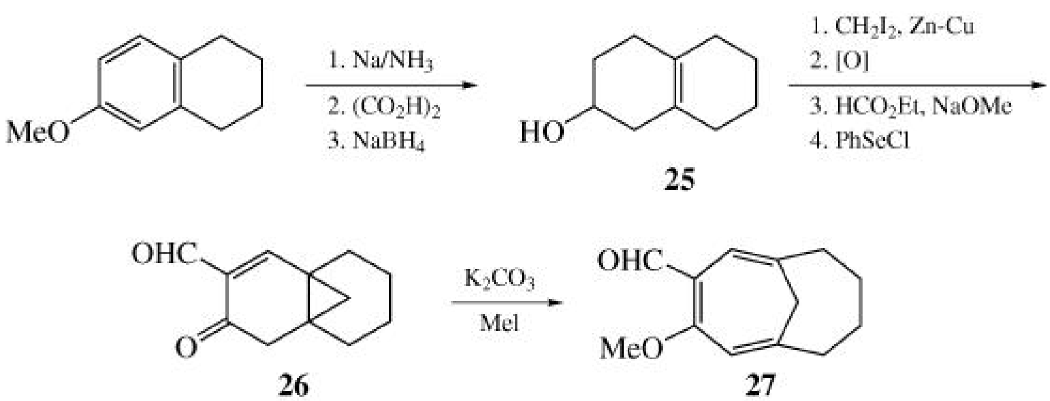


Ingenol



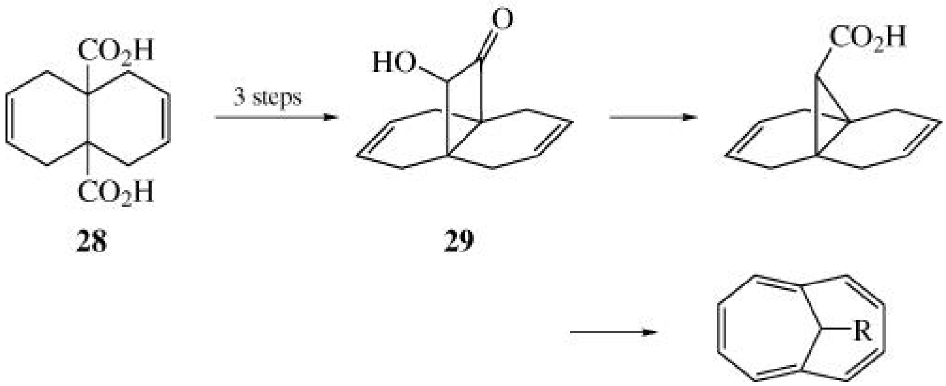
1, 6-methanol[10]annulene

Typical of the approaches to the 1,6-methano[10]annulene system is the model study directed toward the novel marine natural product spiniferin-1. (46) Birch reduction followed by enol ether hydrolysis and reduction converts 6-methoxytetralin into compound **25**. Functional group manipulation and cyclopropanation afford **26**, which upon enolization triggers tautomerization to the cycloheptatriene target **27** (Eq. 28).



(28)

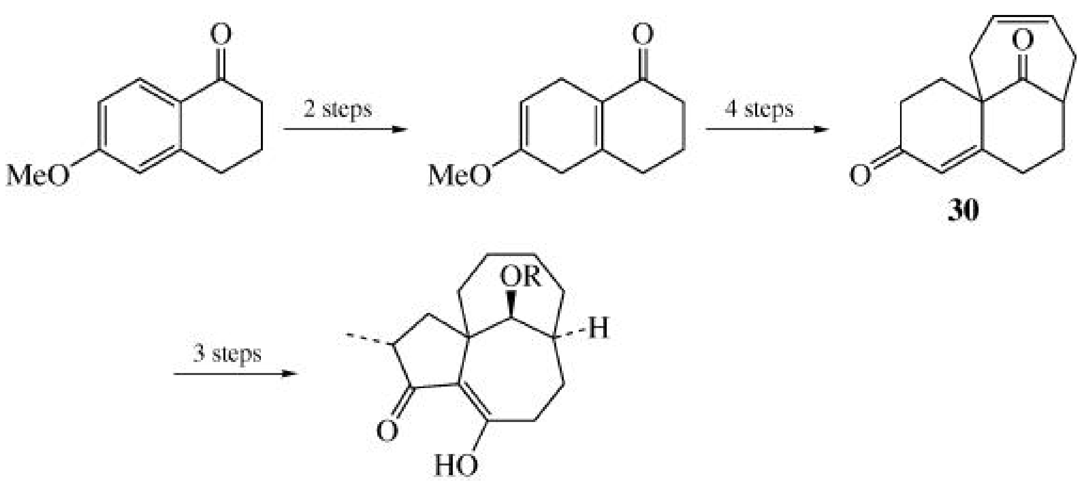
Recently, a variation on this theme has been developed for preparing 1,6-methano[10]annulenes substituted at the C-11 position. (47) In this approach, diacid **28** is transformed into propellane **29** in three steps. Ring contraction, oxidation, and isomerization to the annulene complete the synthesis.



28 **29**

Various approaches specifically focused on the bicyclo[4.4.1]undecane substructure of the ingenane diterpenes have also been reported. Several of these feature a cycloheptannulation step that is achieved via sequential bis-alkylation of a cyclohexanone or cycloheptanone precursor.

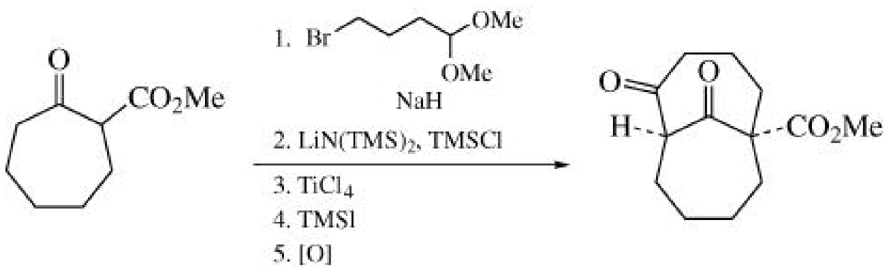
In one case, the ABC ring system of ingenol was assembled starting from 6-methoxytetralone and involving a six-step bis-alkylation sequence leading to dione **30**. Several additional steps, including an intriguing ring contraction–ring expansion, afforded the tricycle **31**. (48)



30

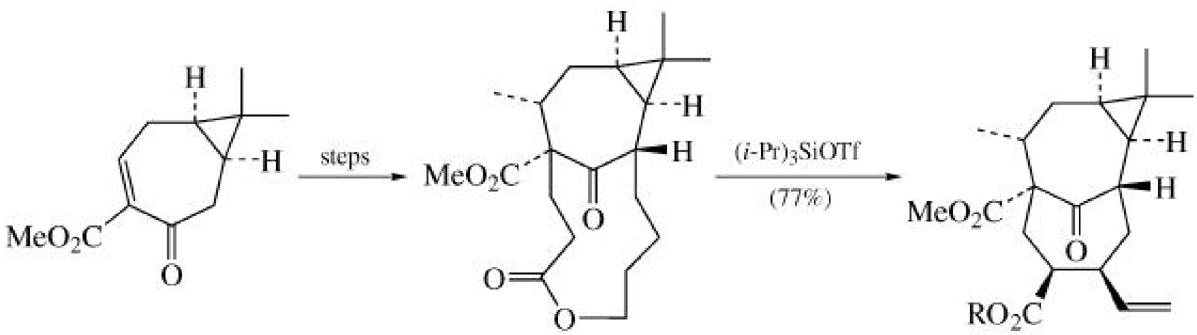
31

A somewhat related sequence for constructing a modestly functionalized bicyclo[4.4.1]undecanone species commencing from a cycloheptanone starting material is depicted in Eq. 29. (49)

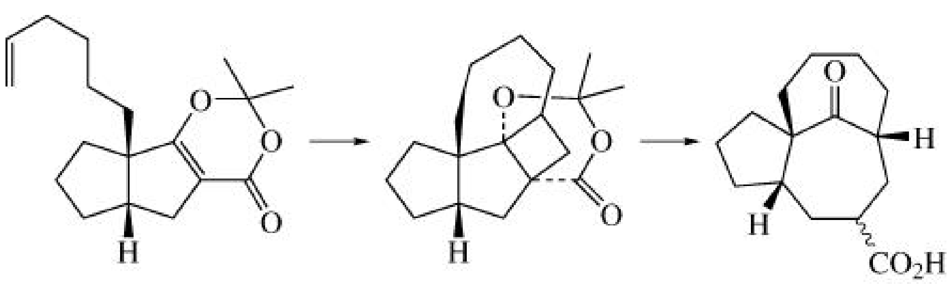


(29)

Ring contraction via Claisen rearrangement has also been effectively employed for the synthesis of the bicyclo[4.4.1]undecane system. In this instance, the resultant product possesses the strained *trans* interbridgehead stereochemistry characteristic of the naturally occurring ingenane diterpenes. (50)

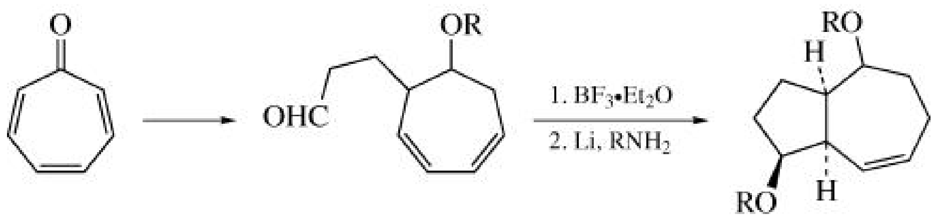


A [2 + 2] photocycloaddition has been used as the key step in a second entry into the ingenane bicyclo[4.4.1]undecane ring system that was elegantly designed to produce the strained “in, out” isomer directly. (51)



The fulvene–diene [6 + 4] cycloaddition yields a bicyclo[5.3.0]decane ring system. In light of the prominence of the hydroazulene substructure in numerous biologically active sesquiterpenes, as well as in the tumor-promoting diterpenes phorbol and ingenol, a large number of alternative entries into this important ring system have emerged and several overviews of this area have appeared. (52-55)

Most traditional methods for assembly of the hydroazulene system can be categorized into one of four basic strategies (with illustrative references): annulation of a cyclopentane ring onto a preexisting seven-membered ring (Eq. 30); (56) cycloheptannulation onto a five-membered ring (Eq. 31); (57) transannular cyclization of a cyclodecane (Eq. 32); (58) and rearrangement of bicyclo[4.3.1]decane or bicyclo[4.4.0]decane precursors (Eq. 33). (52)



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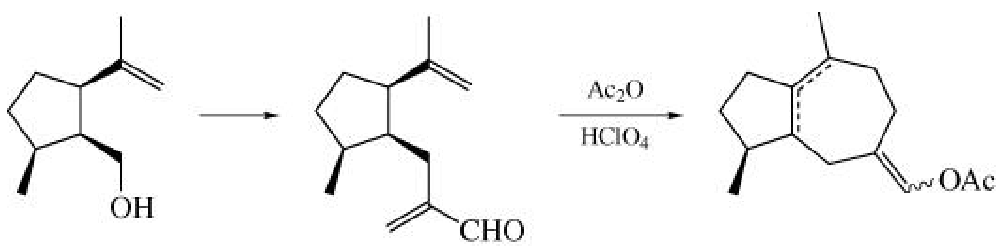

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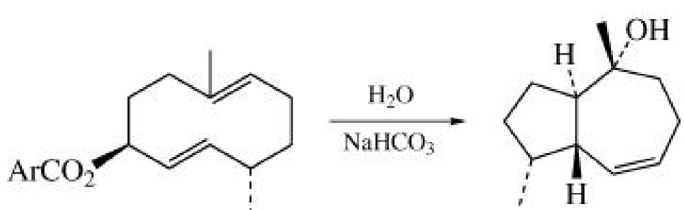

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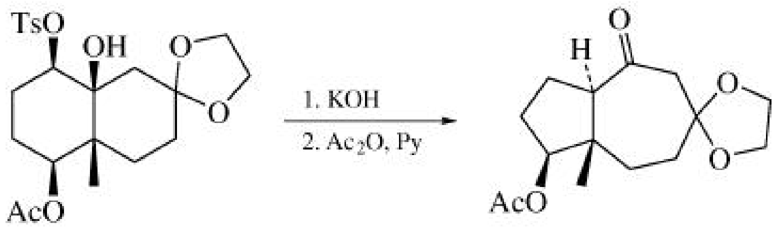
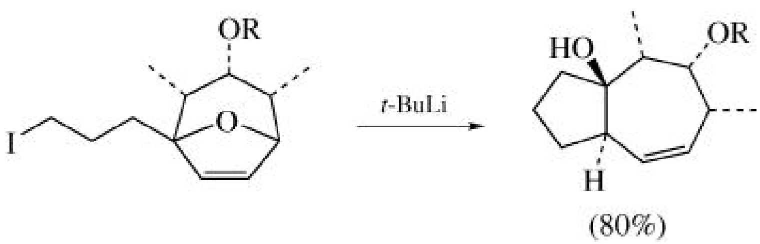
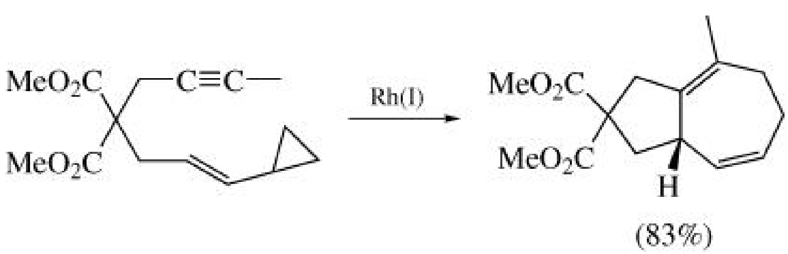


(33)

Several more recent contributions have appeared that feature novel methods for executing the key ring-forming process. An anionic, intermolecular ring-opening procedure affords highly functionalized hydroazulene products from oxabicyclo[3.2.1]octane systems. (59)



A novel and very promising entry into hydroazulenes exploits a Rh(I)-mediated, intramolecular [5 + 2] cycloaddition of an alkyne to a vinylcyclopropane moiety. (60)



Although the choice of which approach to employ for assembling a bicyclo[5.3.0]decane ring system ultimately depends on the specific substitution pattern required, the fulvene–diene [6 + 4] cycloaddition offers the advantages of convergency, ease of substrate synthesis, and well-defined reaction characteristics that are attractive in many situations.

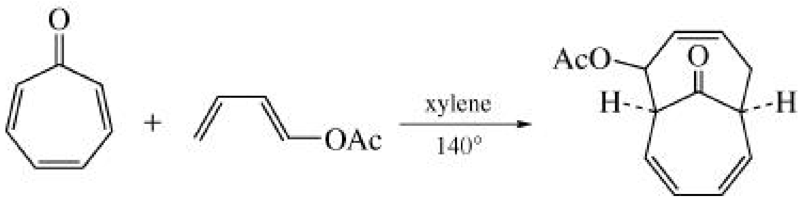
5. Experimental Conditions

For most thermal, metal-free [6 + 4] cycloadditions, a freshly distilled, non-polar solvent of appropriate boiling point is preferred. Benzene, toluene, and xylene are most frequently employed. Since forcing conditions can often promote other pericyclic events (i.e., [4 + 2] cycloadditions) at the expense of the high-order pathway, it is recommended that lower-boiling solvents be screened first for efficacy with each substrate. While the optimum conditions for thermal, metal-free [6 + 4] cycloadditions vary greatly as a function of substrate, transition-metal-mediated photocycloadditions have well-defined conditions for achieving optimal results. Freshly distilled hexanes is the solvent of choice for most applications. Occasionally, a small amount of ether cosolvent may be needed to solubilize a particular complex. Maximum yields of adducts are obtained when the reaction mixture is purged with an inert gas (Ar or N_2) prior to and during photolysis. Pyrex or uranium glass-filtered light affords optimum yields in all cases examined. Employing quartz-filtered light gives inferior yields, owing to the instability of the cycloadduct complexes to the reaction conditions.

With electron-rich diene partners, maximum product yields are obtained when the reaction mixture is stirred under a blanket of carbon monoxide for several hours after completion of the irradiation step.

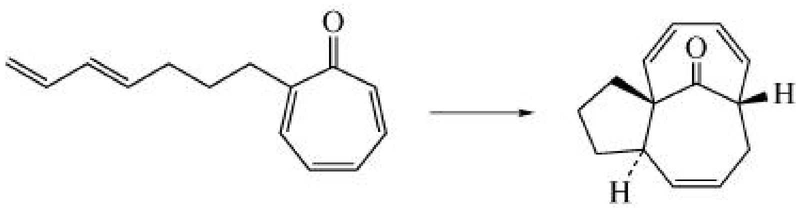
Demetalation of most cycloadduct–metal complexes is accomplished with trimethyl phosphite; however, in some cases better results are obtained by bubbling air through an ether solution of the crude reaction product. *CAUTION*. Lower-alkyl ethers readily form explosive peroxides under these conditions. An ether so treated should never be distilled; peroxides can be removed from it by passing it through a column of basic activated alumina (60a) or by treating it with indicating molecular sieves . (60b)

6. Experimental Procedures



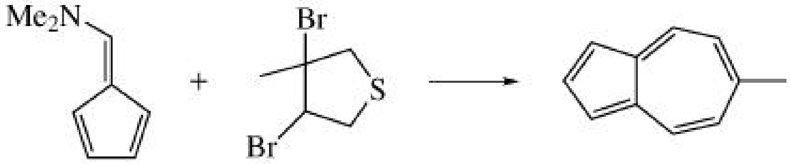
6.1.1. 7β -Acetoxy-(1H α ,6H α)-bicyclo[4.4.1]undeca-2,4,8-trien-11-one (Thermal, Metal-Free Tropone-Diene Cycloaddition). (61)

A solution of 2,4,6-cycloheptatrien-1-one (tropone) (10 g, 94 mmol) and (*E*)-1-acetoxy-1,3-butadiene (15.8 g, 140 mmol) in xylene (300 mL) was heated at reflux for five days. Removal of solvent in vacuo and purification of the crude product by flash-column chromatography (4/1, hexanes/ethyl acetate) afforded 12.1 g (59%) of the cycloadduct as a pale yellow oil: IR (neat) 3031, 2937, 1735, 1707, 1437 cm^{-1};^{1}H NMR($CDCl_3$) δ 2.07 (s, 3 H), 2.56 (m, 2 H), 3.54 (br q, J = 6.3 Hz, 1 H), 3.67 (br t, J = 6.3 Hz, 1 H), 5.67 (m, 4 H), 5.78 (m, 1 H), 6.10 (m, 2 H). High-resolution mass spectrum: Calcd for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0940.



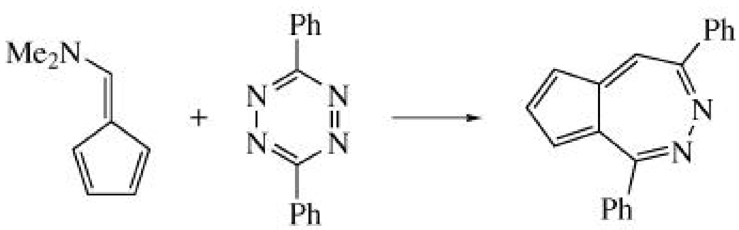
6.1.2. 1,2,3,8,9,11a-Hexahydro-3a,8-methano-3aH-cyclopentacyclodecen-12-one (Intramolecular, Thermal Tropone–Diene Cycloaddition). (27)

2-(Hepta-4,6-dienyl)cyclohepta-2,4,6-trien-1-one (200 mg, 1 mmol) was heated in benzene (4 mL) at reflux for 10 hours. The solvent was removed in vacuo and the crude product was purified by flash-column chromatography (4/1 petroleum ether/ether), affording 172 mg (86%) of cycloadduct: IR (CCl_4) 2959, 1704, 1695 cm^{-1};^{1}H NMR($CDCl_3$) δ 1.43–1.88 (m, 4 H), 1.94 (m, 1 H), 2.20–2.40 (m, 2 H), 2.67 (m, 1 H), 2.88 (m, 1 H), 3.49 (q, J = 6.5 Hz, 1 H), 5.41–6.05 (m, 6 H). Anal. Calcd for $C_{14}H_{16}O$: C, 83.94; H, 8.06. Found: C, 83.97; H, 8.05.



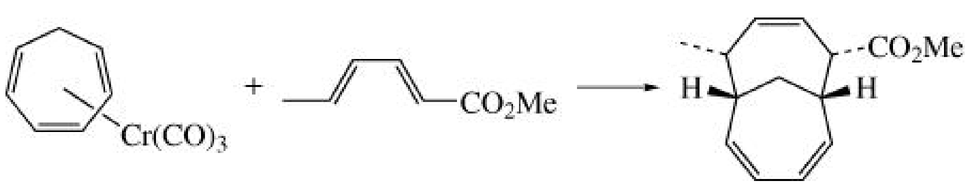
6.1.3. 6-Methylazulene (Electron-Rich Fulvene–Electron-Poor Diene Cycloaddition). (31)

3-Methyl-3,4-dibromotetrahydrothiophene (3.0 g, 10 mmol) was dissolved in benzene (75 mL). The solution was cooled to 0–5°, and triethylamine (3 mL, 20 mmol) was added. This solution was stirred for 2 hours, the precipitate removed by filtration, and the resulting solution added to 6-dimethylaminofulvene (1.5 g, 12.5 mmol). This solution was stirred at room temperature under a gentle stream of nitrogen for 72 hours, at which time the reaction mixture was evaporated to dryness. The crude product was dissolved in 4:1 petroleum ether–chloroform, insoluble material was removed by filtration, and the solution was chromatographed on alumina (petroleum ether). This afforded 0.36 g (25%) of product.



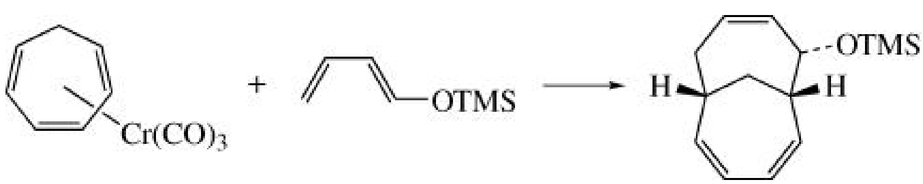
6.1.4. 4,7-Diphenyl-5,6-diazaazulene (Electron-Rich Fulvene–Heterodiene Cycloaddition). (33)

A solution of 6-dimethylaminofulvene (0.15 g, 1.2 mmol) and 3,6-diphenyltetrazine (0.29 g, 1.2 mmol) in benzene (20 mL) was stirred at 25° under argon in the dark for 5 days. Removal of solvent in vacuo and purification by column chromatography (chloroform) afforded 0.14 g (40%) of product: mp 289–92° (chloroform). Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.96; H, 5.16; N, 9.87.



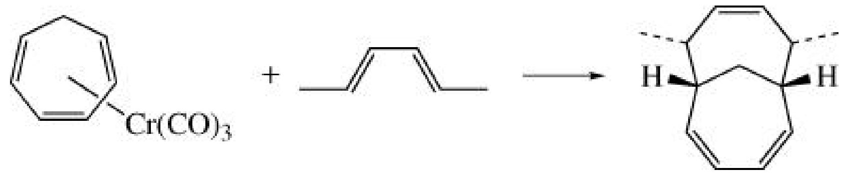
6.1.5. 7 α -(Methoxycarbonyl)-10 α -methyl-(1H β ,6H β)-bicyclo[4.4.1]undeca-2,4,8-triene (Metal-Promoted Photocycloaddition Employing an Electron-Deficient Diene). (23)

A Canrad–Hanovia medium-pressure mercury lamp operating at 450 W was placed in a water-cooled immersion well constructed of Pyrex glass and equipped with a uranium glass sleeve. To this reaction vessel was added a solution of (η ^{6}-1,3,5-cycloheptatriene) tricarbonylchromium(0) (570 mg, 2.5 mmol) and methyl sorbate (284 mg, 2.25 mmol) in hexanes (320 mL). The solution was purged through vigorous bubbling with Ar and irradiated with continuous bubbling for 30 minutes. The resultant orange solution was filtered and the solution reduced in vacuo to a volume of 20–50 mL. At this time, the mixture was stirred with trimethyl phosphite (10 mL) at 25° for 10 hours. Concentration in vacuo and purification by flash-column chromatography (9/1 hexane/ether) afforded 469 mg (96% based on diene) of a colorless oil: IR (film) 3018, 1739, 1435 cm^{-1};^{1}H NMR($CDCl_3$) δ 1.22 (d, J = 7.2 Hz, 3 H), 2.23 (m, 3 H), 2.55 (m, 1 H), 2.69 (m, 1 H), 3.20 (m, 1 H), 3.60 (m, 1 H), 3.74 (s, 3 H), 4.50 (m, 1 H), 5.78 (m, 4 H), 5.92 (m, 1 H). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.08; H, 8.21.



6.1.6. 7 α -Trimethylsilyloxy-(1H β ,6H β)-bicyclo[4.4.1]undeca-2,4,8-triene (Metal-Promoted Photocycloaddition Employing an Electron-Rich Diene). (23)

A solution of (η ^{6}-1,3,5-cycloheptatriene) tricarbonylchromium(0) (310 mg, 1.36 mmol) and 1-trimethylsilyloxy-1,3-butadiene (1.21 g, 8.5 mmol) in hexanes (350 mL) was irradiated (Pyrex) under conditions described above for 30 minutes. The mixture was saturated with carbon monoxide and stirred under a blanket of this gas for 15 hours. The resultant solution was concentrated to 50 mL in vacuo and stirred with trimethyl phosphite (10 mL) at 25° for 10 hours. The mixture was then further concentrated in vacuo, and purification by flash-column chromatography (19/1 hexanes/ethyl acetate) afforded 273 mg (86%) of a colorless oil: ^{1}H NMR δ 0.16 (s, 9 H), 2.13–2.49 (m, 4 H), 2.72 (br s, 1 H), 2.82 (br s, 1 H), 4.67 (m, 1 H), 5.55 (m, 2 H), 5.84 (m, 3 H), 6.05 (m, 1 H). Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.45. Found: C, 72.05; H, 9.37.



6.1.7. 7 α ,10 α -Dimethyl-(1H β ,6H β)-bicyclo[4.4.1]undeca-2,4,8-triene (Thermal, Metal-Promoted Cycloaddition Employing a Hydrocarbon Diene). (23)

A solution of (η^6-1,3,5-cycloheptatriene) tricarbonylchromium(0) (0.154 g, 0.67 mmol) and (*E, E*)-2,4-hexadiene (1.5 mL, 13 mmol) in *n*-butyl ether (10 mL) was refluxed for 36 hours, at which time the reaction mixture was cooled to room temperature and the solvent was removed in vacuo. Flash-column chromatography (pentane) of the crude product afforded 0.115 g (70%) of a colorless oil: ^{1}H NMR δ 1.23 (d, *J* = 7.3 Hz, 6 H), 2.10–2.30 (m, 2 H), 2.55 (m, 2 H), 2.70–2.85 (m, 2 H), 5.28 (m, 2 H), 5.81 (m, 2 H), 5.91 (m, 2 H). High-resolution mass spectrum: Calcd for $C_{13}H_{18}$: 174.1408. Found: 174.1410.

7. Tabular Survey

[6 + 4] Cycloaddition reactions of cyclic trienes, fulvenes, miscellaneous 6 π reactants, and metal complexes are grouped in Tables I–IV and follow the order of topics discussed in the Scope and Limitations section. Tables I and II are further divided into subcategories related to the types of 4 π reaction partners involved. Table I has three subsections: (A) All-Carbon Trienophiles, (B) 1,3-Dipolar Trienophiles, including TMM equivalents, and (C) Intramolecular Reactions. Table II has four subcategories: (A) All-Carbon Trienophiles, (B) 1,3-Dipolar Trienophiles, (C) Heterodienes, and (D) Intramolecular Reactions. Miscellaneous substrates that could not be placed in either Table I or II are collected in Table III, and Table IV presents metal-mediated [6 + 4] cycloadditions.

Within each table, the reactions are listed according to increasing carbon number in the triene (6 π) substrate and the count is based on the total number of carbon atoms in these reactants. Table IV is an exception to this arrangement in that spectator ligands around the metal center are **not** included in the total carbon count.

Within each carbon-number group, the trienes are listed in order of increasing hydrogen count. Yields are given in parentheses and a dash indicates that no yields or experimental conditions were given in the original reference.

Some entries involve structurally large reactant substructures. In these cases, the explicit substructure is provided in the relevant reactant location and indicated in condensed form in the product(s).

The literature has been reviewed from 1952 through mid-1995.

The following abbreviations are used in the tables:

C_2H_3	Vinyl
C_3H_5	Cyclopropyl
C_5H_4N	2-Pyridyl
Cp	Cyclopentadienyl
Et_2O	Diethyl ether
DME	1,2-Dimethoxyethane
rt	Room temperature
THF	Tetrahydrofuran
TBDMS	*tert*-Butyldimethylsilyl

Ts	*p*-Toluenesulfonyl

Table I. [6 + 4] Cycloadditions of 2,4,6-Cycloheptatrien- 1-One and Derivatives

View PDF

Table II. [6 + 4] Cycloadditions of Fulvene Derivatives

View PDF

Table III. Miscellaneous [6 + 4] Cycloaddition Reactions

View PDF

Table IV. Metal-Mediated [6 + 4] Cycloaddition

View PDF

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES

A. All-Carbon Trienophiles

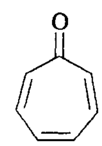
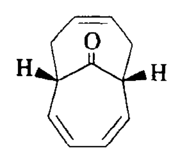
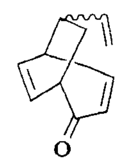
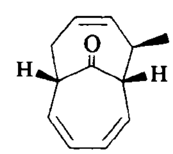
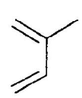
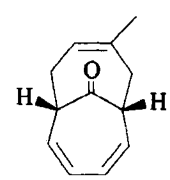
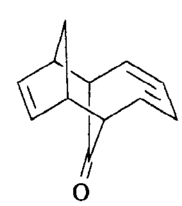
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		Xylene, 130°, 10 h	 (75) +  (8)	62
		Xylene, 130°, 10 h	 (60)	62
		Xylene, 130°, 10 h	 (86)	62
		C_6H_6, 80°, 5 d	 (—)	5, 6

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

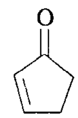
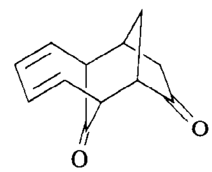
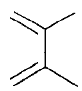
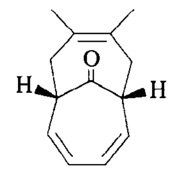
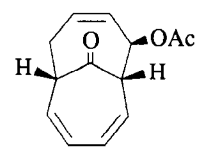
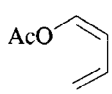
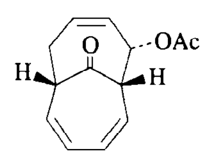
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Toluene, 10 Kbar, 100°, 10 h	 (7)	63
		Xylene, 140°, 12 h	 (75)	16
		Xylene, 140°, 5 d	 (59)	61, 27, 16, 64, 65
		Xylene, 140°, 24 h	 (12)	16, 65

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

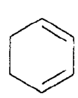
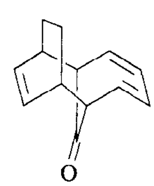
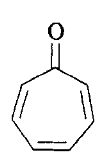
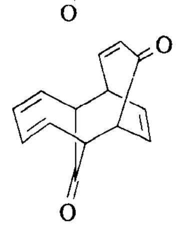
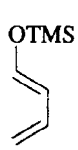
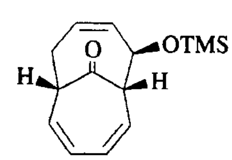
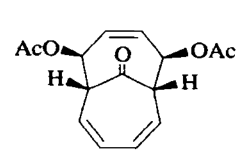
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (30)	66, 5, 67
		MeCN, 28 h, *hv*	 (17)	68, 69
		C_6H_6, 80°, 4 d	 (80)	16
		Xylene, 140°, 27 h	 (25)	16

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

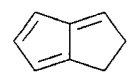
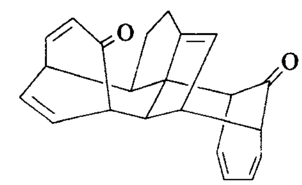
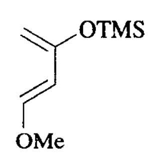
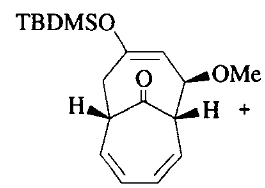
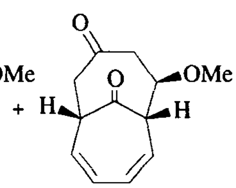
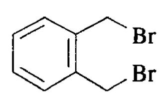
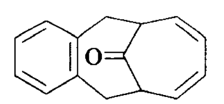
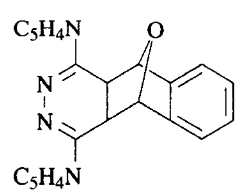
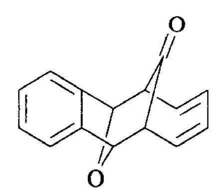
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pentane, rt, 30 d	 (68)	70
		Toluene, 80°, 96 h	 (32) +  (8)	16
		Zn, DMF, rt	 (29)	71
		rt	 (12)	72

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

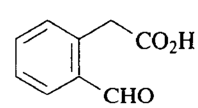
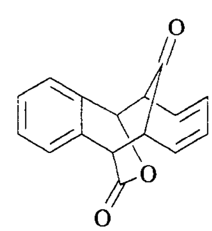
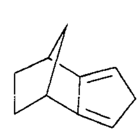
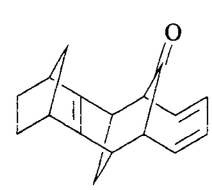
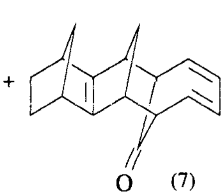
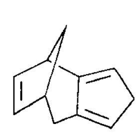
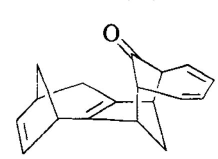
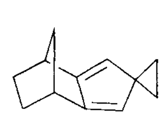
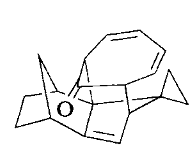
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Ac_2O, 140°, 1 h	 (28)	73
		C_6H_6, rt, 9 d	 (37) +  (7)	74
		rt	 (—)	75
		C_6H_6, 80°, 6 d	 (17)	76

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

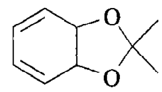
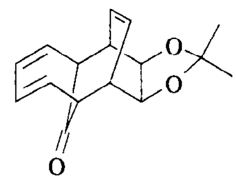
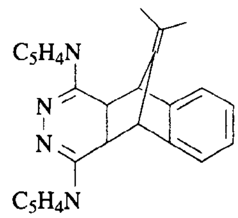
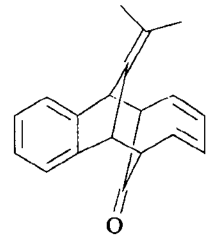
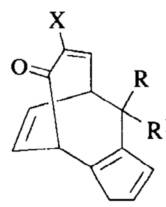
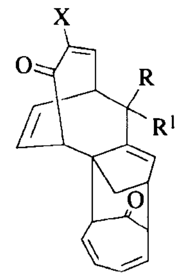
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 80°, 4 d	 (62)	77
		rt	 (100)	78, 79
				
	R / R[1] / X			
	Me / Me / H	THF, 50°, 2 d	(—)	80
	Me / H / H	THF, 60°, 12 h	(61)	81
	Ph / H / H	MeOH, 60°	(86)	81
	Me / Me / Cl	MeOH, 50°, 3 d	(42)	82

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

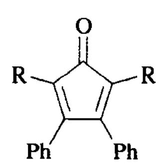
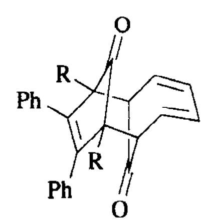
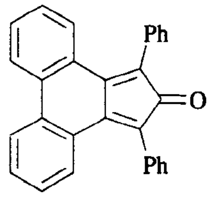
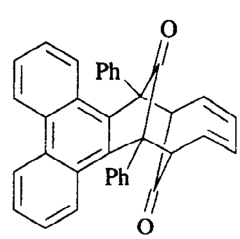
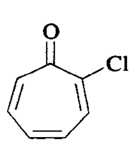
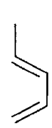
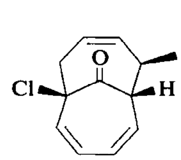
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
				
	R			
	Me	Acetone, 60°, 8 h	(95)	80
	Et	Acetone, 60°, 7 h	(88)	83
	CO_2Me	C_6H_6, 80°, 10 h	(88)	83
		C_6H_6, 80°, 20 h	 (70)	84
		—	 (—)	85

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

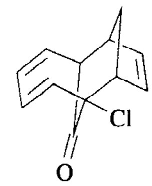
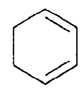
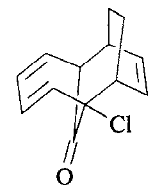
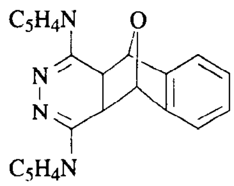
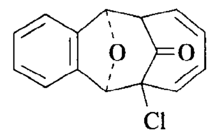
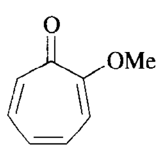
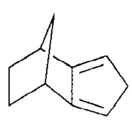
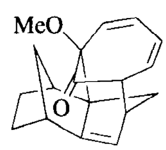
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		105°, 3 h	 (11)	28, 85
		100°, 9 h	 (58)	85
		rt	 (25)	72
C_8 		C_6H_6, 80°, 6 d	 (25)	76

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

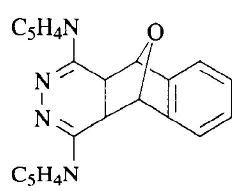
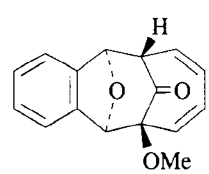
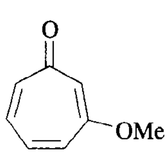
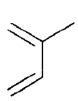
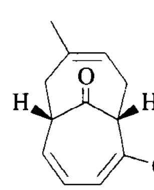
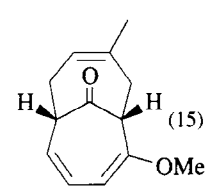
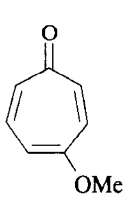
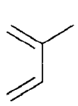
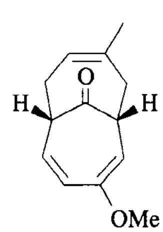
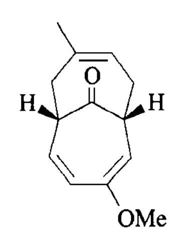
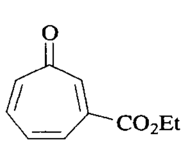
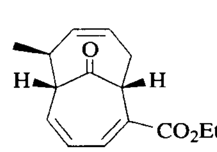
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		rt	 (17)	72
		C_6H_6, 160°, 140 h	 (15) +  (15)	29
		C_6H_6, 175°, 120 h	 (15) +  (5)	29
C_{10} 		C_6H_6, 120°, 16 h	 (21)	29

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

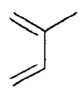
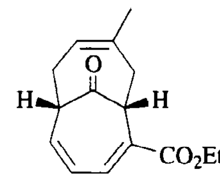
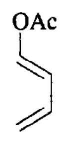
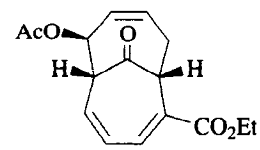
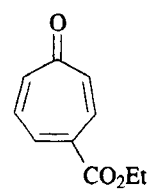
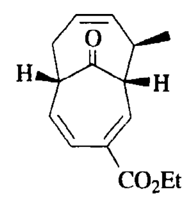
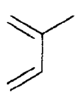
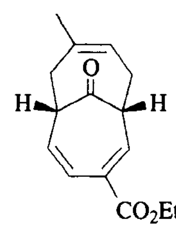
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 110°, 15 h	 (38)	29
		Toluene, 110°, 16 h	 (20)	29
		C_6H_6, 110°, 62 h	 (28)	29
		C_6H_6, 110°, 40 h	 (25)	29

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

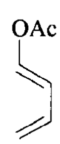
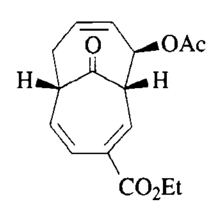
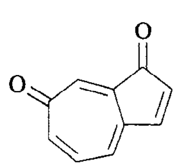
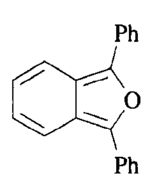
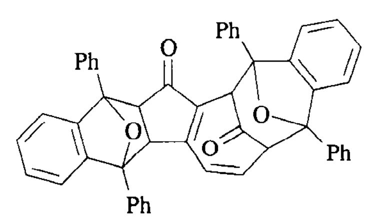
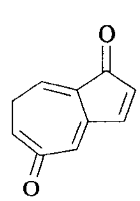
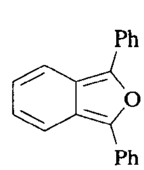
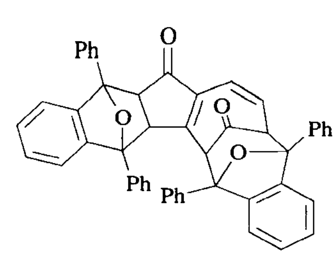
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 80°, 48 h	 (22)	29
		$C_2H_4Cl_2$, rt, 1 h	 (14)	86
		$C_2H_4Cl_2$, rt, 1 h	 (40)	86

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

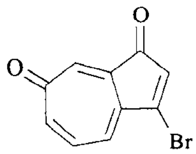
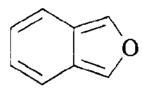
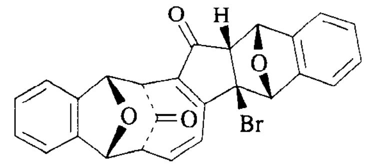
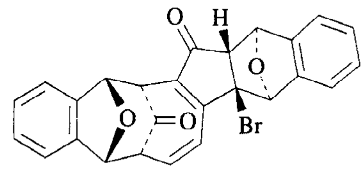
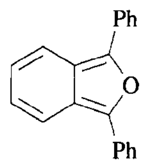
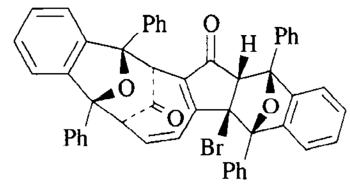
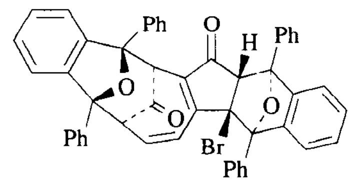
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Chlorobenzene, 130°, 4 h	 (30) +	87
			 (11)	
		Chlorobenzene, 130°, 4 h	 (11) +	88
			 (30)	

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

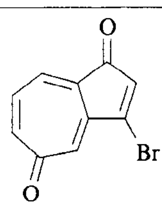
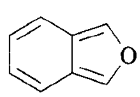
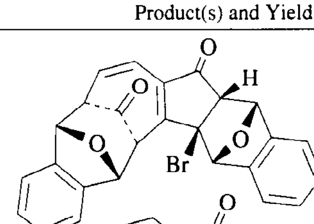
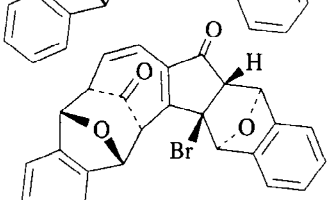
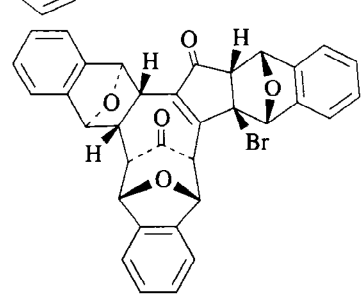
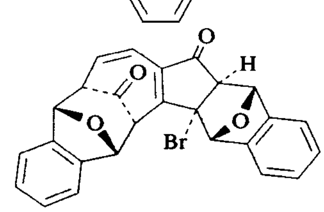
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Chlorobenzene, 130°, 4 h	 (25) +	87
			 (28) +	
			 (9) +	
			 (11)	

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

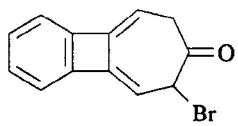
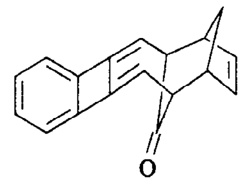
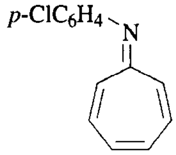
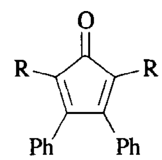
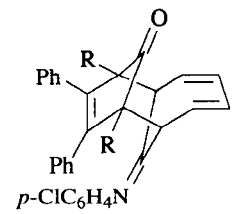
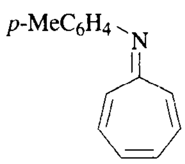
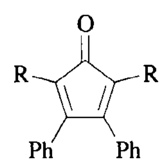
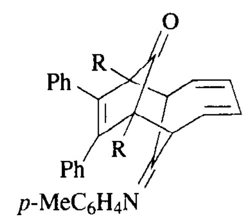
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		CH_2Cl_2, Et_3N, 0°	 (20)	89
	 R Me CO_2Me	C_6H_6, 80°, 96 h	 (50) (51)	90
C_{14}				
	 R Me Et CO_2Me	C_6H_6, 80°, 96 h	 (45) (50) (61)	90

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

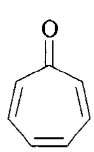
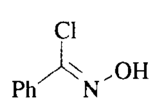
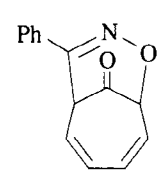
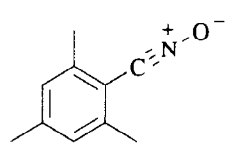
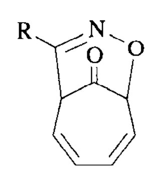
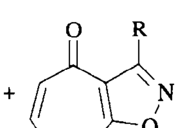
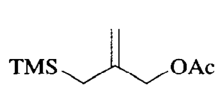
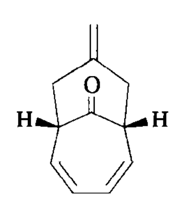
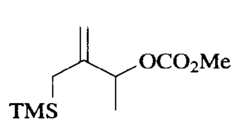
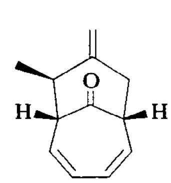
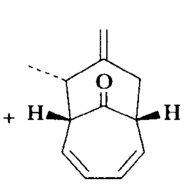
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		C_6H_6, Et_3N, rt, 48 h	 (3.5)	91
		C_6H_6, 15 d	 (0.6) +  (57) R = 2,4,6-$Me_3C_6H_2$	91
		Toluene, $Pd(OAc)_2$, $(i\text{-}C_3H_7O)_3P$, 80°, 3 h	 (68)	92
		Toluene, $Pd(OAc)_2$, $(i\text{-}C_3H_7O)_3P$, 80°, 6 h	 (23) +  (23)	92

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

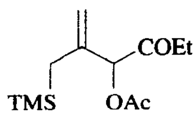
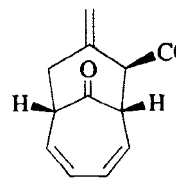
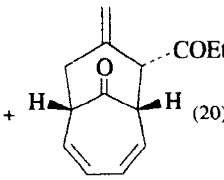
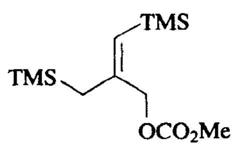
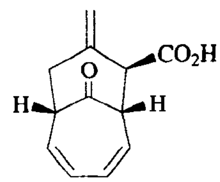
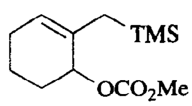
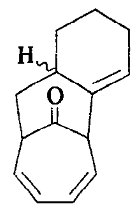
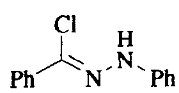
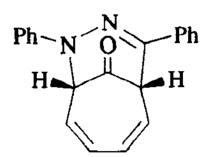
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Toluene, $Pd(OAc)_2$, (i-$C_3H_7O)_3P$, 80°, 3 h	 (60) +  (20)	92
		Toluene, $Pd(OAc)_2$, (i-$C_3H_7O)_3P$, 80°, 6 h	 (84)	92
		Toluene, $Pd(OAc)_2$, (i-$C_3H_7O)_3P$, 80°, 3 h	 (81)	92
		C_6H_6, Et_3N, rt, 12 h	 (5)	93, 8, 94

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

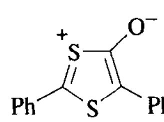
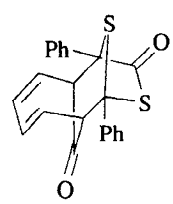
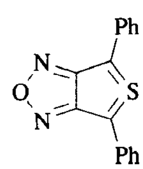
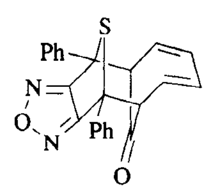
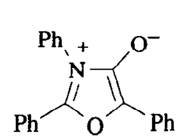
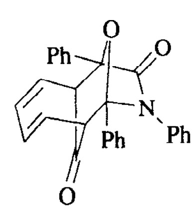
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Toluene, 110°, $Cu(OAc)_2$	 (19)	95
		C_6H_6, 80°, 48 h	 (30)	96
		rt	 (49)	95

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

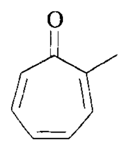
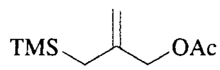
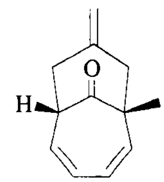
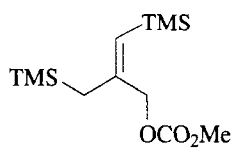
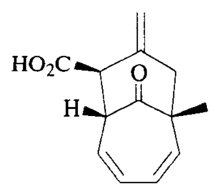
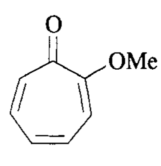
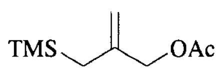
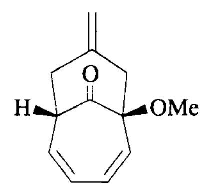
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Toluene, Pd(OAc)$_2$, (i-C_3H_7O)$_3$P, 80°, 10 h	 (74)	92
		Toluene, Pd(OAc)$_2$, (i-C_3H_7O)$_3$P, 80°, 12 h	 (62)	92
		Toluene, Pd(OAc)$_2$, (i-C_3H_7O)$_3$P, 80°, 6 h	 (41)	92

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

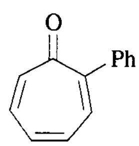
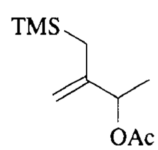
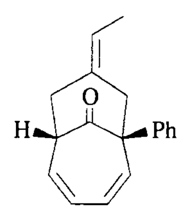
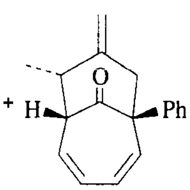
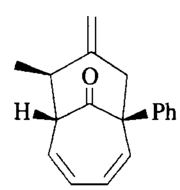
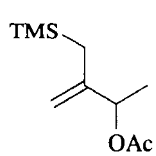
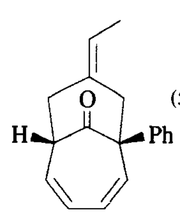
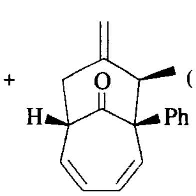
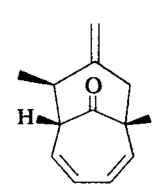
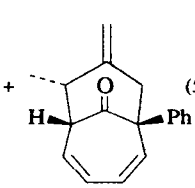
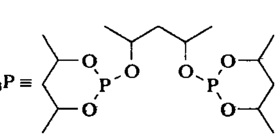
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		Toluene, Pd(OAc)$_2$, (i-C_3H_7O)$_3$P, 110°	 (7) +  (36) +  (11)	97
		Toluene-C_6H_6, 15 kbar, (η^3-C_3H_5PdCl)$_2$, (RO)$_3$P, 50°	 (57) +  (16) +  (6) +  (5)	97
	(RO)$_3$P ≡ 			

TABLE I. [6+4] CYCLOADDITIONS OF 2,4,6-CYCLOHEPTATRIEN-1-ONE AND DERIVATIVES (*Continued*)

C. Intramolecular Reactions

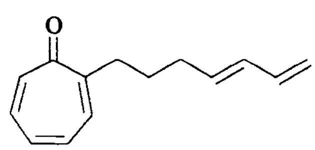
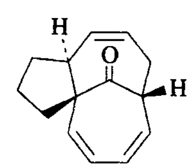
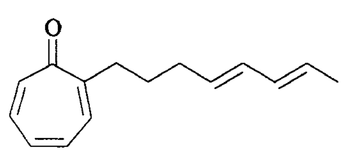
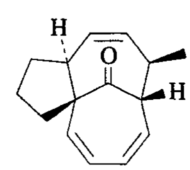
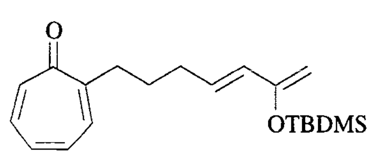
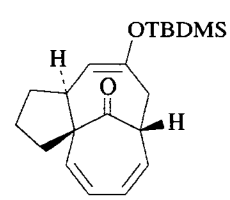
	Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{14}			Xylene, 140°, 6 h		(81)	27
C_{15}			Toluene, 150°, 36 h		(88)	30
C_{20}			C_6H_6, 80°, 6 h		(92)	30

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES

A. All-Carbon Trienophiles

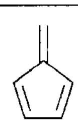
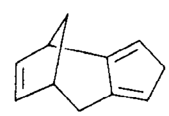
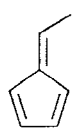
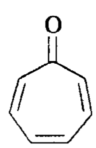
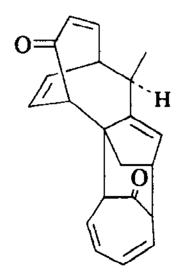
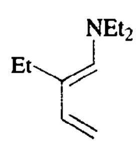
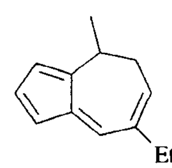
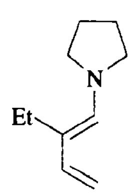
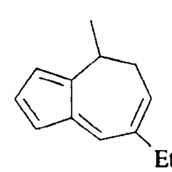
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 		rt, 5 d	 (—)	98
C_7 		60°, 12 h	 (61)	81, 82
		rt, 24 h	 (52)	99
		Et_2O, rt	 (52)	100

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

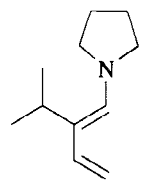
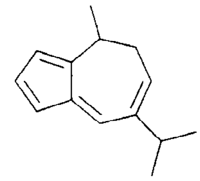
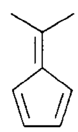
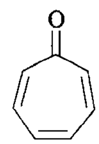
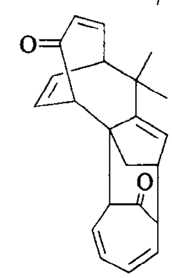
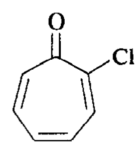
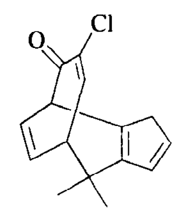
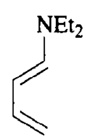
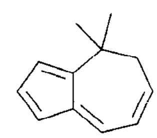
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_2O, rt	 (50)	100
C8 		THF, 50°, 2 d	 (—)	101, 37, 82
		50°, 3 d	 (—)	102
		rt, 2 d	 (65)	19, 99

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

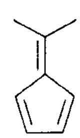
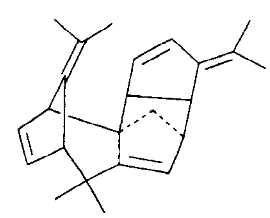
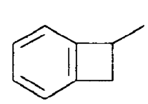
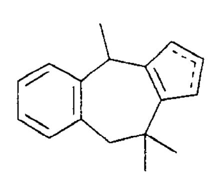
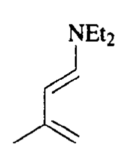
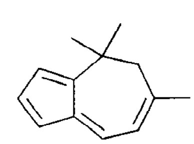
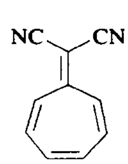
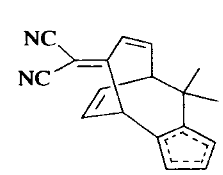
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		60°, 6 mon.	 (35)	103, 104
		Toluene, 185°, 5 h	 (—)	34
		rt, 48 h	 (65)	99
		$CHCl_3$, rt, 1 d	 (—)	105

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

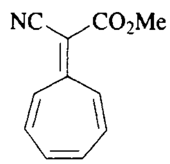
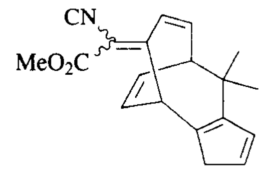
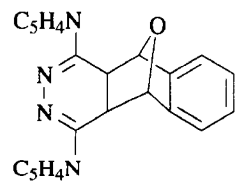
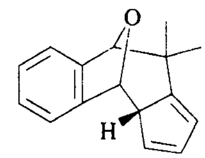
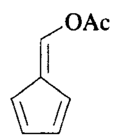
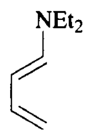
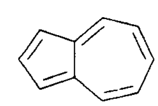
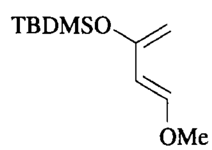
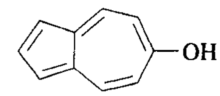
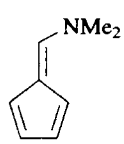
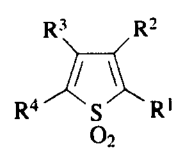
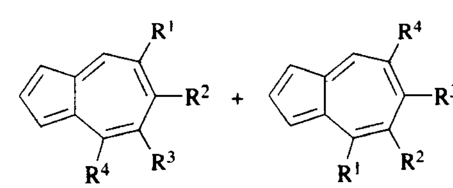
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		$CHCl_3$, rt, 7 d	 (—)	106
		160°, 4 h	 (—)	32
		$CHCl_3$, rt	 (12)	107
		—	 (—)	107

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
			 I + II	

R^1	R^2	R^3	R^4	Conditions	I	II	Refs.
H	H	H	H	THF, 67°, 3 h	(33)	(0)	108
H	H	H	H	$CHCl_3$, rt, 12 h	(10)	(0)	31
Me	H	H	H	$CHCl_3$, 50°, 72 h	(5)	(0)	31
H	Me	H	H	$CHCl_3$, rt, 72 h	(25)	(0)	31
H	Et	H	H	$CHCl_3$, rt, 48 h	(12)	(0)	31
H	Ph	H	H	$CHCl_3$, rt, 12 h	(27)	(0)	31
H	Me	Me	H	$CHCl_3$, 50°, 48 h	(8)	(0)	31
H	Cl	Cl	H	$CHCl_3$, 25°, 12 h	(60)	(0)	31
H	Cl	Cl	H	THF, 67°	(46)	(0)	108
H	Ph	Ph	H	$CHCl_3$, rt, 24 h	(13)	(0)	31
Me	H	Me	H	$CHCl_3$, 50°, 48 h	(0)	(10)	31
Cl	Cl	Cl	Cl	C_6H_6, rt,	(11)	(0)	109

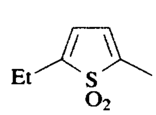
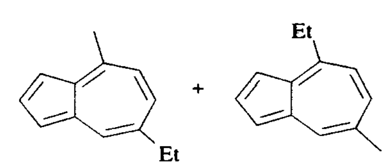
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_5H_5N, 115°	 (16) + (4)	100

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES *(Continued)*

A. All-Carbon Trienophiles

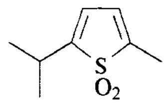
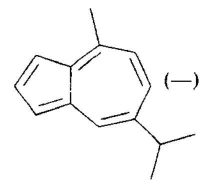
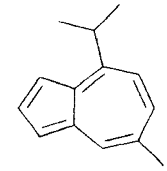
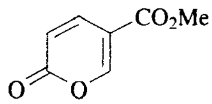
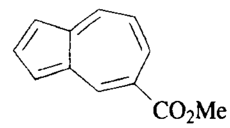
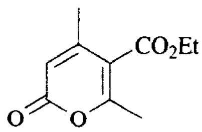
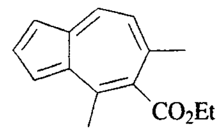
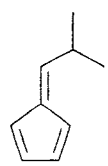
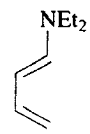
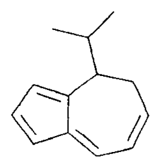
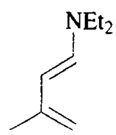
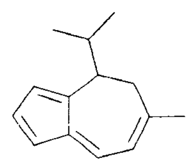
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		(—)	 (—) +  (—)	100
		C_6H_6, rt, 5 d	 (9)	110
		C_6H_6, rt	 (—)	110
C_9 		rt, 24 h	 (23)	99
		rt, 48 h	 (21)	99

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES *(Continued)*

A. All-Carbon Trienophiles

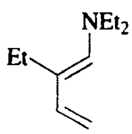
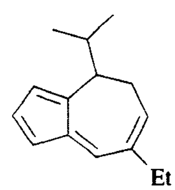
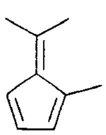
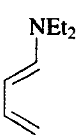
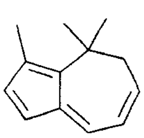
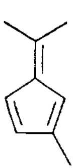
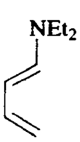
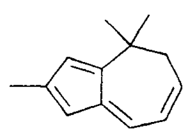
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		rt, 24 h	 (34)	99
		rt, 14 d	 (9)	99
		40°, 4 d	 (12)	99

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

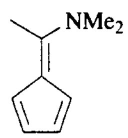
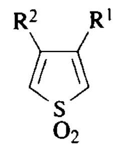
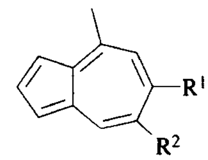
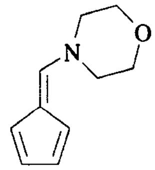
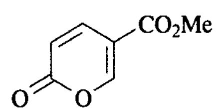
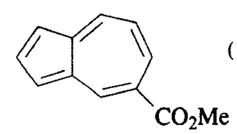
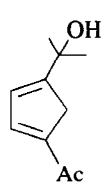
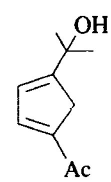
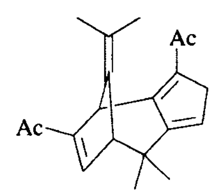
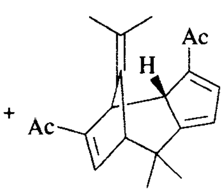
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
				31
	R^1 R^2		R^1 R^2	
	H H	$CHCl_3$, rt, 12 h	H H (4)	
	Me H	$CHCl_3$, rt, 72 h	Me H (10)	
	Et H	$CHCl_3$, rt, 96 h	Et H (12)	
	Ph H	$CHCl_3$, rt, 48 h	Ph H (5)	
			H Ph (1)	
	Me Me	$CHCl_3$, 50°, 72 h	Me Me (7)	
	Cl Cl	$CHCl_3$, rt, 12 h	Cl Cl (15)	
C_{10} 		C_6H_6, rt, 5 d	 (17)	110
		$CHCl_3$, 1 h	 (—) +  (—)	111

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

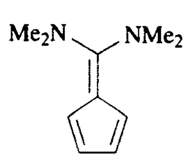
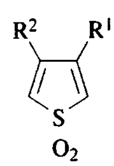
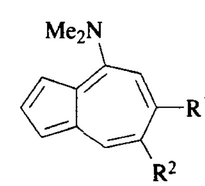
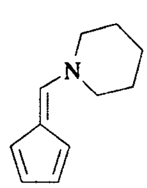
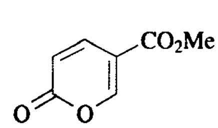
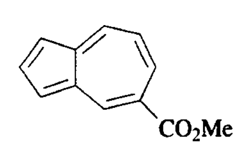
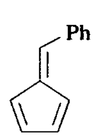
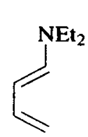
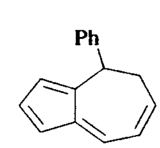
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
				31
	R^1 R^2		R^1 R^2	
	H H	$CHCl_3$, rt, 12 h	H H (10)	
	Me H	$CHCl_3$, rt, 24 h	Me H (5)	
	Et H	$CHCl_3$, rt, 48 h	Et H (8)	
	Ph H	$CHCl_3$, rt, 12 h	Ph H (6)	
			H Ph (1)	
	Ph Ph	$CHCl_3$, rt, 48 h	Ph Ph (10)	
C_{11} 		C_6H_6, rt, 5 d	 (12)	110
C_{12} 		CCl_4, 1 d	 (62)	19, 99

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

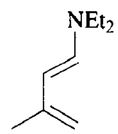
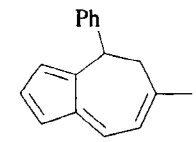
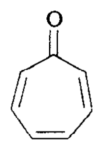
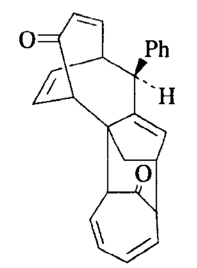
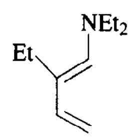
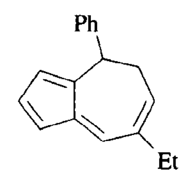
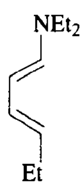
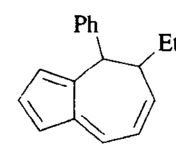
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		rt, 24 h	 (21)	99
		MeOH, 60°	 (86)	81
		rt, 12 h	 (46)	81
		rt, 48 h	 (43)	81

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

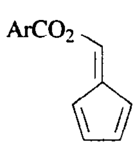
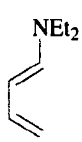
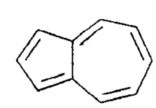
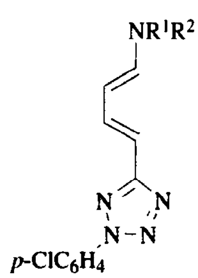
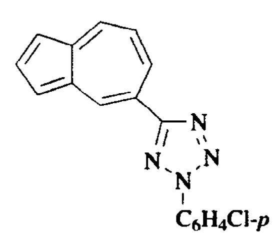
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}  Ar = p-$O_2NC_6H_4$		C_6H_6, rt	 (68)	107
				112
	R^1 / R^2			
	Me / Me	C_6H_6, rt, 7 h	(50)	
	$(CH_2)_4$	C_6H_6, rt, 3 h	(33)	
	$(CH_2)_2O(CH_2)_2$	C_6H_6, 50°, 6 h	(14)	
	Et / Et	C_6H_6, rt, 7 h	(65)	
	$(CH_2)_5$	C_6H_6, 50°, 6 h	(14)	

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

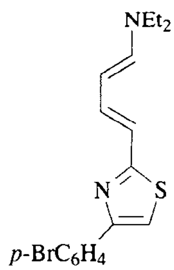
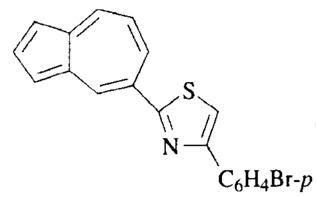
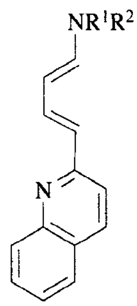
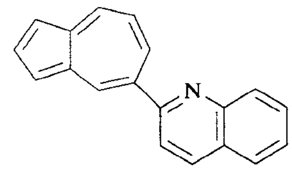
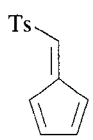
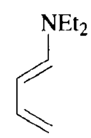
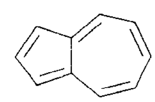
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 50°, 8 h	 (46)	112
				112
	R^1 R^2			
	$(CH_2)_4$	C_6H_6, rt, 8 h	(10)	
	$(CH_2)_5$	C_6H_6, rt, 10 h	(12)	
		CCl_4, rt	 (14)	107

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

A. All-Carbon Trienophiles

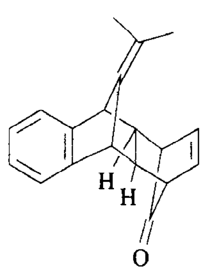
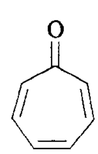
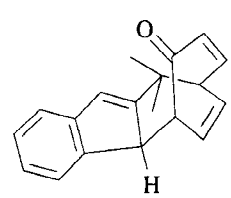
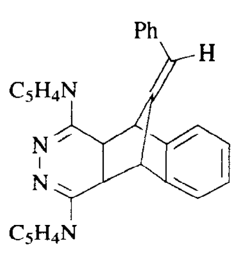
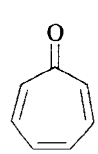
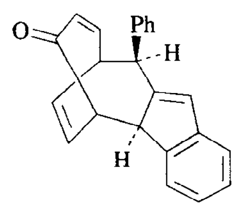
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19} 		120°	 (100)	113, 78
C_{30} 		rt	 (—)	79

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

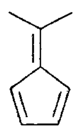
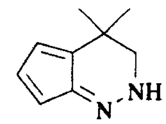
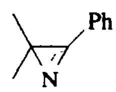
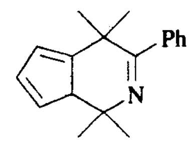
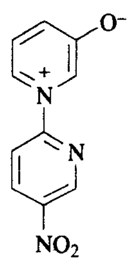
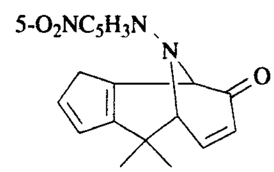
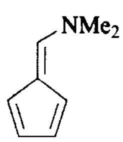
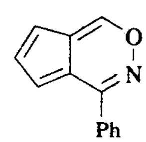
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	CH_2N_2	Et_2O, 0°, 7 d	 (—)	37, 114
		Cyclohexane, *hv*	 (—)	115
		(—)	 (—)	116
	$Ph\text{-}C{\equiv}\overset{+}{N}\text{-}O^-$	Et_2O	 (60)	117

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

B. 1,3-Dipolar Trienophiles

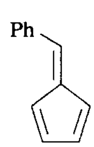
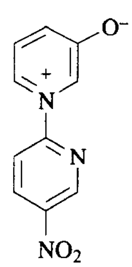
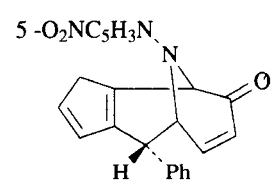
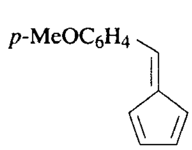
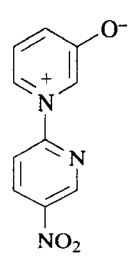
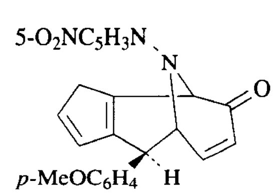
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		(—)	 (—)	116
C_{13} 		(—)	 (—)	116

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

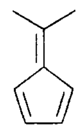
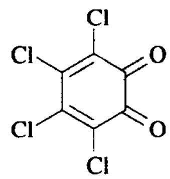
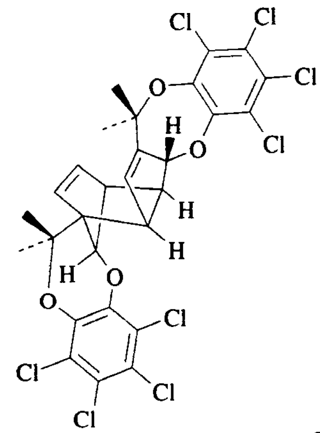
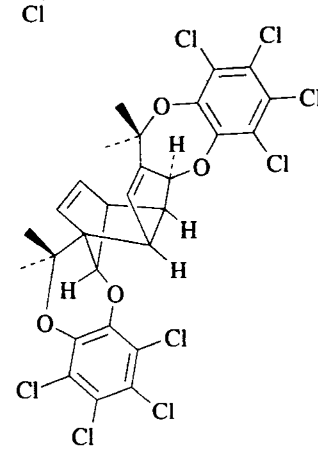
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		THF, rt, 3 h	 (23) +  (36)	118

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

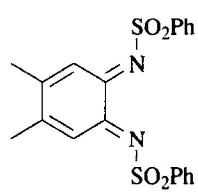
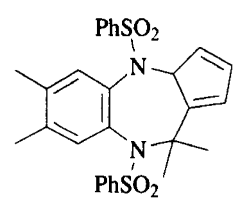
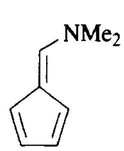
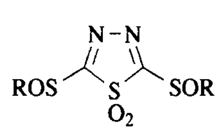
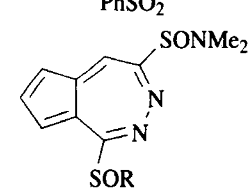
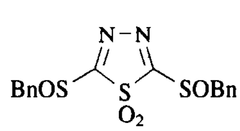
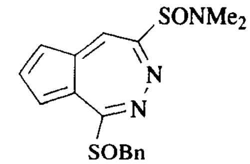
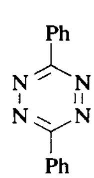
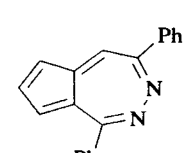
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, rt	 (93)	119
				120
	R			
	Me	Acetone, rt, 0.5 h	(60)	
	Et	Acetone, rt, 15 h	(—)	
		$CHCl_3$, 50°, 15 h	 (—)	120
		C_6H_6, rt, 5 d	 (40)	33

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

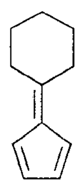
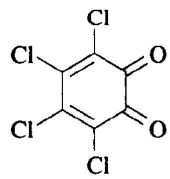
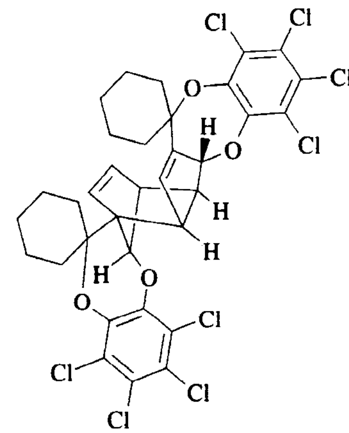
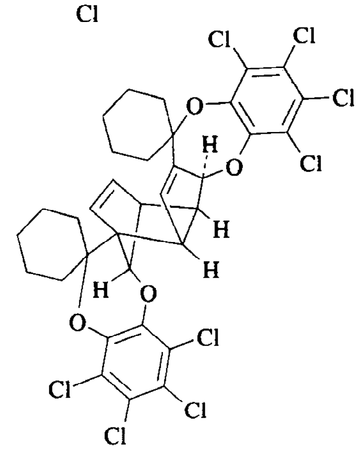
	Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			DME, rt, 30 h	 (18) +	118
				 (25)	

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

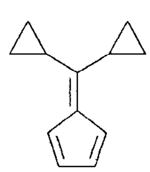
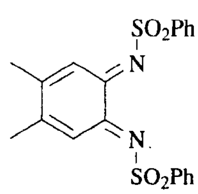
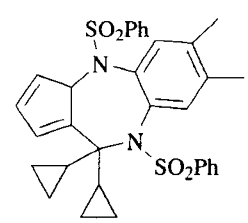
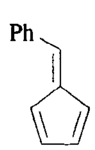
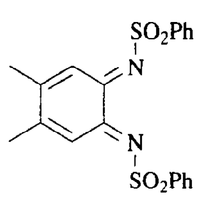
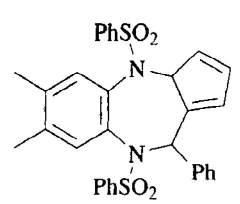
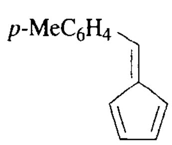
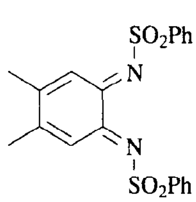
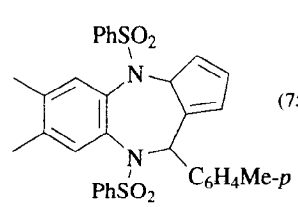
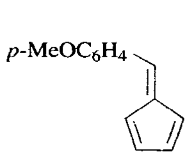
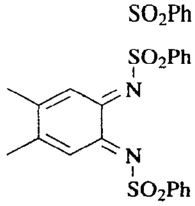
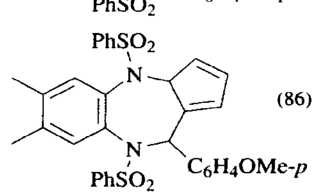
	Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			C_6H_6, rt	 (69)	119, 121
			MeCN, rt, 24 h	 (71)	122
C_{13}			MeCN, rt, 24 h	 (75)	122
			MeCN, rt, 24 h	 (86)	122

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

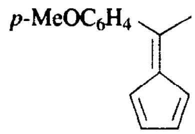
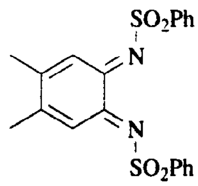
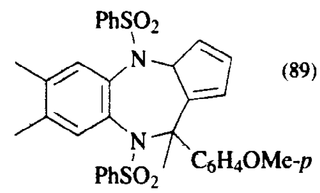
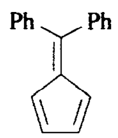
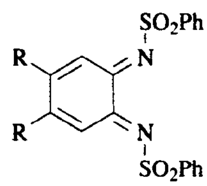
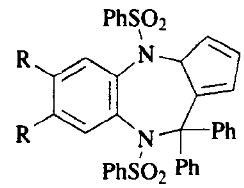
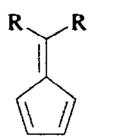
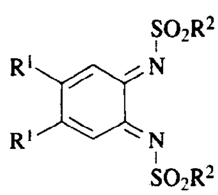
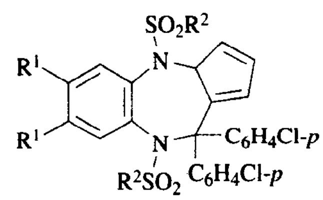
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 		C_6H_6, rt	 (89)	119
C_{18} 				121, 119
	R			
	Me	C_6H_6, rt	(49)	
	Cl	C_6H_6, rt	(62)	
 R = p-ClC_6H_4				119, 121
	R^1 R^2			
	Me Ph	C_6H_6, rt	(83)	
	Me p-$O_2NC_6H_4$	C_6H_6, rt	(50)	
	Me p-$MeOC_6H_4$	C_6H_6, rt	(55)	

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

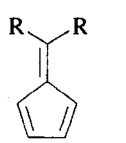
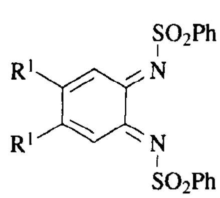
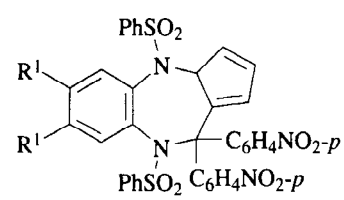
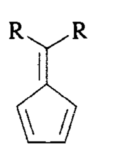
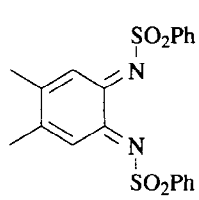
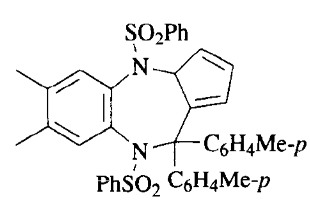
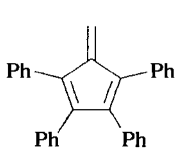
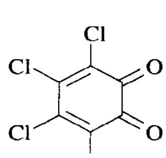
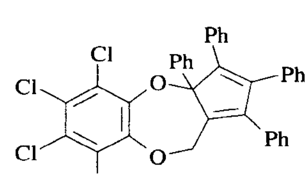
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = p-$O_2NC_6H_4$				119, 121
	R^1			
	Me	C_6H_6, rt	(92)	
	Cl	C_6H_6, rt	(70)	
C_{20}  R = p-MeC_6H_4		C_6H_6, rt	 (60)	119, 121
C_{30} 		C_6H_6, rt, 10 h	 (24)	122a

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

C. Heterodienes

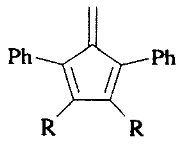
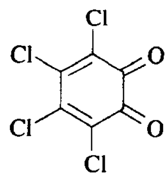
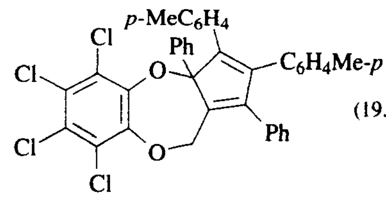
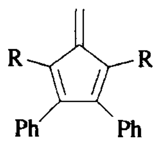
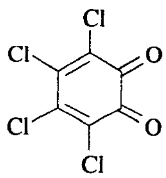
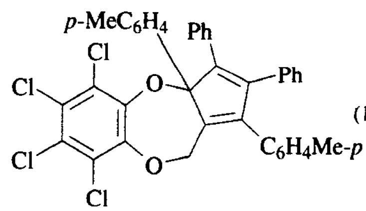
	Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{32}	 R = *p*-MeC_6H_4		C_6H_6, rt	 (19.5)	122a
	 R = *p*-MeC_6H_4		C_6H_6, rt	 (12.5)	122a

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

D. Intramolecular Reactions

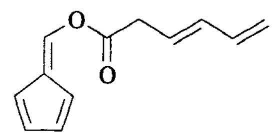
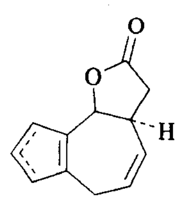
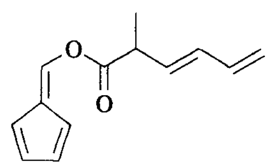
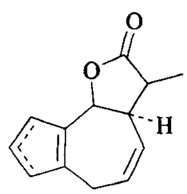
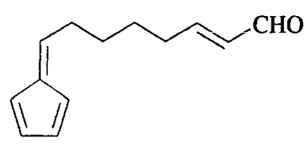
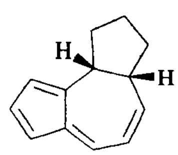
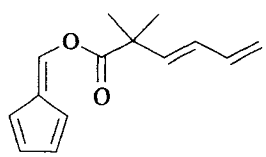
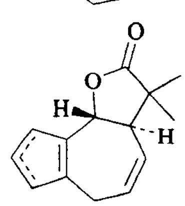
	Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			Toluene, 160°	 (52)	123
C_{13}			Toluene, 160°	 (38)	123
			1. Et_2NH, K_2CO_3, C_6H_6 2. C_6H_6, 40°	 (55)	36
C_{14}			Toluene, 160°, 4 h	 (56)	123

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

D. Intramolecular Reactions

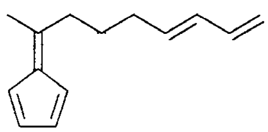
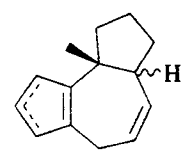
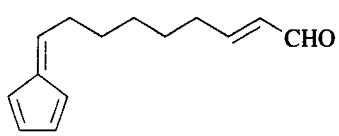
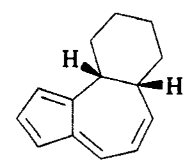
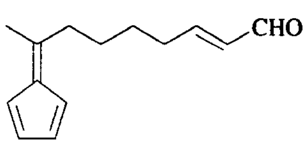
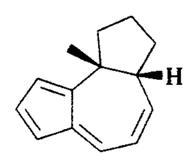
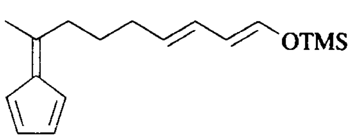
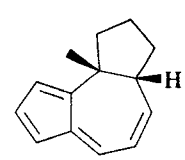
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)		Refs.
		Toluene, 210°, 48 h		(45)	36
		1. Et_2NH, K_2CO_3, C_6H_6 2. C_6H_6, 40°		(46)	36
		1. Et_2NH, K_2CO_3, C_6H_6 2. C_6H_6, 40°		(54)	36
C_{17} 		C_6H_6, 40°		(—)	36

TABLE II. [6+4] CYCLOADDITIONS OF FULVENE DERIVATIVES (*Continued*)

D. Intramolecular Reactions

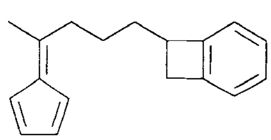
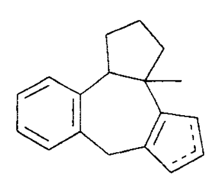
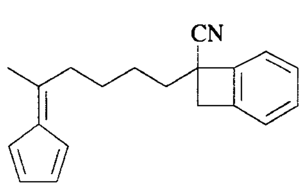
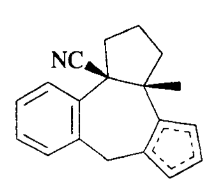
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{18} 		Toluene, 195°, 12 h		(44)	35
C_{19} 		o-$Cl_2C_6H_4$, 180°, 7 h		(60)	35

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS

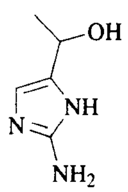
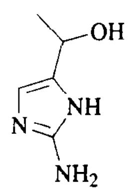
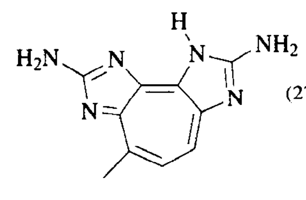
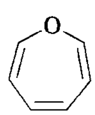
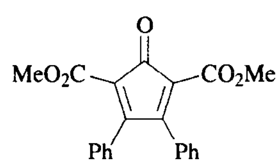
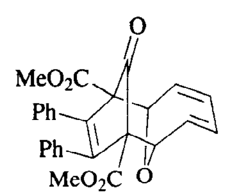
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		H_2SO_4, 100°, 12 h	 (27)	124
C_6 		C_6H_6, rt, 1 d	 (12)	125

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

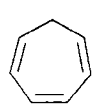
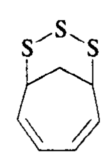
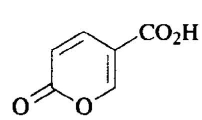
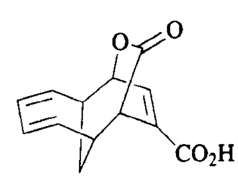
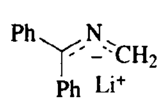
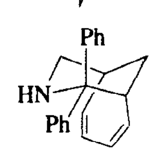
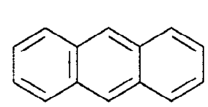
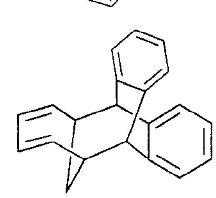
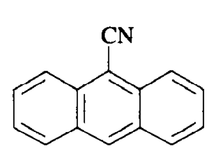
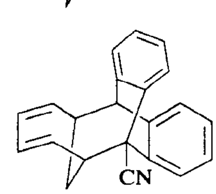
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	S_3	Sulfolane, pyridine, 70°, 72 h	 (21)	126
		Xylene, 180°	 (1)	127
		Et_2O, −45°	 (47)	128
		C_6H_6, rt, *hv*	 (34)	129
		C_6H_6, rt, *hv*	 (4)	130

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

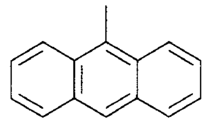
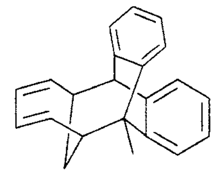
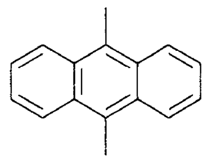
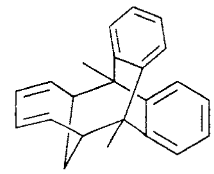
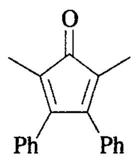
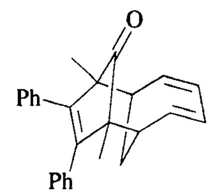
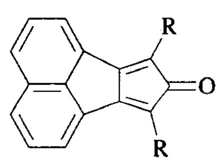
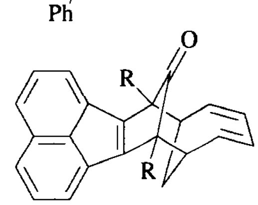
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, rt, *hv*	 (9)	131
		C_6H_6, rt, *hv*	 (—)	131
		170°, 36 h	 (33)	132
				133
	R			
	Et	80°, 39 h	(21)	
	CO_2Et	rt, 108 h	(57)	

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

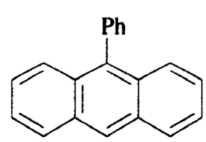
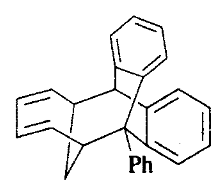
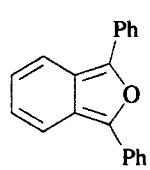
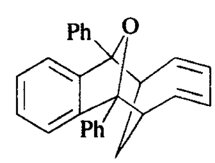
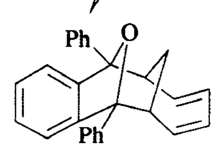
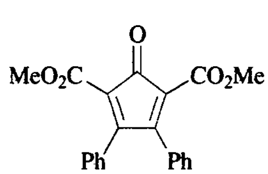
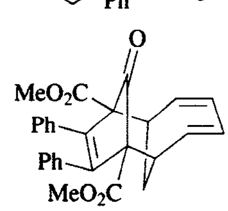
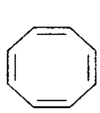
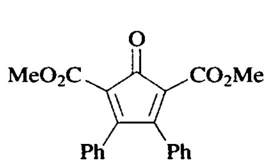
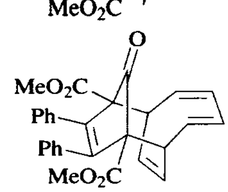
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, rt, *hv*	 (38)	131
		EtOH, *hv*	 (16) +  (20)	134, 135
		rt, 10 d	 (57)	136
C_8 		C_6H_6, 80°	 (46)	137, 138

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

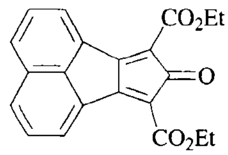
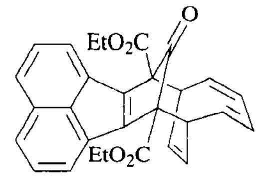
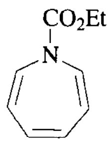
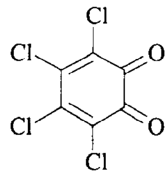
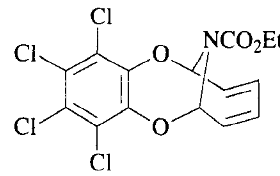
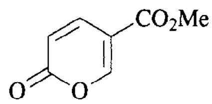
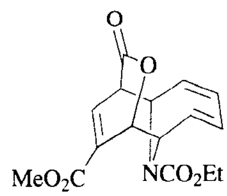
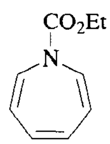
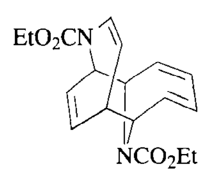
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 80°, 8 h	 (16)	136
C_9 		C_6H_6, rt, 70 min	 (46)	139
		C_6H_6, 80°, 57 h	 (20)	140, 141
		125°	 (—)	142

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

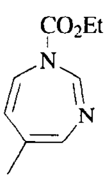
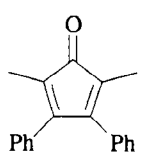
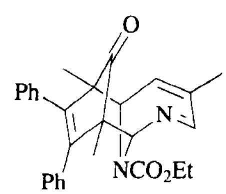
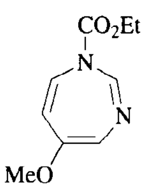
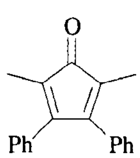
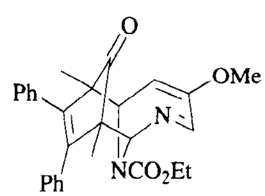
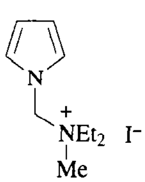
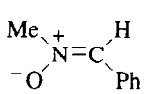
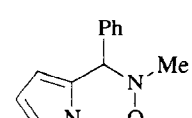
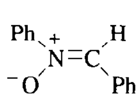
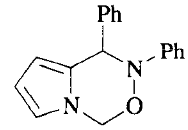
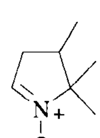
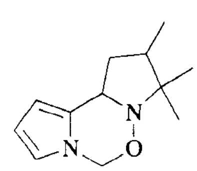
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		Xylene, 140°, 6 d	 (7)	143
		Xylene, 140°, 6 d	 (30)	143
C_{10} 		DMSO, 120°	 (87)	144
		DMSO, 120°	 (92)	144
		DMSO, 120°	 (91)	144

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

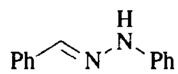
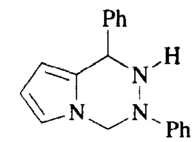
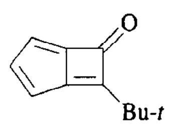
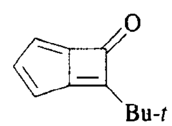
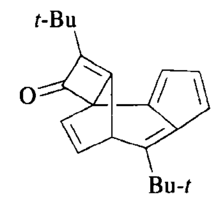
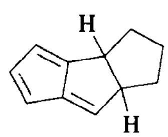
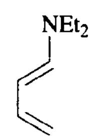
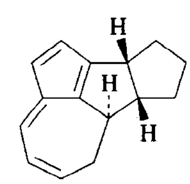
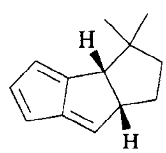
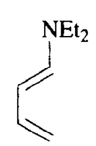
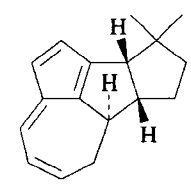
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		DMSO, 120°	 (82)	144
C_{11} 		CH_2Cl_2, rt	 (40)	145
		C_6H_6	 (31)	146
C_{13} 		C_6H_6	 (66)	146

TABLE III. MISCELLANEOUS [6+4] CYCLOADDITION REACTIONS (*Continued*)

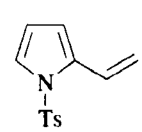
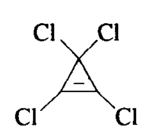
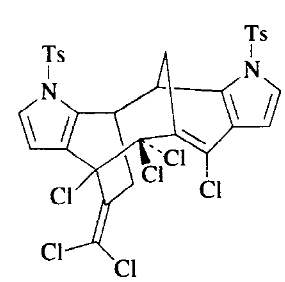
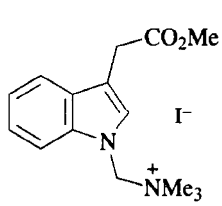
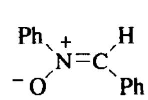
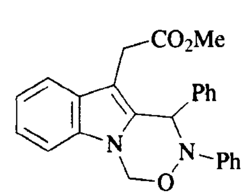
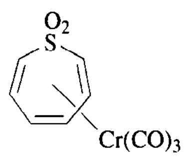
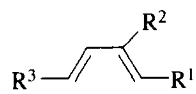
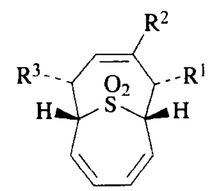
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CCl_4, 69°	 (—)	147
C_{15} 		DMSO, 120°	 (22)	144

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
		1. C_6H_{14}, CH_2Cl_2, *hν* 2. O_2, Et_2O		23, 42

R^1	R^2	R^3	Yield (%)
H	Me	H	(77)
OAc	H	H	(78)
CO_2Me	H	H	(38)
CO_2Me	H	Me	(21)
OTMS	H	H	(65)

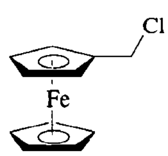
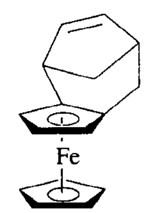
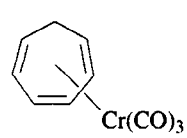
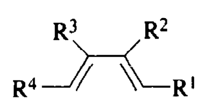
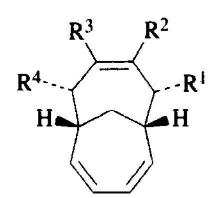
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, rt	 (—)	148

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
		**A**. 1. C_5H_{12}, *hν* 2. Me_3P **B**. 1. C_6H_{14}, *hν* 2. $(MeO)_3P$ **C**. *n*-Bu_2O, 142°		

R^1	R^2	R^3	R^4	Conditions	Yield (%)	Refs.
H	H	H	H	**A**	(21)	149, 150
Me	H	H	H	**A**	(38)	150
H	Me	H	H	**A**	(59)	150
Me	H	H	Me	**B**	(86)	23
Me	H	H	Me	**C**	(70)	23
H	Me	Me	H	**A**	(32)	150
CH=CH_2	H	H	H	**A**	(41)	150
OMe	H	H	H	**B**	(64)	22
OAc	H	H	H	**B**	(67)	22
OAc	H	H	H	**C**	(59)	23
CO_2Me	H	H	H	**B**	(83)	22
CO_2Me	H	H	H	**C**	(55)	23
OTMS	H	H	H	**B**	(86)	23
H	OTMS	H	H	**B**	(82)	23
CO_2Me	H	H	Me	**B**	(96)	23
CO_2Me	H	H	Me	**C**	(60)	23
OAc	H	H	O Ac	**B**	(65)	22, 23
CO_2Me	H	H	CO_2Me	**B**	(89)	23

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

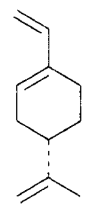
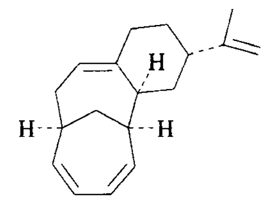
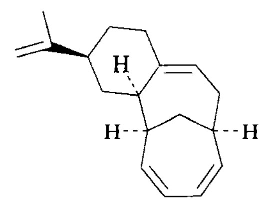
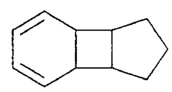
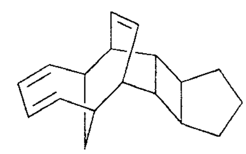
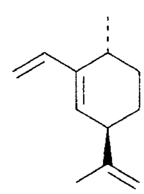
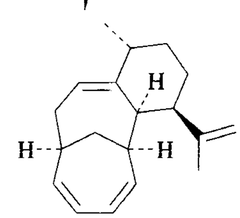
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (15) +	22
			 (45)	
		1. C_5H_{12}, *hv* 2. $(MeO)_3P$	 (21)	151
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (63)	22

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

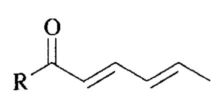
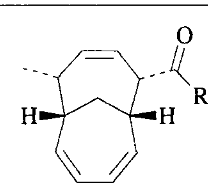
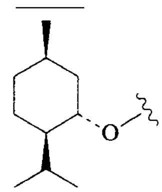
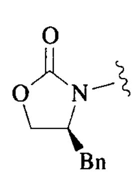
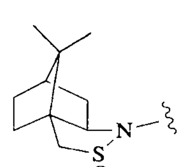
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$		23
	R			
			(50)	
			(75)	
			(74)	

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

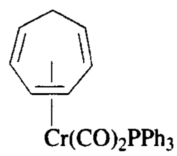
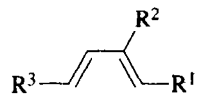
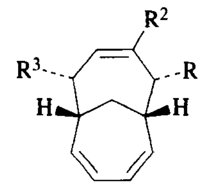
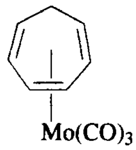
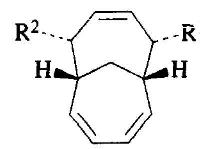
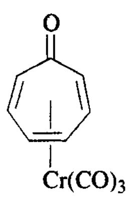
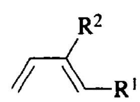
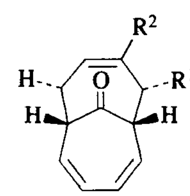
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R^1 / R^2 / R^3 CO_2Me / H / Me H / OTMS / H	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (72) (53)	23
	 R^1 / R^2 OTMS / H Me / H Me / CO_2Me	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (51) (32) (27)	23
	 R^1 / R^2 Me / H H / Me	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (20) (40)	23

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

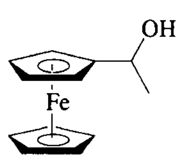
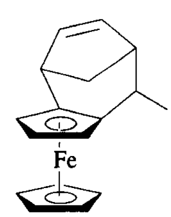
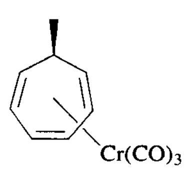
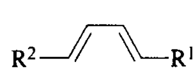
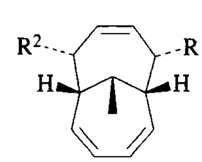
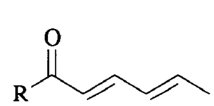
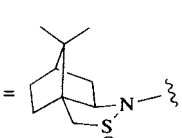
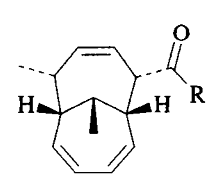
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, Ph_3CBF_4	 (—)	148
C_8				
	 R^1 / R^2 OMe / H Me / CO_2Me	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (47) (97)	 22 23
	 R = 	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (75)	23

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

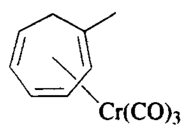
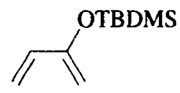
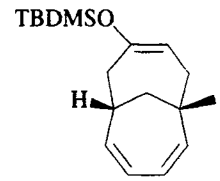
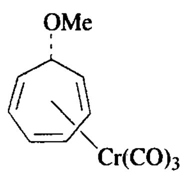
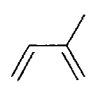
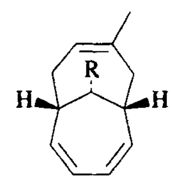
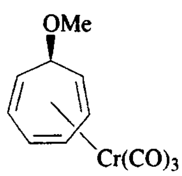
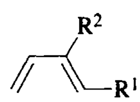
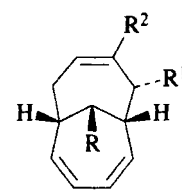
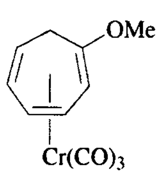
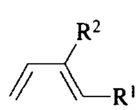
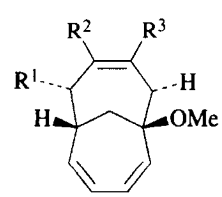
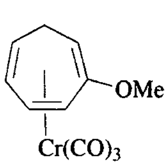
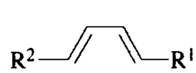
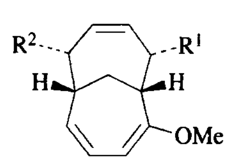
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, $h\nu$ 2. $(MeO)_3P$	 (35)	23
		1. C_6H_{14}, $h\nu$ 2. $(MeO)_3P$	 (66) R = OMe	22
 	 R^1 / R^2: OAc / H; H / Me	1. C_6H_{14}, $h\nu$ 2. $(MeO)_3P$	 R = OMe (60) (60)	22

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, $h\nu$ 2. $(MeO)_3P$		23

R^1	R^2
H	OTBDMS
Me	H
OTMS	H
H	Me

R^1	R^2	R^3	
H	OTBDMS	H	(52)
Me	H	H	(45)
OTMS	H	H	(38)
H	Me	H	(36)
H	H	Me	(12)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, $h\nu$ 2. $(MeO)_3P$		23

R^1	R^2
Me	CO_2Me
OTMS	H

R^1	R^2	
Me	CO_2Me	(44)
CO_2Me	Me	(45)
OTMS	H	(45)
H	OTMS	(44)

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

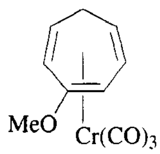
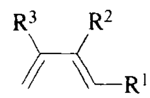
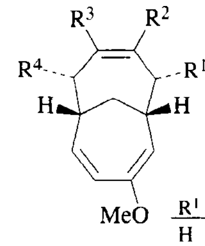
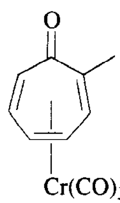
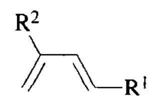
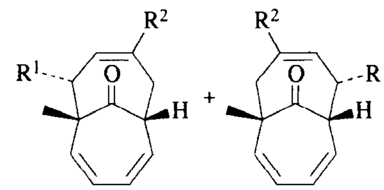
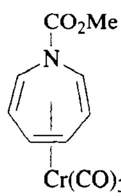
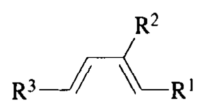
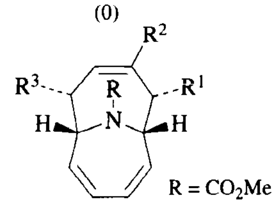
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R[1] R[2] R[3] H Me Me OTMS H H	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 R[1] R[2] R[3] R[4] H Me Me H (93) OTMS H H H (40) H H H OTMS (39)	23
	 R[1] R[2] H Me Me H	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (32.5) (32.5) (0) (23)	23
	 R[1] R[2] R[3] H OTMS H OAc H H OTMS H H Me H CO_2Me	1. C_6H_{14}, Et_2O, *hv* 2. O_2, Et_2O	 R = CO_2Me (87) (75) (79) (83)	23, 42

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

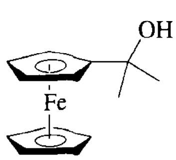
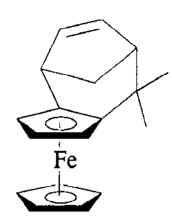
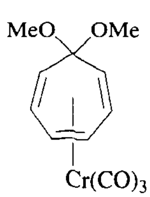
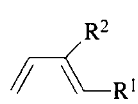
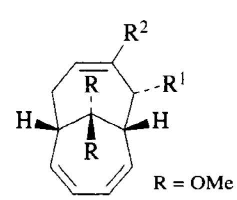
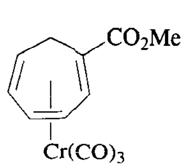
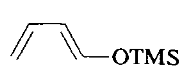
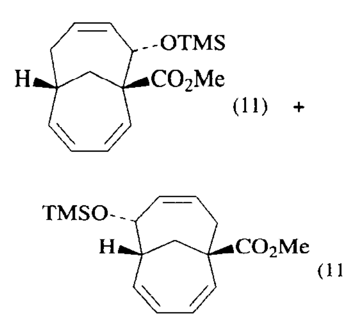
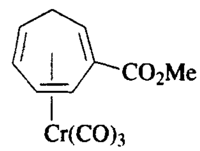
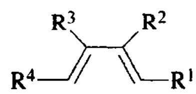
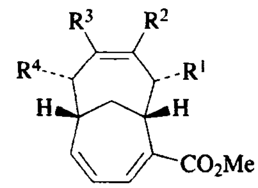
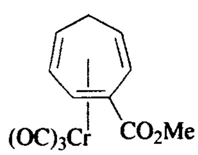
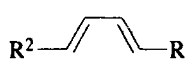
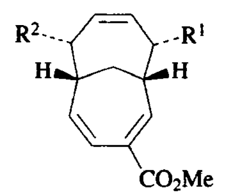
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_2Cl_2, $Ph_3C^+ BF_4^-$	 (—)	148
C_9 	 R[1] R[2] Me H H Me	1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 R = OMe (50) (67)	22
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (11) + (11)	23

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$		23

R^1	R^2	R^3	R^4
OTMS	H	H	H
Me	H	H	Me

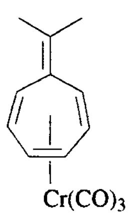
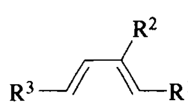
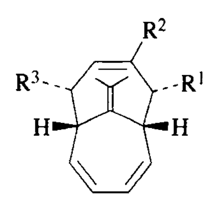
R^1	R^2	R^3	R^4	Yield
OTMS	H	H	H	(37)
H	H	H	OTMS	(38)
H	Me	Me	H	(74)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$		23

R^1	R^2
Me	Me
Me	CO_2Me

R^1	R^2	Yield
Me	Me	(90)
Me	CO_2Me	(45)
CO_2Me	Me	(45)

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 		1. C_6H_{14}, *hv* 2. $(MeO)_3P$		24

R^1	R^2	R^3	Yield
H	H	H	(49)
Me	H	H	(62)
Me	H	Me	(61)
H	Me	H	(50)

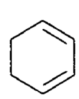
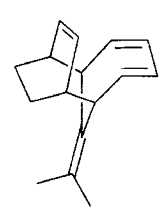
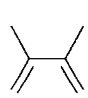
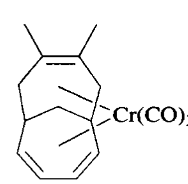
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (74)	24
		1. C_6H_{14}, *hv* 2. CO	 (68)	152

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

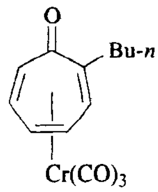
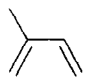
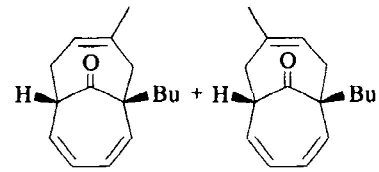
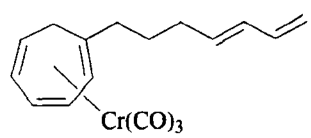
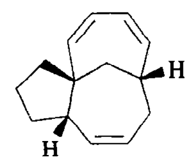
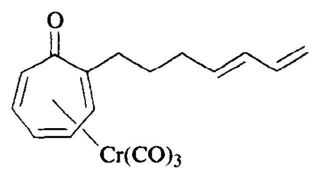
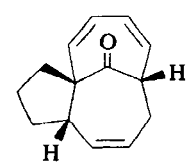
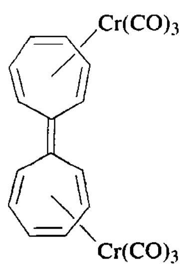
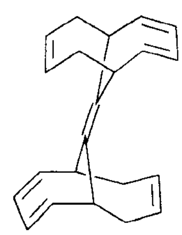
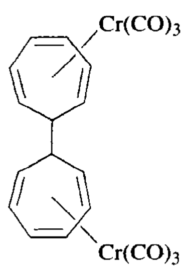
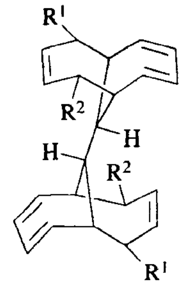
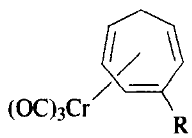
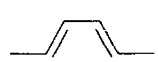
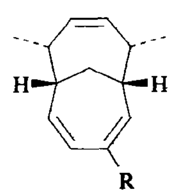
Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (33) (32)	23
C_{14}				
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (85)	153
		1. C_6H_{14}, *hv* 2. $(MeO)_3P$	 (52)	153

TABLE IV. METAL-MEDIATED [6+4] CYCLOADDITIONS (*Continued*)

Triene	Trienophile	Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, *hv*	 (34)	154
	 R^1 R^2 H H Me H Me Me	1. THF, *hv* 2. $(MeO)_3P$	 (48) (39) (42)	155
 R = (+)-2,10-camphor sultam		1. C_6H_{14}, Et_2O, *hv* 2. O_2, Et_2O	 (82) >98% de	41a

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