The Oxidation of Alcohols by Modified Oxochromium(VI)–Amine Reagents

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1. Introduction

The development of oxochromium(VI)-amine reagents as oxidants in organic synthesis has evolved since the early studies of Sisler (1-3) which described the use of adducts of heterocyclic nitrogen bases and chromium(VI) oxide. The later work of Sarrett and coworkers in steroid synthesis soon established the utility of chromium(VI) oxide-pyridine adducts (1) as the first selective oxochromium(VI)-amine reagents. (4) Several modifications of the Sarrett oxidation (5-8) followed Sarrett's original report and varied mainly in solvent type and mode of preparation. All had the advantage of providing selectivity for the oxidation of primary and secondary alcohols without the undesirable side reactions promoted by chromic acid. Subsequently Corey and Fleet (9) reported the oxidizing properties of the chromium(VI) oxide-3,5-dimethylpyrazole complex which, like the dipyridine complex, later proved to be an effective oxidant for allylic alcohols. (10)

The search for a milder and more efficient oxidant than the Sarrett-type oxochromium(VI) reagent systems as well as the nonchromium oxidants based on dimethyl sulfoxide (11, 12) or dimethyl sulfide (13) led to an examination of the utility of pyridinium chlorochromate (PCC) in selective oxidations of alcohols. (14, 15) When compared with the Sarrett/Collins systems, PCC (2) was superior in terms of ease of preparation, shelf stability and economy. Since the introduction of PCC in 1975 the reagent has become a commercially available "textbook" compound and is usually the reagent of choice for routine large and small scale oxidations of alcohols to carbonyl compounds. (16) Unlike the oxochromium(VI)-pyridine adducts, PCC is an acid salt, and its properties have proven advantageous in a number of tandem oxidative reactions such as oxidative transpositions (17-19) and oxidative cationic cyclizations. (20) Several reviews address the versatility of PCC and its extension to many different types of oxidative conversions in single and multistep organic syntheses. (21) Such reports cover carbohydrate oxidation, (21) oxidative rearrangements of tertiary cyclopropyl carbinols, (22) oxidation of organoboron compounds to carbonyl compounds, (23) allylic oxidation, (24, 25) benzylic oxidation, (26-28) oxidation of enol ethers to esters and lactones, (29, 30) and oxidative cleavage of substituted furans (31) and oximes. (32, 33)

While PCC was gaining widespread use, the utility of pyridinium dichromate

(34) (PDC, 3) in solvents such as dimethylformamide (DMF) and dichloromethane was reported. PDC/DMF was useful for oxidizing allylic alcohols to the corresponding, α , β -unsaturated carbonyl compounds and non-conjugated aldehydes and primary alcohols to the corresponding carboxylic acids. In contrast to PDC/DMF, PDC/ CH₂Cl₂ oxidized secondary alcohols to the corresponding ketones, and primary alcohols to the corresponding aldehydes. PDC is safely prepared and handled, shelf-stable and commercially available. The utilization of PDC has been extended beyond the simple oxidation of alcohols, and it is now employed for transformations such as oxidative transpositions, (35) catalytic oxidation, (36) conversion of aldehydes to esters, (37) allylic oxidation, (38) acetal cleavage, (39) and carbohydrate oxidation. (40)

Many other types of substituted pyridines, nitrogen heterocycles and amines form chromates, dichromates, and chlorochromates which allow many different types of oxidative processes for a wide range of substrate molecules. Chlorochromates of 2,2¢-bipyridine (4), (41) 4-(dimethylamino)pyridine (5), (42) napthyridine, (43) pyrazine, (44) N-benzyltriethylammonium, (45) tetrabutylammonium (6), (46) trimethylammonium (7) (47) and 2-cyanopyridine (48) have been prepared and used for the selective oxidation of allylic alcohols, furan cleavage, oxidative ether formation, and oxidation of thiols, sulfides, and sulfoxides. (49) As with the chlorochromates, the original pyridinium dichromate studies prompted the preparation of many more dichromates for examination as mild oxidants or oxidants with unique selectivity. For example dichromates based on 2- and 4-benzylpyridine, (50) quinoline (8), (51) nicotinic acid (9), (52) tetrabutylammonium, (53) tetrakis(pyridine)silver, (54) and imidazole (10) (55) were contrived in order to realize modified reactivity as compared to PDC. As substituting the ligand species associated with oxochromium(VI) produces significant differences in reactivity, so too will changes in the nature of the oxochromium species afford reagents of special reactivity. Oxochromium(V) reagents (56) and fluorochromates (11) (57) have been prepared and are efficient reagent systems for oxidative lactonizations and Etard-type oxidations of substituted toluenes.

The present concern with the toxicity and environmental implications of oxochromium(VI) has provided encouragement for the study and use of catalytic oxochromium reagents in conjunction with stoichiometric co-oxidants such as peroxides. (58) Such technology is welcome, particularly when applied to the largescale preparations found in industry where the disposal of byproducts is a constant problem.

Separation of the reduced chromium species, many of which are intractable tars, from the desired products has long posed a problem when using many of the "textbook" oxochromium(VI) reagents. A major advantage of the PCC

reagent was the usage of less than half the equivalents required of the Collins reagent, thus providing less expense and less polymeric reduced chromium byproducts to separate and dispose.

Modified oxochromium(VI)-amine reagents on polymer supports (59) have been prepared and examined with the objective of providing a regenerable reagent system which is serviceable on a practical scale. Chromates, dichromates, and chlorochromates of cross-linked polyvinylpyridine resin (60) were studied as reagent systems for the oxidation of simple alcohols to carbonyl compounds with the primary focus on stoichiometry and regeneration of active reagent from the used resin.

A significant improvement in routine oxidations utilizing PCC and PDC entails the addition of adsorbents such as Celite[®], (61) alumina, (62) silica gel, (63) molecular sieves, (64) or zeolites. (65) The distinct advantages associated with the use of adsorbents in oxochromium(VI)-amine-mediated oxidations are the facile removal of the polymeric reduced chromium byproducts, buffering effects, and desiccation effects. The necessity for easy removal of the reduced chromium tars which accompany many oxochromium(VI)-amine oxidations and may entrain a portion of the desired product has been mentioned previously.

The importance of buffers (66) and desiccants in oxochromium(VI) oxidations is apparent when considering substrates bearing acid-sensitive protecting groups, acid-sensitive E/Z isomerizable double bonds, or aldehyde moieties. Reactive aldehydes which form acetals or hemiacetals will undergo further oxidation to carboxylic acid or ester derivatives (67, 68) as side reactions, thereby reducing yields.

Thus virtually any number of oxochromium(VI)-amine reagents may be prepared by varying the amine ligand and/or acid species associated with oxochromium(VI), and many of these compounds have been tested using simple substrate alcohols for oxidation to carbonyl compounds. More often than not the initial investigation stops at the point of evaluating simple substrates, and further use of the reagent is encumbered by expense or lack of demonstrated applicability with complex substrates. A substantial test of a new oxidant's utility is the response of multifunctional intermediates usually found in complex total synthesis.

Representative Oxochromium(VI)-Amine Reagents



Synthetic chemists engaged in multistep schemes will continue to examine and evaluate a reagent's applicability with respect to protecting group integrity, reactivity with heteroatoms such as nitrogen, phosphorus, and sulfur, and the avoidance of unwanted side reactions such as dehydration, cationic olefin cyclization, carbon-carbon bond cleavage, or overoxidation.

This chapter surveys the many applications of oxochromium(VI) complexes in oxidative conversions of alcohols to carbonyl compounds. Alternative reagent systems based on modifications involving ligands, buffering agents, or adsorbents, as well as nonchromium(VI) oxidants are discussed. A variety of

substrates have been included in the Tables so as to guide the synthetic chemist in selecting reagents and conditions that will be optimal for a given transformation. Oxidative conversions of alcohols through transpositions and cationic cyclizations giving carbonyl compounds as endproducts are included.

2. Mechanism

2.1. Alcohol Oxidations

Westheimer first demonstrated the presence of oxochromium(VI) ester intermediates in chromic acid-mediated oxidations of 2-propanol to acetone. Westheimer and coworkers prepared solutions of isopropyl chromate in benzene and observed its decomposition to acetone upon addition of pyridine. (69) Based on rate observations, the proposed mechanism involves formation of the chromate ester (rapid) (Eq. 1); and base-catalyzed decomposition of the chromate ester intermediate to acetone by release of a proton (Eq. 2). Chromate esters have also been

$$\begin{array}{c} R^{1} \\ R^{2} \\ H \end{array} \xrightarrow{OH} + H_{2}CrO_{3} \xrightarrow{R^{1}} \\ H \end{array} \xrightarrow{O-Cr=O}_{I} \\ R^{2} \\ H \end{array} \begin{array}{c} O \\ O-Cr=O \\ OH \end{array}$$
(1)

implicated in PCC oxidations of isopropanol, 1-butoxy-2-propanol (70) and substituted mandelic acids (71) in aprotic solvents such as chlorobenzene or nitrobenzene with acid catalysis. In contrast to Westheimer's findings, a direct hydride transfer mechanism involving delivery from the substrate alcohol to a protonated chlorochromate species has also been proposed. (72) Intramolecular hydride delivery after prior formation of a chromate ester may also occur (Eq. 3). (73, 74) The

kinetic isotope effects exhibited for α , α '-dideuterioalcohols indicate that the rate-determining step is C-H bond cleavage. (75) The stoichiometry of the PCC oxidation of 1-octanol in methylene chloride at reflux requires only the theoretical amount of reagent. (76) While these results are in contrast to the original reports of using 1.5 equivalents of reagent, the more vigorous conditions presumably minimized the entrainment of PCC in the reduced

chromium polymer. Although the ideal conditions provide quantitative conversion to the product aldehyde with a single equivalent of PCC, treatment of more complex substrates that are sensitive to rearrangement or that bear acid-sensitive protecting groups will possibly suffer side reactions at the elevated temperatures. (76)

During Collins oxidations the chromate ester may form through a postulated monopyridine intermediate that is formed by disproportionation of the dipyridine complex upon addition of the substrate alcohol (Eq. 4). (77) The second equivalent

of pyridine may then act as the base which abstracts the α -proton, or the proton transfer may be intramolecular. (78, 79)

In summary, the nature and decomposition of the chromate ester intermediate may be dictated by the acidity of the reagent, the protic nature of the solvent, or the basicity of the ligands associated with oxochromium(VI). (80, 81)

2.2. Oxidative Annulation of Alcohols

The acidity of pyridinium chlorochromate may be used to advantage for the oxidative annulation of substrate alcohols with suitably disposed double bonds. A typical case involves the oxidative cyclization of (–)-citronellol to (–)-pulegone. (82, 83) The overall conversion entails the unbuffered oxidation of citronellol to the aldehyde, cationic cyclization of the aldehyde to the intermediate isopulegol, and oxidation and isomerization of the isopulegol to pulegone (Scheme 1). The oxidative cyclization has been extended to a number of unsaturated aldehyde substrates but is limited to the formation of six-membered rings. Cyclization of the intermediate unsaturated aldehydes is observed only in cases in which a tertiary cation is formed as the initial cyclic intermediate.

Scheme 1.



2.3. Oxidative Transposition of Tertiary Allylic Alcohols

The oxidative transposition of tertiary allylic alcohols (84-88) (Eq. 5) may follow one of two mechanistic pathways, which are presumably dependent on the acidity



of the oxochromium(VI) reagents employed. The use of the mildly acidic PCC may result in the reaction proceeding by Path A (Scheme 2) in which the substrate is ionized— either through the initial formation of the chromate ester or prior solvolysis of the tertiary alcohol. The resulting carbonium ion then recombines with the chromium(VI) ion at the secondary position which is then oxidized through the normal pathway to the product enone. Path B may be followed in cases in which the basic oxochromium(VI) reagents such as the Collins reagent or pyridinium dichromate are used. The formation of an initial tertiary chromate ester is followed by a 1,3-sigmatropic rearrangement to give the secondary ester, which is then oxidized, to the product enone as in Path A. Scheme 2.



2.4. Oxidative Cyclizations of Olefinic Alcohols to Cyclic Ethers

Although oxametallocyclobutane intermediates have been implicated in oxochromium(VI)-mediated oxidations of isolated double bonds, (89) the formation of the same types of intermediates may be invoked in the substituent-directed oxidative cyclization of 4-alken-1-ols to substituted tetrahydrofurans (Eq. 6). (90, 91)



A plausible mechanism for this type of transformation involves formation of the tertiary oxochromium(VI) ester followed by a *syn* addition of the chromate ester across the double bond (Scheme 3). (92) The intermediate oxametallacyclobutane thus formed collapses and suffers further oxidation to form the bicyclic ketone intermediate. Extensive studies have been made of the scope and mechanism of the substituent-directed oxidation with both

oxochromium(VI) reagents and other high-valent metal oxidants. (93) Although other mechanistic routes considered involve Criegee intermediates or epoxidation prior to cyclization, the less acidic pyridinium dichromate is not as effective as PCC in promoting the reaction, and the Collins reagent does not promote the cyclization. Scheme 3.

 $\xrightarrow{L_{0}}_{O=Cr}^{L_{0}} \xrightarrow{O}_{O-Cr}^{L_{0}} \xrightarrow{O}_{O-Cr}^{O} \xrightarrow{H_{0}} \xrightarrow{O}_{O} \xrightarrow{O$

3. Scope and Limitations

Oxochromium(VI)-amine reagents are mildly to moderately acidic oxidants with their degree of acidity largely dependent on the associated nitrogen base ligands. Reagents with multiple basic sites in the form of heterocyclic ligands contain their own internal buffer system. However, large excesses of the reagents and extended reaction times are usually required. In contrast to active manganese dioxide, oxochromium(VI)-amine reagent systems promote the isomerization of Z- α , β -unsaturated aldehyde products to the E isomers in the oxidation of allylic alcohols. Notwithstanding the tendency to promote the isomerization of double bonds, oxochromium(VI)-mediated conversions of allylic alcohols require fewer equivalents of reagent and shorter reaction times (94) than do reactions with active MnO₂. Although the basicity of the chromium trioxide/dipyridine systems allows for the oxidation of many substrates containing a variety of protecting groups, amine chlorochromate reagents usually require the addition of a buffer to enhance survival of the protecting group. (95) The addition of external buffers has facilitated the use of oxochromium(VI) reagents with substrates bearing tetrahydropyranyl (THP) protecting groups, silvl ethers such as the *tert*-butyldimethyl-silvl (TBDMS) group, and many types of ketal protecting groups. While PCC will promote oxidative cationic cyclizations of olefinic alcohols and aldehydes (Eq. 7), use of the buffering agent will retard these reactions and mediate only



the oxidations of the alcohol to the carbonyl compound. For example, the buffered oxidation of citronellol results in its conversion to the corresponding aldehyde citronellal while the unbuffered oxidation results in its cyclization to pulegols. (96)

Oxochromium(VI) reagents are undesirable for the oxidation of carbohydrate-derived alcohols to the corresponding carbonyl compounds. However, the addition of molecular sieves (97) or acetic anhydride (98) will expedite these conversions in conjunction with PCC, PDC or Sarrett-type reagents. The use of additives such as alumina, (61) Celite[®], (60) silica gel (62) or clays (64) has proven effective in oxochromium(VI)-amine oxidations since these materials adsorb much of the reduced chromium tars, which entrain the reactants and products thereby lowering yields. In cases where

oxochromium(VI) reagents alone are ineffective in oxidizing carbohydrate-derived alcohols to the corresponding carbonyl compounds, and the addition of molecular sieve or acetic anhydride to these oxidations does not promote the oxidation, there are alternatives.

For oxidations in the nucleoside series, Swern (99) or Moffatt (100) oxidations have typically been employed for the conversions of 5ϕ -alcohols to 5ϕ -aldehydes (Eq. 8). Again the nucleoside substrates possess a high degree of oxygenation,



and together with the heterocyclic base portion of these substrates, deactivation of the oxidation reagent can take place by complexing with the Cr(VI) species at several points in the substrate.

The employment of oxochromium(VI) reagents is usually not successful in cases where the substrates contain a heterocyclic or primary, secondary, or tertiary amine group as in many types of alkaloid intermediates. In some cases the chromium(VI) species may preferentially bind to the substrate rather than the ligand, hence an exchange reaction takes place rather than the preferred oxidation. The most effective reagents for the oxidation of nitrogen-containing substrates are the Swern, Moffatt, or Dess-Martin (101) reagents.

The response of substrate alcohols containing juxtaposed double bonds in affording products of functional group transposition or intramolecular etherification has greatly expanded the scope of oxochromium(VI)-amine reagent oxidations. Tertiary allylic alcohols suffer oxidative transposition (84-86) when treated with PCC, Collins reagent, PDC, or CrO₃/dimethylpyrazole thus giving conjugated carbonyl compounds (Eq. 5). The substrates may be generated by 1,2-addition of organometallics to cyclic enones or by the addition of vinyl Grignards to ketones. The oxidative transposition has been extended to substrates such as tertiary cyclopropyl carbinols, allenyl carbinols, dienols, enynols, and dithiane-substituted carbinols. (84-88, 102, 103) The yields of the transposed products may be enhanced by the addition of buffers, or silica gel, or the application of ultrasound.

Oxochromium(VI)-amine reagents have been used to prepare substituted

tetrahydrofurans by oxidative cyclization of 5-monohydroxy- and 5,6-dihydroxyalkenes. (104) The oxidative cyclization of a diol to a THF diol using the Collins reagent or PCC with high stereoselectivity has been reported (Eq. 9). Oxidative



THF formation has been used in preparing a key intermediate from a chiral geraniol derivative for the total synthesis of venustatriol. (105) A transannular oxidative cyclization (Eq. 6) which occurred in substrates that possessed both unsaturated sites for oxidative attack as well as with hydroxylic sites that acted as ligands for the oxochromium species has been reported. (90) This putative substituent-directed transannular oxidative cyclization of cyclooctenol substrates to bicyclic THFs offers examples of *syn*-alkoxyhydroxylation of alkenes with the high level of selectivity characteristic of intramolecular reactions. Further advances in the area of *syn*-oxidative cyclizations have been made in the area of hydroxypolyene polycyclizations (106) mediated by PCC where a cascade of cyclizations affords two rings (Eq. 10).



4. Comparison with Other Methods

4.1. Manganese Dioxide

The complexity and sensitivity of the many types of intermediates in a multistep synthesis places a high demand on an oxidant with regard to mildness and selectivity. Many types of reagents or reagent systems are available as alternatives in case the oxochromium(VI)-amine reagent fails to effect the desired alcohol-to-carbonyl compound transformation. Oxochromium(VI)-amine reagents promote the Z to E isomerization of double bonds during the oxidation of primary allylic alcohols to the corresponding aldehydes. Active manganese dioxide (107) has largely been the reagent of choice for the oxidation of sensitive allylic alcohols to the corresponding carbonyl compounds without the undesirable olefinic isomerization. In some cases epoxidation (86) is a significant side reaction when employing PCC or the Collins reagent for the oxidation of allylic alcohols, and MnO_2 is again the effective alternative. In contrast to oxochromium(VI)-amine reagents, which promote the oxidative rearrangement of tertiary allylic alcohols to the corresponding carbonyl compounds, active managanese dioxide is not known to effect this allylic transposition and is therefore selective for the allylic alcohol oxidation. The drawbacks associated with MnO_2 are the requirement for large excesses of reagent, extended reaction times, variations in the activity of the reagent and the nonpolar hydrocarbon solvents. The workup and purification of the products following a MnO₂ oxidation is among the most facile in oxidation chemistry.

4.2. Moffatt/Swern Oxidation

The dimethyl sulfoxide (DMSO)-based oxidants such as the Moffatt and Swern reagents are effective alternatives to the oxochromium(VI) reagent systems. In general the Moffatt oxidation system employs DMSO in conjunction with a diimide, usually dicyclohexylcarbodiimide, while the Swern oxidation utilizes DMSO with oxalyl chloride. In cases where primary alcohols are oxidized to aldehydes, overoxidation to the carboxylic acid does not take place and substrates that are sensitive to acidic or hydrolytic conditions do not suffer side reactions. The Moffatt and Swern reagent systems have generally proven superior to the oxochromium(VI) reagents for the oxidation of highly oxygenated compounds such as carbohydrates and nucleoside derivatives as well as compounds containing nitrogen, sulfur, and active methylene groups. Since oxochromium(VI) reagents may also promote the oxidation of allylic and benzylic (108) C-H sites in addition to the oxidation of hydroxy groups, many complex substrates bearing both sites would demand the higher selectivity of the DMSO-based oxidant to accomplish the desired hydroxyl oxidation. Carbohydrate alcohols with multiple sites protected as acetates, ethers or ketals oxidize very slowly or not at all when treated with the chlorochromates, and hydrolysis of any acid-sensitive functionality usually predominates over

the requisite oxidation of the hydroxyl function. The employment of oxochromium(VI)-amine reagents for the oxidation of substrate alcohols bearing nitrogen heterocycles or amines has consistently been problematic. As in the carbohydrate series little or no oxidation takes place because of binding of the substrate to the oxochromium-amine reagent or exchanging of the substrate with the reagent's ligands. Amino alcohol derivatives, (109) which are otherwise poor substrates for oxochromium reagents, respond well to Swern conditions, thus providing the corresponding carbonyl products in fair to excellent yields. The major drawbacks encountered with the Moffatt/Swern systems are the sometimes annoying odors and the troublesome removal of DMSO and byproducts, requiring lengthy purification.

4.3. Dess-Martin Oxidation

The Dess-Martin reagent (12) has provided a viable alternative to both the oxochromium(VI) and DMSO-based systems. (101) Since its introduction, the



reagent has had an ever-increasing frequency of use for the oxidation of complex intermediates in multistep syntheses. Like the Moffatt/Swern reagents, the Dess-Martin reagent has been effective in oxidizing the alcohol function of highly oxygenated compounds with multiple acid-sensitive protecting groups.

The immediate advantages of the Dess-Martin periodinane are ease of workup and purification of carbonyl products, shorter reaction times, and the need for only one equivalent of reagent. Allylic alcohols are oxidized without isomerization of the double bond and are oxidized preferentially in the presence of saturated alcohols, as are benzylic alcohols also. (110) Complex synthetic intermediates with cumulated double bonds, (111) high degrees of oxygenation with silvl ether, (112) benzyl ether, and isopropylidene protecting groups, (113, 114) sensitive diene functionality, (115, 116) enediyne functionality, (117) trifluoromethyl groups, (118) and sulfur-based protecting (119) groups respond well to the Dess-Martin reagent. Substrate alcohols of high complexity containing nitrogen heterocycles are converted to the expected aldehyde products in good yield. (120) The main drawback associated with the Dess-Martin reagent is the potential for detonation during its preparation. (121) In summary, employment of the Dess-Martin reagent has made possible the completion of many complex multistep syntheses, and it is a superior method for the procurement of small amounts of sensitive synthetic intermediates.

4.4. Catalytic Methods

The expense, toxicity, and disposal considerations associated with many highvalent metal oxidants has prompted the investigation of catalytic methods for the oxidation of alcohols. A typical catalytic system employs 0.05–0.1% of the metal oxidant and a stoichiometric co-oxidant such as air, oxygen, or peroxides such as hydrogen peroxide, tert-butyl hydroperoxide or a peracid. With respect to complex substrates an important consideration is employment of the stoichiometric co-oxidant— a species that may compromise selectivity by promoting unwanted side oxidations such as allylic or benzylic oxidation, epoxidation, hydroxylation, or cleavage of sensitive double bonds and unwanted oxidation of heteroatoms. Thus employment of even the most "ideal" catalytic system may be confined to substrates with only a limited amount of sensitive functionality, therefore limiting its versatility in complex syntheses. Chromium and ruthenium-catalyzed oxidations of alcohols to carbonyl compounds in organic synthesis have been extensively studied. The applications of catalytic oxochromium(VI) reagents in many types of oxidative conversions such as benzylic oxidation, oxidative cleavage and the oxidation of alcohols have been reviewed. (122) Good yields of carbonyl compounds from the corresponding alcohols were obtained using catalytic systems composed of chromium trioxide/tert-butyl hydroperoxide, (123) pyridinium dichromate/bis(trimethylsilyl)peroxide, (124) or chromate esters/peracetic acid. (125) These methods were tested only on simple substrates, and their selectivity in the oxidation of complex substrates has yet to be evaluated. Ruthenium-based oxidants such as tetra-n-butylammonium perruthenate (TBAP) (126) and tetra-n-propylammonium perruthenate (TPAP) (127) in conjunction with N-methylmorpholine-N-oxide as a co-oxidant have been evaluated using both simple substrates and substrates of high molecular complexity. Yields of aldehydes and ketones from the corresponding primary and secondary alcohols using the catalytic TPAP system have ranged from modest to excellent. In evaluating the TPAP system, comparisons were made with the Swern reagent. Substrates containing heterocyclic nitrogen, tetrahydropyranyl and various silyl protecting groups, benzyl ethers, benzylidene acetals, enediynes, and cyclopropanes responded well to the catalytic TPAP system, which was a distinct improvement over the Swern system on a case-by-case basis. In the interest of cost, environmental and toxicity concerns, and expenditure of time during purification, catalytic studies will continue to be a focus in new oxidation technology.

5. Experimental Considerations

5.1.1. General

Commercially available ACS grade pyridine is adequate for the preparation of the chlorochromates and dichromates. Dry pyridine is recommended for the preparation of the chromium trioxide-dipyridine complexes. The purity of many of the commercially supplied substituted pyridines is sufficient for preparation of the reagents. The oxochromium(VI)-amine reagents that are isolated are stored in a desiccator protected from light. Although many oxochromium(VI)-amine reagents darken over time on storage, the loss of activity is minimal. Dry technical flake chromium trioxide gives the best results for preparation of the oxidants and is best stored in a desiccator.

5.1.2. Safety

Care should be taken when adding chromium trioxide to any solvent or solution of organic reactants— the ignition of pyridine by its addition to chromium trioxide is well documented. Weighing papers with residual chromium trioxide adhering to them should never be thrown into the wastepaper basket since ignition may occur. The mammalian toxicity of oxochromium(VI) compounds is well documented. (128) Gloves should be worn when handling the reagents, and one should avoid breathing the dust associated with any of the more microgranular reagents. Chromium waste should be diligently collected and held for disposal as solid waste (silica gel residues from reactions, workups and chromatography) and liquid waste components (filtrates from chlorochromate and dichromate preparation and aqueous workup extracts). Reduced chromium residues can be removed from glassware with concentrated HCl or a rapid rinse with 10-15% HF followed by disposal of the washings in the liquid waste container. Chromium(VI) waste can also be reduced to chromium(III) for disposal by treatment with aqueous sodium bisulfite at low pH. (129)

6. Experimental Procedures

6.1.1. The Collins Reagent (1) (7)

Chromium trioxide (80 g, 0.8 mol, dried over P_2O_5) was added (Caution!) slowly in small portions to anhydrous pyridine (600 mL) with stirring at 15–20°. The orange complex was isolated by washing several times by decantation with petroleum ether, filtration, and drying in vacuo at 10 mm (higher vacuum causes surface decomposition) while protecting from light. The complex hydrates on standing in air and forms pyridinium dichromate, which is less soluble in dichloromethane than the dipyridine complex.

6.1.2. Pyridinium Chlorochromate (PCC, 2) (14)

Chromium(VI) oxide (100 g, 1 mol) was added to HCI (6 M, 1.1 mol) rapidly while stirring. After 5 minutes the homogeneous solution was cooled to 0° followed by addition of pyridine (79.1 g, 1 mol) over 10 minutes. Recooling to 0° gave a yellow-orange solid, which was collected by suction filtration using a sintered glass funnel and dried in vacuo. Prolonged exposure to light promotes darkening of the material with minimal loss of activity.

6.1.3. Pyridinium Dichromate (PDC, 3) (34)

Pyridine (80.6 mL) was gradually added to a cooled solution of chromium(VI) oxide (100 g, 1.0 mole) in 100 mL water at room temperature. The solution was then diluted with acetone (400 mL) and cooled (-20°). After 3 hours the orange crystals were collected by suction filtration, washed with acetone, and dried in vacuo to yield 127.2 g (67%) of PDC.

6.1.4. 2,2¢-Bipyridinium Chlorochromate (BPCC, 4) (41)

Chromium(VI) oxide (10.0 g, 0.11 mol) was added in one portion while stirring to HCI (6 N, 18.4 mL, 0.11 mol). After dissolution of the chromium(VI) oxide was complete, 2,2¢-bipyridine (15.6 g, 0.1 mol) was added while stirring vigorously. The resultant yellow slurry was filtered using a sintered glass funnel and washed with ice cold distilled water (2 × 15 mL). The filter cake was dried in vacuo (room temperature) for 3 hours and afforded 26.8 g (92%) of BPCC as a yellow powder. The material is best stored protected from light in a desiccator over P_2O_5 .

6.1.5. 4-(Dimethylamino)pyridinium Chlorochromate (DMAPCC, 5) (42)

Chromium(VI) oxide (3.27 g, 32.7 mmol) was added to 1.65 M aqueous hydrochloric acid (20 mL) while stirring. The resulting red-orange solution was cooled to 0° and 4-dimethylaminopyridine (4.0 g, 32.8 mmol) was added in one portion while stirring vigorously. The yellow-orange slurry was then vacuum-filtered using a sintered glass funnel and washed with ice-cold distilled water (2 × 10 mL), followed by drying the filter cake in vacuo at room

temperature. The yield of the yellow-orange complex, which should be stored in a desiccator protected from light, was 7.76 g (92%).

6.1.6. Tetrabutylammonium Chlorochromate (TBACC, 6) (53)

Chromium(VI) oxide (5.0 g, 0.05 mol) in concentrated hydrochloric acid (10 mL) was added slowly to a stirred solution of tetrabutylammonium hydrogen sulfate (16.95 g, 0.05 mol) in 5 N hydrochloric acid at 20°. To the orange solid formed, 5 N hydrochloric acid (50 mL) was added. The precipitate was isolated by suction filtration and recrystallized from ethyl acetate/hexane; yield: 15.1 g (80%); mp 184–185°.

6.1.7. Trimethylammonium Chlorochromate (TMACC, 7) (47)

Reagent grade CrO_3 (100 g, 1 mol) was added with stirring to 6 N HCl (184 mL, 1.1 mmol) at 0°. To this solution was added slowly trimethylamine hydrochloride (99.5 g, 1 mol) over a period of 0.5 hour and stirring was continued for 0.5 hour at 0°. The precipitated orange solid was isolated by filtration, washed with $CH_2Cl_2(3 \times 60 \text{ mL})$ and dried in vacuo for 2 hours at room temperature The chromium(VI) content was determined iodometrically to be >99%; yield: 178 g (86%); mp 162°.

6.1.8. Quinolinium Dichromate (QDC, 8) (51)

To a stirred solution of CrO_3 (100 g, 1 mol) in water (100 mL) cooled in ice, quinoline (86 mL, 727 mmol) was added in small portions. The solution was diluted with acetone (400 mL), cooled to -20° and the orange solid which separates was filtered, washed with acetone, dried in vacuo, and recrystallized from water to yield 234 g (72%) of quinolinium dichromate; mp 160–161°.

6.1.9. 3-Carboxypyridinium Dichromate (NDC, 9) (52)

Chromium(VI) oxide (480 g, 0.48 mol) was dissolved in water (48 mL) followed by the addition of nicotinic acid (29.52 g, 240 mmol) at 0–5° to the resulting red-orange solution while mechanically stirring. After 15 minutes acetone (100 mL) was added to the red-orange suspension and the mixture was stirred at 0–5° for 15 minutes. The product was separated by filtration, washed with acetone (4 × 200 mL), and then methylene chloride (100 mL) to afford 3-carboxypyridinium dichromate (47 g, 85%) as a yellow-orange solid; mp 215–217° (dec).

6.1.10. Imidazolium Dichromate (IDC, 10) (129)

Imidazole (13.6 g, 0.2 mol) was slowly added to a cooled solution of chromium(VI) oxide (20.0 g, 0.2 mol) in water (16 mL). After 0.5 hour the reaction mixture was diluted with acetone (20 mL) and cooled to -20° . The yellow crystals were collected, washed with acetone (40 mL), and dried in vacuo at room temperature to give imidazolium dichromate (28.3 g, 80%); mp 130–131° (dec.).

6.1.11. Pyridinium Fluorochromate (PFC, 11) (56)

Chromium(VI) oxide (15.0 g, 0.15 mol) was dissolved in water (25 mL) in a polyethylene beaker, and 40% hydrofluoric acid (11.25 mL, 0.225 mol) was added with stirring at room temperature. Within 5 minutes a clear orange solution resulted. To this solution pyridine (12.3 mL, 0.15 mol) was added slowly with stirring. The mixture was heated on a steam bath for 15 minutes, then cooled to room temperature, and allowed to stand for 30–35 minutes. The bright orange crystalline pyridinium fluorochromate was isolated by filtration, pressed between folds of filter paper, and dried in vacuo for 1 hour; yield: 27.9 g (93.5%); mp 106–108°.

6.1.12. The Sarrett Reagent (CrO₂·2Pyr) (4)

Chromium(VI) oxide (3.1 g, 31 mmol) was carefully added in portions to pyridine (30 mL, 370 mmol) while stirring or swirling at 15–20°. The addition **must** be in this order or combustion may result. Dissolution of the anhydride proceeded first, followed by slow exothermic formation of the yellow complex. The temperature was kept below 30° during the addition of the subsequent portions of the CrO_3 . At the end of the addition, a slurry of the complex in pyridine remained to which the substrate was added.

6.1.13. The Cornforth Reagent (6)

Chromium(VI) oxide (50 g, 0.5 mol) dissolved in water (30 mL) was added gradually with stirring to pyridine (500 mL) cooled in an ice water bath. The resulting yellow slurry can be used to oxidize up to 165 mmol of substrate alcohol.

6.1.14. 3,5-Dimethylpyrazole-Chromium Trioxide Oxidation of α -Phenethanol (9)

3,5-Dimethylpyrazole (580 mg, 6 mmol) was added to a suspension of chromium(VI) oxide (600 mg, 6 mmol) in methylene chloride (20 mL) and the mixture was stirred at room temperature under argon for 30 minutes. To the resulting dark red solution was added a solution of phenethanol (263 mg, 2.2 mmol) in dichloromethane (2 mL) in one portion and the reaction mixture was stirred at room temperature (30 minutes). The solvent was removed under reduced pressure, the brown residue was extracted with ether (50 mL), and the resulting mixture was filtered. The filtrate was dissolved in pentane and filtered again through a short silica column. Evaporation of the solvent gave acetophenone (260 mg, quantitative) identical with an authentic sample by NMR, IR and pure by GLC analysis.

6.1.15. Selective Oxidation of p-(3-Hydroxypropyl)benzyl Alcohol with Imidazolium Dichromate (55)

To a solution of p-(3-hydroxypropyl)benzyl alcohol (165 mg, 1 mmol) in N,N-dimethylformamide (3 mL) was added imidazolium dichromate (705 mg, 2 mmol) and the mixture was stirred at room temperature (4 hours). After completion of the reaction, water (30 mL) was added to the reaction mixture

and the product was extracted three times with diethyl ether. The ether extracts were washed with water and aqueous NaHCO₃, dried over anhydrous MgSO₄, and evaporated to dryness. The crude product was subjected to silica gel column chromatography with dichloromethane-ethyl acetate (4:1) as eluent to yield *p*-(3-hydroxypropyl)benzaldehyde (112 mg, 68%); NMR (CDCl₃): δ 1.8–2.3 (m, 2 H), 2.77 (s, 1 H), 2.93 (t, 2 H, J = 6 Hz), 3.80 (t, 2 H, J = 6 Hz), 7.4–7.98 (m, 4 H), 10.10 (s, 1 H). IR (film) 1700 cm⁻¹. δ and 3-(4-Formylphenyl)propanal (4 mg, 3%): ¹H NMR(CDCl₃) = 2.45–3.21 (m, 4 H), 7.31–7.85 (m, 4 H), 9.81 (s, 1 H), 9.95 (s, 1 H).

6.1.16. Selective Oxidation of p-(3-Hydroxypropyl)benzyl Alcohol with DMAPCC (5) (42)

To a suspension of 4-(dimethylamino)pyridinium chlorochromate (1.24 g, 4.8 mmol) in dry dichloromethane (7.0 mL) was added p-(3-hydroxypropyl)-benzyl alcohol (200 mg, 1.2 mmol). Stirring was continued (2 hours) at room temperature under a nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (10 mL) and the brown granular chromium reduction products were removed by vacuum filtration through a Celite[®] pad. Concentration of the solvent and column chromatography on silica gel (hexane/ethyl acetate, 2:1) furnished 121 mg (62%) of p-(3-hydroxypropyl)benzaldehyde as an oil. The spectral data were the same as those of the product reported above with imidazolium dichromate.

6.1.17. Ultrasound-Promoted Pyridinium Chlorochromate-Silica Gel Oxidation of 3,4-Dimethoxybenzyl Alcohol (Veratryl Alcohol) (62)

PCC (1.93 g, 9 mmol) was ground with silica gel (70–230 mesh, 1 weight equiv.) in a mortar. The resulting free running light orange solid was suspended in methylene chloride (20 mL) at 18° (water bath), and the titanium probe tip of an ultrasonic processor was inserted 1 cm beneath the surface of the suspension. The probe was activated (maximum intensity), and veratryl alcohol (1.0 g, 6 mmol) in CH_2CI_2 (5 mmol) was added in one portion. After 20 minutes the probe was deactivated and the brown suspension was diluted with ether (20 mL) followed by vacuum filtration through a Büchner funnel (60 × 50 mm) packed with Celite[®]. The granular brown residue was washed with ether (150 mL) and the resulting filtrate concentrated,

flash-chromatographed and vacuum Kugelrohr-distilled to give veratraldehyde (0.91 g, 92%) (hexane/EtOAc, 1:1).

6.1.18. Oxidation of Borneol with the Ratcliffe CrO_3 /Pyridine Reagent System (8, 130)

Chromium(VI) oxide (2.99 g, 30 mmol) was added to a magnetically stirred solution of pyridine (5.0 g, 6.3 mmol) in methylene chloride (150 mL). The flask was then stoppered with a drying tube containing Drierite and the resulting deep burgundy solution was stirred for 15 minutes at room temperature. A solution of borneol (0.77 g, 5 mmol) in dichloromethane (5.0 mL) was then

added in one portion whereupon a tarry black deposit appeared immediately. The reaction mixture was stirred for an additional 15 minutes and then decanted from the tarry residue which was washed with diethyl ether (200 mL). The combined organic solution was then washed with 5% aqueous sodium hydroxide (3 × 100 mL), 5% aqueous hydrochloric acid (100 mL), 5% aqueous sodium bicarbonate solution (100 mL), saturated aqueous sodium chloride solution (100 mL), and then dried over anhydrous magnesium sulfate. Alternatively the decanted methylene chloride solution was concentrated in vacuo and the residue then diluted with ether and filtered to remove insoluble chromium salts. The filtrate was submitted to the successive washings as above. Evaporation of the solvent then gave the crude material which was recrystallized to yield 639 mg (84%) of pure camphor.

6.1.19. Oxidation of 4-Hydroxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene with PFC (10) (56)

In a 250 mL round-bottom flask fitted with a reflux condenser and stirrer was placed a suspension of pyridinium fluorochromate (16.15 g, 81.2 mmol) in dichloromethane (30 mL). To the suspension was added a solution of 4-hydroxytricyclo[$5.2.1.0^{2.6}$]deca-3,8-diene (8.0 g, 54.05 mmol) in dichloromethane (40 mL) while stirring vigorously. Stirring was continued for 90 minutes. The reaction was monitored by thin-layer chromatography on silica gel using benzene/ethyl acetate (90/10) as eluent. To the resultant mixture, dry ether (100 mL) was added and the mixture was filtered through a short silica gel column (7 cm × 2 cm²). The filtrate was evaporated on a steam bath and the oily residue, which solidified on standing, was recrystallized from pentane to yield the bicyclic ketone: 7.3 g (92%); mp 79–80° (lit. 80°).

6.1.20. Oxidation of n-Butanol with QDC (8) (51)

To a stirred solution of quinolinium dichromate (23.8 g, 53.5 mmol) in dichloromethane (48 mL) was added dropwise a solution of *n*-butanol (3.7 mL, 45 mmol) in dichloromethane (7 mL). The mixture was heated at reflux (4 hours), cooled to room temperature, diluted with ether, and filtered through silica gel. The solvent was evaporated and the residue distilled to give 2.24 g (69%) of *n*-butyraldehyde.

6.1.21. Oxidation of 1-Phenyl-1,3-propanediol to 3-Hydroxy-1-phenyl-1-propanone with TBACC (6) (53)

To a solution of 1-phenyl-1,3-propanediol (0.298 g, 2 mmol) in chloroform (10 mL), TBACC (2.28 g, 6 mmol) was added at room temperature and the solution was heated at reflux for 1 hour. The product was isolated by evaporating the solvent at reduced pressure and treating the crude oily residue with diethyl ether and Celite[®]. The suspension was filtered and the Celite[®]pad was washed with ether (3 × 30 mL). Evaporation of the ether afforded 0.09 g of product. Additional treatment of the Celite[®] with hot benzene (3 × 5 mL) afforded a further 0.085 g of product which was combined and purified by

column chromatography on silica gel (chloroform/acetone, 95:5) to give pure 3-hydroxy-1-phenyl-1-propanone; yield: 0.152 g (52%); b.p. 80–82°/2 torr.

6.1.22. Pyridinium Chlorochromate/3,5-Dimethylpyrazole Oxidation of Androst-4-ene-3 β ,17 β -diol (66)

Pyridinium chlorochromate (388 mg, 1.8 mmol) was added to a solution of androst-4-ene-3 β ,17 β -diol (174 g, 0.6 mmol) in dichloromethane (50 mL) with 3,5-dimethylpyrazole (1.0 g, 10.4 mmol) at 2–3°. After stirring under nitrogen (30 minutes), a saturated NaCl solution was added and the mixture was thoroughly extracted with chloroform. The resulting extracts were dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure to give a brown residue. The residue was subjected to column chromatography using a solvent gradient of ether in toluene followed by recrystallization to give pure testosterone (151 mg, 87%).

6.1.23. cis-1-Benzoylmethyl-3-phenoxy-4-phenylazetidin-2-one [Oxidation of a β -Lactam Alcohol with NDC (9)] (52)

To a suspension of 3-carboxypyridinium dichromate (2.32 g, 5.0 mmol) in methylene chloride (15 mL) was added pyridine (3.2 mL, 40 mmol) followed by *cis*-1-benzoylmethyl-3-phenoxy-4-phenylazetidine-2-ol (686 mg, 2.0 mmol), and the resulting mixture was stirred at room temperature while monitoring by TLC (silica gel; ethyl acetate/hexane, 1:1). The mixture was then filtered through a pad of silica gel (70–230 mesh) and the filtrate washed with water (15 mL), 6 N HCI (15 mL), and saturated NaHCO₃ (15 mL). The organic layer was separated and dried with sodium sulfate. Evaporation of the solvent gave 613 mg of *cis*-1-benzoylmethyl-3-phenoxy-4-phenylazetidine-2-one (90%).

6.1.24. Oxidation of Geraniol with Pyridinium Chromate on Silica Gel (131)

To a solution of geraniol (770 mg, 5 mmol) in methylene chloride (7.5 mL) was added pyridinium chromate-silica gel (7.2 g, 10 mmol) and acetic acid (0.24 g, 4 mmol). The mixture was mechanically shaken for 4 hours at room temperature followed by addition of diethyl ether (15 mL) and shaking (2 minutes). The suspension was then filtered and the combined filtrate was washed successively with 5% aqueous HCl (8 mL), water (2×5 mL), and brine (5 mL). The solvent layer was then passed through a small bed (0.8 × 4 cm) of alumina (Brockmann Grade II) and washed with ether (10 mL). From the combined filtrates the solvent was stripped off and the residue was distilled to furnish citral (0.678 g, 89%) of 98.5% GLC purity; bp 125° (bath) 10 minutes.

6.1.25. Pyridinium Chromate on Silica Gel (132)

To a solution of chromium(VI) oxide (50.0 g, 0.5 mol) in water (300 mL), silica gel (250 g) was added and the mixture was shaken mechanically for 1 hour at room temperature (30–35°). The excess water was then removed by a rotary

evaporator (90°/80 mm) which provided 312 g of an orange free-flowing powder. The entire amount of material was placed in a three-necked flask and covered with light petroleum (600 mL). The mixture was cooled to 20°, and pyridine (79.0 g, 1.0 mol) was slowly introduced with stirring under anhydrous condition while maintaining the temperature between 20 and 24° (30 minutes). The mixture was stirred for an additional hour, filtered, and the solid washed with light petroleum (2 × 300 mL). Drying under vacuum gave a dark brown free-flowing powder (358 g) which was stored in a brown bottle. One gram of this preparation was equivalent to 0.1396 g of chromium(VI) oxide.

6.1.26. (2E,4Z)-2,4,11-Dodecatrien-1-al (BPCC Oxidation of 2E,4Z-2,4,11-Dodecatrien-1-ol) (133)

(2E,4Z)-2,4,11-Dodecatriene-1-ol (54 mg, 0.30 mmol) dissolved in dichloromethane (3 mL) was stirred with 2,2¢-bipyridinium chlorochromate (234 mg, 0.80 mmol) for 2 hours. Preparative TLC on Kieselgel 60 (ether/petroleum ether, 1:2) provided 50 mg (87%) of the aldehyde product: bp 58°/0.1 Torr.

6.1.27. Oxidative Transposition of 1,5,5-Trimethylcyclohex-2-en-1-ol to Isophorone with PCC (2) (85)

To a magnetically stirred slurry of pyridinium chlorochromate (4.3 g, 20.0 mmol) in dichloromethane (30 mL) was added 1,5,5-trimethylcyclohex-2-en-1-ol (1.4 g, 10.0 mmol) in dichloromethane (10 mL) at room temperature. The resulting dark red-black mixture was stirred at room temperature (2.0 hours) and then diluted with an equal volume of ether. The ethereal solution was decanted from the black resinous polymer, which in turn was washed with ether (3 × 20 mL). The combined ethereal phases were washed successively with two 100 mL portions of 5% aqueous sodium hydroxide, 5% aqueous HCl (100 mL), saturated aqueous NaHCO₃(2 × 50 mL), and dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure and the residue was bulb-to-bulb distilled to afford 1.33 g (96%) of isophorone of greater than 97% purity and whose spectral properties were identical with an authentic sample.

6.1.28. Oxidation of Alcohols with TMACC (7) (47)

In a 50 mL two-necked flask equipped with a reflux condenser, TMACC (2.93 g, 15 mmol) and molecular sieves 4Å (200 mg, previously activated at 350°) were suspended in CH_2Cl_2 (20 mL). The alcohol was added to the magnetically-stirred suspension followed by the addition of acetic acid (0.2 mL) and the mixture was heated at reflux until the reaction was complete. To monitor the reaction, an aliquot was quenched with 10% aqueous $Na_2S_2O_3$ (10 mL), extracted with ether (3 × 15 mL) and tested for contents by using toluene or napthalene as the internal standard. After the reaction was complete, the mixture was cooled to room temperature and diluted with anhydrous ether (100 mL). The solvent was decanted and the brown solid was

washed with Et_2O as it becomes granular. The product was isolated by filtration through Celite[®]. The Celite[®] pad was washed with $Et_2O(3 \times 20 \text{ mL})$, the combined organic layer dried (Na_2SO_4), and the solvent was removed by distillation at reduced pressure followed by distillation of the products.

6.1.29. Oxidation of

1,2-O-Isopropylidene-5-O-methoxycarbonyl-D-xylo-furanose with PCC/Benzene (134)

A vigorously stirred suspension of pyridinium chlorochromate (520 g, 2.4 mol) (7.6 g/L)brought reflux in benzene was to and 1,2-O-isopropylidene-5-O-methoxycarbonyl-D-xylofuranose (240 g, 0.97 mol) was added. After 2.5 hours, the reaction mixture was filtered through Celite[®], and the reaction mixture and Celite[®] were washed with benzene (3 × 400 mL). The filtrate was concentrated in vacuo to 800 mL and then passed through a pad of silica 60 (300-400 g). The silica was washed with ethyl acetate and the combined filtrates were evaporated to provide the crude ketose which was recrystallized from heptane in 73% yield: mp 81-82.5°.

7. Tabular Survey

Entries are arranged according to increasing carbon count of the substrate.

Yields are given in parentheses, and a dash (—) indicates that no yields or experimental conditions were provided in the original reference.

The following abbreviations are used in the table.

Ac	acetyl
Bn	benzyl
Bz	benzoyl
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
HMPA	hexamethylphosphoric triamide
MOM	methoxymethyl
TBDMS	tert-butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl
THP	tetrahydropyranyl
TMS	trimethylsilyl
Ts	<i>p</i> -toluenesulfonyl

Oxochromium(VI)-Amine Reagents:

BPCC 2,2¢-bipyridine chlorochromate

DMAPCC 4-(dimethylamino)pyridine chlorochromate

- IDC imidazole dichromate
- NDC nicotinic acid dichromate
- PCC pyridinium chlorochromate
- PDC pyridinium dichromate
- PFC pyridinium fluorochromate
- PVPCC polyvinylpyridinium chlorochromate
- QDC quinolinium dichromate
- TBACC tetrabutylammonium chlorochromate
- TMACC trimethylammonium chlorochromate

Table . Oxidations with Oxochromium(VI)Amine Reagents

View PDF

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
С _S он	DMAPCC (3 eq), CH ₂ Cl ₂ 3 h	S (73)	43
ОН	PCC, CH ₂ Cl ₂ , 40°		136
0	PCC (2.5 eq), AI_2O_3 , $C_6H_{6,}$ 1.5 h	н " (45)	137
о с о	PCC (1.6 eq), NaCl 25°, 1.7 h		138
OH OCN	PCC (1.5 eq), CH ₂ Cl ₂ , 25°, 3 h		139
₩ № 0Н	PCC (2.0 eq), NaOAc 25°, 1.5 h	H (70)	140
ОН	PCC, CH ₂ Cl _{2.} 25°	H (47)	141
	PCC	" (—)	142
ОН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 15 min	$ \begin{array}{c} & H \\ & & (-) \end{array} $	143
\bigcirc	PCC (3.0 eq), CH ₂ Cl ₂ 60-70°, 7 h	(70)	25
ОН	PCC (1.1 eq), CH ₂ Cl ₂ rt, 2 h	0 H (73)	144
$F_3C - S - N $ OH	PCC (2.0 eq), CH ₂ Cl ₂ 25°, 24 h	$F_{3}C \xrightarrow{ I }{ I }_{O} (22)$	145
D D OH	PCC, CH ₂ Cl ₂ , rt		146
ОН	PCC	H ()	147
ØH	PCC (1.5 eq), 3 h	мара (70) О (70)	148
ОН	PCC (2.5 eq), CH ₂ Cl ₂ 2.5 h	H ()	149
ОН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1.5	⊢ ⊢ (−)	150
ОН	PCC	$\bigcup_{H} \bigoplus_{H} \bigoplus_{(43)}$	151
ОН			152, 153
СІ ОН	PCC, CH ₂ Cl ₂		154
OH OH	PCC (2.5 eq) 3 Å mol. sieves, rt, 24 h	O (78)	155

OXIDATIONS WITH OXOCHROMIUM	I(VI)AMINE REAGENTS
UNDATIONS WITH ONOCINOMON	

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
(<i>S</i>) - (-) OH	PCC, NaOAc	(S) - (+) H O (80)	156
МеО	PCC, CH ₂ Cl ₂ , rt, 2.5 h	н мео0 (47)	157
OH MeO OMe	CrO ₃ •2Pyr (7 eq) rt, 10 min	MeO OMe (45)	158
(R)OH	PDC, DMF	$(R) - H \qquad (-)$	175
ОН	PCC (2.5 eq), CH ₂ Cl ₂ 0°, 7 h	H (53)	159
остон	CrO ₃ •2Pyr (6.0 eq) rt, 15 min		160
Br (E) OH	PCC, CH ₂ Cl ₂	$\operatorname{Br} \underbrace{(E)}_{O} H \qquad (47)$	161
Br OH		Br (Z) H (75)	161
ОН	PDC, CH ₂ Cl ₂ , rt, 24 h	$\bigcup_{H} \overset{O}{\overset{(10)}{\overset{(10}{\overset{(10)}{\overset{(10}{\overset{(10)}{\overset{(10}{\overset{(10)}{\overset{(10}{\overset{(10)}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}}{\overset{(10}{\overset{(10}}{\overset{(10}}{\overset{(10}{\overset{(10}{\overset{(10}}{\overset{(10}{\overset{(10}}{\overset{(10}{\overset{(10}}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}}{\overset{(10}{\overset{(10}}{\overset{(10}}{\overset{(10}}{\overset{(10}}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}{\overset{(10}}{\overset{(10}}{\overset{(10}}{\overset{(10}}{\overset{(10}{(10$	162
HOOH	PCC (3.7 eq), CH ₂ Cl ₂ rt, 2 h	$\stackrel{O}{\longrightarrow} \stackrel{O}{\longrightarrow} \stackrel{O}{\longleftarrow} \stackrel{(60)}{H}$	163
СОУСОН	PCC	$ \bigcup_{i=1}^{O} \bigcup_{i=1}^{H} \prod_{i=1}^{H} (-) $	164
ОН	PCC (1.5 eq), CH ₂ Cl ₂ 20°, 3 h	(83)	165
.0 ОН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 14 h	O H (76)	166
	PDC		167
ОН	CrO ₃ •2pyr	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	168
AcO	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2.5 h	AcO (44)	157
EtO ₂ COH	PCC (2.5 eq), NaOAc CH ₂ Cl ₂ , 2 h	EtO_2C (79)	169
	PCC (1.5 eq), CH ₂ Cl ₂ rt, 14 h	" (70)	170
ОЧ	PCC (2.0 eq), NaOAc CH ₂ Cl ₂ , 2 h	$ \begin{array}{c} $	169
OH O TOH	n	(82)	171

OXIDATIONS WIT	H OXOCHROMIUM(VI)	AMINE REAGENTS (Continued)
		,

 C_6

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OH NO ₂	PCC. SiO ₂ , ultrasound 25°, 4 h	0 (60) NO ₂	64
ОН	PCC, CH ₂ Cl ₂		172
ОН	PCC	0 (65)	173
ОН	QDC (1.0 eq), CH ₂ Cl ₂ rt, 4 h	H (70)	52
(S) - (-) OH	PCC (1.5 eq). CH ₂ Cl ₂ 2 h	() O	174
тмѕ он	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1 h	H H TMS O (67)	176
но ОН	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 1-2 h	H0 (68)	14
	PCC (3.2 eq), CH ₂ Cl ₂ 35 min		177
	PCC, CH ₂ Cl ₂	" (62)	178
r-BuO OH		<i>ι</i> -BuO − − − − − − − − − − − − − − − − − − −	179
МеООН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2.5 h	MeO (44)	157
ELO		E10 (10)	157
	PCC (1.5 eq), CH ₂ Cl ₂	0 (96)	180
С ₇ — — — — — — — — — — — — — — — — — — —	PCC		181
⟨OH	PCC (1.5 eq). CH ₂ Cl ₂ rt, 2 h	$\langle \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x}$	182
Br	QDC, DMF	Br O H	73
CI-OH	DMAPCC (5.0 eq) CH ₂ Cl ₂ , 21 h	$CI \longrightarrow H$ ()	43
FOH	PFC, DMSO	$F \longrightarrow H^{O}$ ()	76
ОН	PCC (1.5 cq), CH ₂ Cl ₂ rt, 21 h	$ \overset{I}{\underset{H}{\longrightarrow}} \overset{O}{\underset{H}{\longrightarrow}} $ (76)	183
⟨ N ₃ OH	PCC (1.7 eq), CH ₂ Cl ₂	(90)	184

OXIDATIONS WITH	OXOCHROMIUM(V	I)AMINE REAGENTS	(Continued)

	Substrate	Conditions	0.11	Product(s) and Yield(s) (%)	Refs.
O2N OH		QDC, DMF		0 (—) H	73
0 ₂ N-	он	DMAPCC (5.0 eq), CH ₂ Cl ₂ 15 h	0 ₂ N-		43
		PFC, DMSO	"	(—)	76
ОН		DMAPCC (3.0 eq) CH ₂ Cl ₂ , 3 h	√ → H	(64)	43
		CrO ₃ •2Pyr (6 eq) CH ₂ Cl ₂ , 15 min	"	(89)	8
		QDC (1.0 eq), CH ₂ Cl ₂ rt, 4 h	"	(45)	52
С— ¹³ СН ₂ ОН		PCC		D (—)	185
но-СССССССССССССССССССССССССССССССССССС		PCC (1.7 eq), CH ₂ Cl ₂ 25°, 3 h	0=	(94) El	186
MeO O=OH		PDC		(8)	187
Br (E)	∽он	PCC, CH ₂ Cl ₂	Br	E H (69)	161
Br (Z)	∕он	ĸ	Br	Z) H (95)	161
Br	ſ	РСС (1.5 еq). NaOAc СН ₂ Сl ₂ , 0 ⁰ . 1 h	Br	(83) So	188
——————————————————————————————————————		PCC, CH_2Cl_2		()	189
Отон		PCC (2.0 cq), CH ₂ Cl ₂ rt. 1.5 h		(64)	190
0 OH		PDC (2.0 eq), CH ₂ Cl ₂ rt. 18 h	0	(84)	191
	ОН	PDC, CH ₂ Cl ₂		H ()	192
	II	PCC, CHCl ₃ , CH ₂ Cl ₂		(70)	193
		PCC (2.0 eq), CH ₂ Cl ₂ 2.5 h		(70)	194
Br		PCC (2.0 eq), CH ₂ Cl ₂	Br	(68)	195
		"	n	(95)	195
-ОН		u		(78)	196

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
NC тон	CrO ₃ •2Pyr	NC ~ H ()	197
NC- OH	PCC (1.2 eq), CH ₂ Cl ₂ 3 h	NCH (70)	198
ОН	PDC, DMF	CO ₂ H (67)	199
D OH OH	PCC		200
	CrO ₃ •2Pyr (12 eq) CH ₂ Cl ₂ , rt, 22 h	0 (67)	201
(б)-	PDC, DMF	(S) - CO ₂ H (85)	202
ОН	PCC (3.0 eq), CH_2Cl_2 rt, 2 h	$\bigcup_{H} \bigcup_{H} \bigcup_{H} (62)$	203
ОН	PCC (2.5 eq), rt, 45 min	H (63)	204
ОН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2 h	(94)	205
	PCC (3.0 eq), CH ₂ Cl ₂ 60-70°, 24 h	(60)	25
	'n	(70)	25
EtO ₂ C	PCC	EtO ₂ C ()	206
CN OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1 h	CN 0 (76)	207
NO ₂ OH CO ₂ Me	РСС (2.25 еq) 3 Å mol. sieves п, 24 h	$\bigcup_{O}^{NO_2} CO_2 Me $ (65)	155
≫~~~~ _{OH}	PCC		208
OH	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , rt, 4 h	Н (58)	209
OH	PCC (1.5 eq). NaOAc CH ₂ Cl _{2.} rt, 15 min	(34)	210
	PCC	" (41)	211
ОН	PCC (1.5 eq), rt, 2 h	О (72) Н (72)	212
ОН	PCC (1.5 eq), AI_2O_3 hexane, 10 h	(83)	137

Substrate	Conditions	Product(s) and Yield(s) (%)	Refe
Substrate	Conditions		
ОН	PCC (1.5 eq), CH ₂ Cl ₂	(81)	213
~ • • • •	rt, 24 h	ů -	
, OH	PCC, NaOAc, CH ₂ Cl ₂ rt, 15 min	S (55)	214
ОН	PCC		164
ОН	w	H 0 (44)	215
Сотон	PCC, NaOAc, CH ₂ Cl ₂		216
NeO ₂ C OH	РСС (1.5 еq), п, 3 h	$\begin{array}{c} (S) - H \\ MeO_2C \end{array} \tag{63}$	218
MeO OH	PCC (1.5 eq), NaOAc		219
✓ → → → → → → → → → → → → → → → → → → →	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , reflux, 0.5 h	$\bigvee_{O}^{O} \xrightarrow{V}_{H}^{O}$ (56)	220
ОН	РСС, СН ₂ Сl ₂ , п, 3 h	0 0 H (75)	221
/	PCC (1.5 eq), CH_2Cl_2 rt, 3 h	" (75)	222
OH O	PCC, NaOAc, CH ₂ Cl ₂ 4 h		223
OH OH	CrO ₃ •2Pyr (9.0 eq) CH ₂ Cl ₂ , 40 min	0 0 0 H (48)	224
ОН	PCC (1.5 eq), CH ₂ Cl ₂ 20°, 3 h	0 (76)	165
ООН	CrO ₃ •2Pyr (2.0 eq) CH ₂ Cl ₂ 15 min		225
	PCC (2.0 eq), CH ₂ Cl ₂ rt, 3 h	H " (91)	226
ОН	PDC (2.0 eq) 3 Å mol. sieves, CH ₂ Cl ₂	0 EtO 0 (72)	227
NO ₂ OH	PCC (2.25 eq) 3 Å mol. sieves, rt, 24 h	$\bigvee_{\substack{\text{O}}}^{\text{NO}_2} (87)$	155
O II P EtO) ₂ OH	PCC (1.2 eq), rt, 4 h	$(EtO)_2 \xrightarrow{P}_{H} O $ (52)	228
ОН	РСС (1.5 eq), CH ₂ Cl ₂ rt, 1-2 h	H (78)	14

	Substrate	Conditions	Product(s) and Vield(s) (%)	Refs
	Substrate	Conditions		Keis.
	ОН	PCC	(91) O	229
	OH <i>t</i> -Bu	РСС (1.5 еq), CH ₂ Cl ₂ гt, 1.5 h	0 /-Bu (89)	230
	ноуссон	PCC, CH ₂ Cl ₂	HOCHO (41)	178
	EtO	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2.5 h	EtOCHO (56)	157
	n-PrO OH		<i>n</i> -PrO CHO (53)	157
C ₈	MeO ₂ COH	PCC (2.5 eq), CH ₂ Cl ₂ rt, 1 h	MeO ₂ C CHO (66)	217
	EtO ₂ C OH	PCC, NaOAc, rt	EtO ₂ C CHO (75)	292
	F ₃ C — CH ₂ OH	PFC, DMSO	F ₃ C-CHO ()	76
	CH ₂ OH	DMAPCC (5.0 eq) CH ₂ Cl ₂ , 15 h	(98)	43
	С	PCC, CH ₂ Cl ₂		231
		PCC (1.5 eq), CH ₂ Cl ₂ 2 h	СНО (89)	232
		PFC, DMSO	——————————————————————————————————————	76
	СН2ОН	QDC, DMF	СНО ()	73
	СН2ОН	DMAPCC (4.0 eq) CH ₂ Cl ₂ . I5 h	СНО ()	43
	MeS — CH2OH	PFC, DMSO	MeS-CHO ()	76
	MeO-CH2OH	DMAPCC (4.0 eq) CH ₂ Cl ₂ , 6 h	MeO-CHO (87)	43
		PFC, DMSO	" (—)	76
	CO ₂ H OH	CrO3•2Pyr, pyridine, 12 h	CO ₂ H 0 (66)	233
	$F \xrightarrow{F} F$ $F \xrightarrow{F} CH_2OH$ CO_2Me	PCC (1.7 eq) CH ₂ Cl ₂ , 2 h	$F \xrightarrow{F} F$ $F \xrightarrow{F} F$ CHO CHO (61)	234
	Br O Br S=0 CH ₂ OH	PCC	$Br \xrightarrow{N} S = 0 \qquad ()$	235

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН	PCC	(70)	236
			237
СН2ОН	PCC (3.0 eq), CH ₂ Cl ₂	(90)	238
СН2ОН	PCC (1.5 eq), CH ₂ Cl ₂ 0°, 7 h	(—) СНО (—)	159
H CH ₂ OH	CrO ₃ •2Pyr (7.2 eq) CH ₂ Cl ₂ , 15 min	H CHO (62)	239
Сн2ОН	CrO ₃ •2Pyr (8.3 eq) CH ₂ Cl ₂ , rt, 15 min	(71) CHO	240
CH2OH	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 2 h	(71)	241
E moli	СгО3•2Руг (6.0 еq) СН₂Сl₂. гt, 20 min	(24) O	242
ОН	РСС (2.0 сq), гt, 24 h	(61)	243
Pr-i OH	PCC (2.6 eq)	$\bigvee_{\mathbf{S}} \Pr(i) $	244
Сн2он	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	(91)	245
	PCC	" (—)	246
O OH	n	0 (50)	247
	CrO ₃ •2Pyr (9.0 cq) CH ₂ Cl ₂ , 0°, 1 h	$O = \bigvee_{O}^{CHO} (83)$	248
OH OAc	PCC (4.0 eq), CH_2Cl_2 , 27 h	O O O O O O O O O O	249
OAc OH	РСС (6.0 еq), СН ₂ СІ ₂ , 26 h	$ \begin{array}{c} $	249
HO HO	PCC, CH ₂ Cl ₂ , rt, 15 min	(60)	250

_	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
H CH ₂ O	н	PCC, CH ₂ Cl ₂	H CHO (69) Br	252
CONH ₂ OH		CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , rt, 2 h	CONH ₂ (61)	253
	CH₂OH	PDC (3.72 eq), DMF rt, 8 h	CO ₂ H (51)	254
$\sim\sim\sim$	СН2ОН	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 1-2 h	CHO (84)	14
OH OH		PDC (1.6 eq), DMF, rt, 6 h		255
CH ₂ OF	ł	РСС, п, 1 h	СНО (77)	203
(H)		PDC (1.6 eq), DMF, rt, 6 h	(77)	255
СН2ОН		PDC (3.5 eq), DMF 25°, 7-9 h	CO ₂ H (90)	35
СЦ. СН2ОН		PCC (2.5 eq), CH ₂ Cl ₂ 0°, 7 hr	(74.2) CHO	159
ОН		PCC	()	256
HOH ₂ C		PCC (1.5 eq), CH ₂ Cl ₂	OHC (74)	257
ОН		РСС (1.5 eq), CH ₂ Cl ₂ п, 16 h	(73)	258
$F_{3C} \xrightarrow[Me]{} N$	∼∽он	PDC (2.0 eq), CH ₂ Cl ₂ rt, 2 h	$F_{3C} \xrightarrow[Me]{H} (87)$	259
	он	PCC		260
OH		РСС (2.0 еq), NaOAc CH ₂ Cl ₂ , п, 6 h	(80)	261
MeO ₂ C	OH OH	PCC (1.5 eq), Celite [®] CH ₂ Cl ₂	$MeO_2C \underbrace{\qquad \qquad }_H O (-)$	262
	jon	PCC, CH ₂ Cl ₂ , 20°, 2 h	MeU ₂ C, , , CHU (63)	263
		PCC, CH ₂ Cl ₂	" (63)	264
	-OH	T	" (89)	265
MeO_2C^{-}		CrO ₃ •2Pyr (6.0 eq)	MeO_2C^{-} (86)	266

OXIDATIONS WI	TH OXOCHROMIUM	(VI)AMINE REAGEN	TS (Continued)
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
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OH O O	PCC (1.5 eq), CH_2Cl_2 rt, 3 d	0 0 0 0 (79)	267
MeO ₂ C-OH	PCC (1.2 eq), CH ₂ Cl ₂ 25°, 3 h	MeO ₂ C	268
MeO ₂ C	CrO ₃ •2Pyr, CH ₂ Cl ₂ 23°, 2 min	MeO_2C (88)	269
MeO ₂ C OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ 23°, 15 min	$MeO_2C \xrightarrow{O} H $ (96)	270
	PCC (1.34 cq), rt, 24 h		271
O OMe	PCC	$\bigcup_{0}^{O} \bigcup_{0}^{OMe} (65)$	272
D	PCC (1.5 eq), NaOAc CH ₂ Cl ₂	O (86)	273
	PCC, CH ₂ Cl ₂	$ \bigcup_{O}^{O} T (94) $	274
	РСС (1.5 сq) 3 Å mol. sieves CH ₂ Cl ₂ , rt, 24 h	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} $ (78)	155
ОН	CrO ₃ •2Pyr		276
~~~~ _{ОН}	CrO3•2Pyr (7.46 eq) CH2Cl2, reflux, 12 h	H (48)	277
OH	PCC, CH ₂ Cl ₂	(43) O	278
ОН	РСС (5.2 еq), CH ₂ Cl ₂ п, 2 h	собо) Н (60)	279
	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2 h	" (—)	280
но	PCC (1.5 eq), CH ₂ Cl ₂ rt, 12 h	(80) O	281
СН2ОН	PCC (2.0 eq), NaOAc CH ₂ Cl ₂ , rt, 2 h	СНО (91)	282
CH2OH	PDC (3.5 eq), DMF 20°, 14 h		283
СН2ОН	PCC (1.5 eq), CH ₂ Cl ₂	СНО (99)	284

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН	РСС (2.2 еq), NaOAc CH ₂ Cl ₂ , п, 12 h	(74)	285
ОН	РСС (2.2 еq), NaOAc CH ₂ Cl ₂ , rt, 24 h	(79)	285
ГМS	PCC	TMS (45)	286
он	PCC, CH ₂ Cl ₂	0 0 0 (96)	287
OH OH	PCC (2.0 eq), CH ₂ Cl ₂ , 3 h	0 (75)	288
i-Pr H	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt	i-Pr H ()	289
CH ₂ OH	PCC	CHO ()	164
EtO CH ₂ OH	PCC (2.0 eq), 1.5 h	EtO 0 (60)	290
о он	PCC (1.5 eq), CH ₂ Cl ₂ 20°, 3 h	o i-Pr (82)	165
НО	PCC, CH ₂ Cl ₂	0 (51)	291
MeO CH ₂ OH	PCC (1.2 eq), CH ₂ Cl ₂	MeO CHO (70)	293
осн ₂ он	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min	CHO 0 0 (65)	294
ОН	PCC (2.0 eq), CH ₂ Cl ₂ rt, 1.5 h		295
CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 1-2 h	CHO (85)	14
О СН2ОН	PCC (2.5 eq), NaOAc CH ₂ Cl ₂ , 2 h	CHO (87)	169
Сн ₂ он	PCC (1.25 eq) 3 Å mol. sieves, CH ₂ Cl ₂	СНО (97) ОО	227
CH2OH	CrO ₃ •2Pyr (11.0 eq) CH ₂ Cl ₂ , 25°	CHO (60)	296
	PCC (2.0 eq), NaOAc 30 min	" (92)	297

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	но н он	PCC (1.0 eq), NaOAc CH ₂ Cl ₂ , 1.5 h	$\rightarrow$ $H$ $O$ $H$ $O$ $H$ $(51)$	105
	CH ₂ OH	PCC	CHO (88)	299
	MeO OH	PCC (3.0 eq), 3 Å mol. sieves CH ₂ Cl ₂ , π, 90 min	0Me (78) MeO 0	300
	HO COMe	PCC (1.25 eq), rt, 24 h	0 0 0 0 (72) 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	301
	Br	PCC (2.0 eq), CH ₂ Cl ₂ 0°, 2 h	Br CHO ()	302
	OH D	PCC, CH ₂ Cl ₂	0 (47)	303
	OH T	PCC	о т (—)	304
	ОН	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min		8
		PCC (1.0 cq), $CH_2Cl_2$ reflux	" (100)	77
	OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min	0 (97)	8
		PCC, SiO ₂ , ultrasound	" (80)	64
	СН2ОН	CrO ₃ •Pyr (6.0 eq), CH ₂ Cl ₂	CHO (70)	305
	OH /-Bu	РСС, СН ₂ Сl ₂ , гt, 2 h	0 /-Bu (40)	306
		PCC (1.5 eq). CH ₂ Cl ₂ , 0°	TMS CHO (71)	307
	о Сн₂он	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	О СНО (72)	308
C9	CH ₂ OH	CrO ₃ •2Руг (6.0 еq) CH ₂ Cl ₂ , гt, 45 min	СНО (—)	456
	TBDMSO CH ₂ OH	PCC, NaOAc, CH ₂ Cl ₂ , rt	TBDMSO CHO ()	292
		PCC, CH ₂ Cl ₂ . 25°, 2 h	$ \begin{array}{c} Br & O \\ O \\ O \end{array} $ ()	310
	ОН	CrO ₃ •2Pyr (3.0 cq) CH ₂ Cl ₂ , 20 h	(60)	351
		PCC (1.5 eq), CH ₂ Cl ₂ , 26 h	$ \underbrace{ \overset{\text{CHO}}{\underset{N \to O}{\overset{+}{\longrightarrow}}} }_{N \to O} O^{-} $ (65)	309
	HOH ₂ C CH ₂ OH Fe(CO) ₃	CrO3•2Pyr (15.0 eq) CH2Cl2, rt, 0.5 h	OHC	311
	ОН	QDC (1.0 eq), $CH_2CI_2$ rt, 4 h	CHO (70)	52
		CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min	~ " (96)	8

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PCC (2.0 eq), Al ₂ O ₃ benzene. 25min.	. (84)	137
	DMAPCC (6.0 eq) CH ₂ Cl ₂ , rt, 15 h	" (62)	43
CH2 OH	РDС (2.0 еq) СН ₂ СІ ₂ , п, 24 h	CH ₂ H (56)	312
0	PCC (3.0 eq), CH ₂ Cl ₂ 60-70°, 24 h	(80)	25
OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ гг, 5 min	(40)	313
O CH2OH	PCC (2.0 eq), CH ₂ Cl ₂ rt, 3 h	ОСНО (—)	314
MeO ₂ C — CH ₂ OH	PFC. DMSO	MeO ₂ C-CHO ()	76
Br	PCC (1.2 eq), CH ₂ Cl ₂ rt, 3 h	CHO (66)	315
McCOHN CH ₂ OH	PFC, DMSO	MeCOHN — CHO (—)	76
СН2ОН	PCC (1.1 eq). CH ₂ Cl ₂	(98)	316
СССОН	РСС (1.5 eq), CH ₂ Cl ₂ п, 3 h	(85)	317
SEt CH2OH	PCC	SEt CHO ()	318
OH OH	PCC. CH ₂ Cl ₂ . 4 h		319
HO	CrO ₃ •2Pyr		320
MeO MeO CH ₂ OH	DMAPCC (4.0 eq) CH ₂ Cl ₂ , 14 h	MeO MeO CHO (91)	43
	PCC, SiO ₂ , ultrasound	" (90)	64
МеО СН2ОН	PCC	MeO CHO () MeO	321
o=€	PCC (1.5eq), CH ₂ Cl ₂ rt, 2 h	0=	322

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН	PCC, CH ₂ Cl ₂ , 20°		323
OH	PCC	0 (86)	324
11	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2 h	" (86)	325
OH	PDC, CH ₂ Cl ₂ , rt, 8 h		326
CH ₂ OH	PCC (3.0 eq), CH ₂ Cl ₂	(90)	238
ОН	PCC, CH ₂ Cl ₂ , rt, 2 h	(79)	327
OH	CrO ₃ •2Pyr	H (50)	87
H CH ₂ OH	PCC	H CHO ()	328
H H	CrO ₃ •2Pyr	$0 \xrightarrow{H} H (-)$	329
ОН	CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , 3 min	(95)	330
OMe	PCC, NaOAc, CH ₂ Cl ₂	(62) OMe	292
CO ₂ Me	PCC (1.5 eq). CH ₂ Cl ₂ , rt	0 (78) CO ₂ Me	331
MeS eO ₂ C S OH	PDC. n, 3 d	MeS MeO ₂ C S O (47)	332
одоҲсн₂он	РDС (2.6 еq). CH ₂ Cl ₂ гt, 18 h	(50)	333
eO ₂ C OH	PCC (1.5 eq), rt, 2 h	MeO ₂ C (93)	242
HO	PDC, CH ₂ Cl ₂ , 0°, 1 h		334
оснаон	PCC, NaOAc, CH ₂ Cl ₂	CHO ()	335
	PCC, NaOAc, rt, 1 h	" (85)	336

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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
О	PCC (2.5 eq) NaOAc. rt. 1 h		337
0 HO HO	CrO3•2Pyr (6.0 eq) CH2Cl2, rt, 15 min		338
HO	PCC (3.0 eq) 3 Å mol. sieves CH ₂ Cl ₂ , rt, 1 h		339
	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 20 min	$X_0^{0} \xrightarrow{1}_{0} X_0^{0} \qquad (-)$	340
n-C ₅ H ₁₁ O ^{CH₂OH}	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	$n-C_5H_{11}$ (65)	139
D	PCC (4.64 eq), NaOAc CH ₂ Cl ₂ , rt, 2 h		341
СН2ОН	CrO ₃ •2Pyr (6.0 eq) pyridine, 0°, 15 min	CHO (83)	342
	CrO ₃ •2Pyr (8.0 eq) CH ₂ Cl ₂ , 0-20°	" (84)	342
	PCC (1.5 eq)	" (65)	343
	PCC (1.7 eq), rt, 3 h	" (55)	344
СН3ОН	РСС (7.0 еq), Celite [®] СН ₂ Сl ₂ , п. 1.75 h	CHO (61)	345
ОН	PDC (3.72 eq). DMF, rt, 8 h	CO ₂ H (56)	254
	РСС (7.4 еq), NaOAc CH ₂ Cl ₂ , п. 4 h	CHO (52)	209
СН20Н	PCC (2.0 eq), CH ₂ Cl ₂ 25°, 2.5 h	CHO (82)	346
CH ₂ OH	CrO ₃ •2Pyr	CHO ()	347
СН2ОН	PDC (2.0 eq), DMF, 0°, 2 h	СНО (81)	348
→< ^Н СН <u>₂</u> ОН	PDC	H CHO ()	349
OH	РDC (1.6 еq). DMF п, 6 h	(70)	255
H H H	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 5 h	Н СНО (73) Н	350

Substrate	Conditions	Product(s) and Vield(s) (%)	Dafe
OH	Conditions		Keis.
A S	PCC (1.5 eq), CH ₂ Cl ₂	(58)	258
CH ₂ OH		(83) CHO	257
СН2ОН	•	СНО (100)	257
CH ₂ OH	PCC (4.0 eq), NaOAc CH ₂ Cl ₂	CHO (73) CHO	352
OH CO ₂ Me	PCC (4 cq), NaOAc CH ₂ Cl ₂ , π, 4 h	O CO ₂ Me (79)	353
CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ 20°, 1-2 h	(81)	14
	DMAPCC (5.0 eq) CH ₂ Cl ₂ , 24 h	" (55)	43
	PCC (3.0 eq), 3 Å mol. sieves NaOAc, CH ₂ Cl ₂ , rt	; " (—)	354
	PCC (1.5 eq), NaOAc 4 Å mol. sieves CH ₂ Cl ₂ , 0°-rt	" (55)	355
MeO OMe OH	PCC (1.4 cq). CH ₂ Cl ₂ rt, 2 h	MeO, OMe 0 (95)	356
оон	PCC		357
HOH ₂ C	PDC (6.0 eq), DMF rt, 24 h	HO ₂ C ()	359
	PCC	" (86)	360
но со сон	PCC (17 eq). CH ₂ Cl ₂ 5-10°. 1 h		361
OMe HO NHCOMe	PCC (2.7 eq), CH ₂ Cl ₂ 3 Å mol. sieves	OMe (60) 0 NHCOMe	362
McO ₂ C CH ₂ OH	PDC. CH ₂ Cl ₂	0 0 CHO (93)	363
	CrO3*2Pyr (6.0 eq) Ac2O. CH2Cl2	$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	364
OH Br	PCC (2.0 eq), CH ₂ Cl ₂ rt, 4 h	H Br (86)	348
CI CH2OH	CrO ₃ •2Pyr	CHO (97)	365

Substrate	Conditions		
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	РСС (2.25 сq) 3 Å mol. sieves CH ₂ Cl ₂ , п, 24 h	$NO_2$ (83)	155
ОН	DMAPCC (6.0 eq) CH ₂ Cl ₂ , 24 h	H (90)	43
ОН	DMAPCC (6.0 eq) CH ₂ Cl ₂ , 12 h	Ч (72) Н (72)	43
сн,он	PCC (1.5 eq), Celite [®] rt, 2.5 h	сно (90)	366
ОН	PDC (1.6 eq), DMF 11, 6 h	(67)	255
Улгон Сумон	PCC (2.8 eq), CH ₂ Cl ₂ , 2 h	· (92)	367
тмя	PDC, DMF, rt, 6 h	TMSCO ₂ H (60)	368
СН2ОН	PCC	()	164
MeO. CH ₂ OH	CrO ₃ •2Pyr (6.0 eq), CH ₂ Cl ₂	MeO. (90)	369
	CrO ₃ •2Pyr	" (98)	370
Ср_о_сн₂он	CrO3•2Pyr (9.0 eq) CH2Cl2, 15 min	(95)	371
	PCC (1.5 eq). NaOAc CH ₂ Cl ₂ , 2 h	" (60)	372
CH ₂ OH	CrO ₃ •2Pyr (11.0 eq) CH ₂ Cl ₂ , 25°	CHO (75)	296
Состористически стран	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , 2 h	СНО (100)	373
осн ₂ он	PDC, DMF	CO ₂ H (65)	374
CH ₂ OH	PDC (1.5 cq), CH ₂ Cl ₂	CHO (70)	375
CH ₂ OH 	PCC, CH ₂ Cl ₂ , 12 h	CHO CHO OMe (85)	376
C TMS Br OH	PCC (1.62 eq), 2.5 h	TMS Br (82)	377
о г-Вио Кн2ОН	PDC, DMF	0 <i>t-BuO</i> N CO ₂ H (61)	378

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
(EtO) ₂	p (E) CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, 16 h	$(EtO)_2 \xrightarrow{p} (E) (83)$	161
(EtO) ₂	$ \sum_{\substack{p \\ \mu \\ \mu}} CH_2OH $	n	$(EtO)_{2} \underbrace{p}_{1} \underbrace{(Z)}_{CHO} (86)$	161
$\sim$	о он	PCC, SiO ₂ , ultrasound	0 CHO (85)	64
$\checkmark$	ОН	CrO ₃ •2Pyr (7.25 eq) CH ₂ Cl ₂ 10 min	сно (69)	379
t-Bu		PCC, CH ₂ Cl ₂ , rt, 11 h	<i>I</i> -Bu (75)	306
Me ₃ Sn	ОН	PCC (1.5 eq), CH ₂ Cl ₂ 16 h	$Me_3Sn \longrightarrow O$ (72)	380
$\downarrow$		PCC. pentane	OH (55)	381
$\lambda_{\rm o}$		PCC (3.5 eq), $C_6H_6$ reflux, 2.5 hr		135
	Et }— CH₂OH	CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , 20°, 16 h	Е (15)	403
H H	OH O O	PCC, CH ₂ Cl ₂	$ \begin{array}{c}                                     $	438
C ₁₀ <i>i</i> -Bu	он	PCC, CH ₂ Cl ₂ rt, 11 h	<i>r</i> -Bu CHO	306
$\times$	-CH ₂ OH	PCC, CH ₂ Cl ₂ , rt	$\sim$ CHO (92)	473
		PCC (1.5 eq), Celite® CH ₂ Cl ₂ , rt, 2 h	" (66)	262
HO F ₃ COC	HN OMe	PCC (1.5 eq), 3 Å mol. sieves CH ₂ Cl ₂ , rt, overnight	$F_3COCHN$ OMe (93)	275
	O CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ 15 min	CHO CHO (23)	382
	CH(OH)CH ₃	PCC (1.8 eq), CH ₂ Cl ₂ rt, 2 h	COCH ₃ ()	383
	CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	CHO (57)	139
	ОН	CrO ₂ •2Pyr, CH ₂ Cl ₂	(65)	384
	OH	PCC, CH ₂ Cl ₂ , 2 h		385
$\sim$	CH ₂ OH	PCC (1.5 ag) CH.Cl.	СНО	

PCC (1.5 eq), CH₂Cl₂

rt, 30 min PCC

(85)

(---)

386

387

 $C_{10}$ 

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (C	Continuad

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph D D-V-CH2OH	РСС (1.65 еq), CH ₂ Cl ₂ п. 1.5 h	Ph D D-CHO (84)	388
OH OH	PCC (2.0 eq), CH ₂ Cl ₂	H D 0 (60)	389
CH ₂ OH	РСС (1.75 еq), CH ₂ Cl ₂ п, 1.5 h	CHO (60)	390
HOH ₂ C CH ₂ OH	DMAPCC (1.5 eq) CH ₂ Cl ₂ , 2 h	HOH ₂ C CHO (62)	43
СН₂ОН	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 24 h	CHO (55)	391
	PCC (5.0 eq), SiO ₂ CH ₂ Cl ₂ , rt, 11 h	" (53)	391
OH O	РСС (5.0 еq), CH ₂ Cl ₂ п, 4 h		392
OH OH	PCC, CH ₂ Cl ₂ , EtOAc	0 (70)	393
он снзон	PDC (1.0 cq), CH ₂ Cl ₂ 15 min	о о о о сно (65)	394
он Оон			394
	PCC		395
CH ₂ OH	PCC, NaOAc	CHO 0 0 (77)	396
O OH	РСС		397
MeO ₂ C H OH	PCC (2.5 eq), 4 Å mol. sieves CH ₂ Cl ₂ , 8 h	MeO ₂ C H O (90)	398
O OH	CrO ₃ , pyridine, HOAe		399
$ \underbrace{\langle \bigcirc}_{II}^{O} \underbrace{O}_{II}^{O} CH_{2}OH_{II}$	PCC, NaOAc, CH ₂ Cl ₂		400
Br	PCC (1.1 cq), CH ₂ Cl ₂ rt. 3 h	Br (81)	315
Br Br	PCC (1.5 eq), CH ₂ Cl ₂ , 2 h	Br ()	401

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН Н	РСС	D H (91)	402
i-Pr-CH2OH	DMAPCC (4.0 eq) CH ₂ Cl ₂ , rt, 14 h	i-Pr — CHO (72)	43
ОН	CrO ₃ •2Pyr (4.0 eq) CH ₂ Cl ₂ , 1 h	(69)	404
PhS CH ₂ OH	PCC (2.4 eq), CH ₂ Cl ₂ 2.5 h	PhS CHO (55)	405
SPr-i CH ₂ OH	PCC	SPr- <i>i</i> ————————————————————————————————————	318
HO HO Ph	PDC (1.0 eq). $CH_2Cl_2$ rt, 3 h	Ph (59)	406
MeO	PDC	MeO	407
	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 10 min	." (83)	408
	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1.5 h	" (82)	409
√ 0 OH	PCC, CH ₂ Cl ₂		410
CH ₂ OH	CrO₃•2Pyr, Celite [®] CH₂Cl₂, 20 min	Сно Сно	411
MeO CO ₂ Me	PDC (3.0 eq), CHCl ₃ reflux, 24 h	MeO (40)	412
CO ₂ Me CHO	PDC (2.2 eq), DMF rt, 26 h	CO ₂ Me CO ₂ H (65)	413
OH O O O	PCC, Celite [®] , NaOAc CH ₂ Cl ₂ , 24 h		414
PhSO ₂ OH	PCC (2.0 eq), CH ₂ Cl ₂	PhSO ₂ H ()	415
MeO MeO MeO	DMAPCC (3.0 eq) CH ₂ Cl ₂ , 14 h	MeO MeO MeO (86)	43

OVIDATIONS	WITHOYOCI	IROMIUM(VI)AN	AINE REAGENTS	(Continued)
UNIDATIONS			IIIIL KLAOLI IS	<i>voonunaeu</i>

Substrate	Conditions	Product(s) and Yield(s) (%)	Re
СН <u>э</u> ОН		СН-ОН	
MeO-OMe	PCC (1.0 eq), CH ₂ Cl ₂	$MeQ \longrightarrow OMe$ (62)	416
	0°, 3 h		
CH ³ OH		СНО	
СН ₂ ОН		СНО	
$0 = \left\langle \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & $	$CrO_3 \bullet 2Pyr, CH_2Cl_2, 0^\circ$	$0 = \bigvee_{0}^{1} \bigcup_{i=0}^{1} 0 Ac \qquad ()$	417
	CrO ₃ •2Pyr	" (90)	418
CI N CH ₂ OH	PCC	(-)	419
CH2OH	PDC (1.25 eq), DMF, -10°	CHO (86)	420
Снон	PCC. NaOAc. CH ₂ Cl ₂ 25°. 3 h	СНО (—)	421
HO	PCC, NaOAc, CH ₂ Cl ₂	(61)	422
ОН	PCC, CH ₂ Cl ₂ , 25°, 2 h	(50)	423
⊂ → → →	PCC		424
CH ₂ OH	PDC (1.5 eq)	(-)	159
	PCC (2.0 eq), CH ₂ Cl ₂ 4°, 12 h	" (48.7)	159
CH ₂ OH		(12.3)	159
Сн2ОН	PCC (3.0 eq). $CH_2Cl_2$ , rt	CHO ()	425
	PCC (3.0 eq), CH ₂ Cl ₂	" (90)	238
,OH	РСС (1.6 еq), Al ₂ O ₃ п, 3 h	(93)	137
СН2ОН	РСС (1.5 eq), NaOAc CH ₂ Cl ₂ , rt, 18 h	СНО (55)	426
$\times$	PCC (1.8 eq), NaOAc CH2Cl2, rt, 3 h	(85)	427

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
, OH	PDC	()	428
OH	PCC (2.0 eq). CH ₂ Cl ₂ rt. 2 h	(70)	429
H H H OH	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , 25°, 1 h	(92)	430
H H H	РСС (1.8 еq), СН ₂ Сl ₂ , п	H 	431
ОН	CrO ₃ •2Руг (6.0 eq) CH ₂ Cl ₂ , гt, 1 h	(84)	432
HOH ₂ C	PCC (1.5 eq), CH ₂ Cl ₂	(96) OHC	257
но	РСС (8.5 еq), CH ₂ Cl ₂ п, 2 h	0 (80)	433
но	CrO ₃ •2Pyr	O ()	434
S OH	РСС (1.5 еq), CH ₂ Cl ₂ п, 1 h	(48)	435
O CH2OH	РСС (4.0 еq), CH ₂ Cl ₂ п, 2 h	о (69) СНО	436
СН2ОН	PCC, NaOAc	СНО (86) СНО	437
ОН	PCC, CH ₂ Cl ₂ , rt, 4.5 h	0 (80)	439
ноон	PCC		440
CH ₂ OH	PCC (2.5 eq), $CH_2Cl_2$ rt, 3.5 h	$-CO_2Et \qquad (94)$	441
O O O O O O O O O O O O O O O O O O O	PCC		442
МеО2С ОН	CrO3•2Pyr (6.0 eq) pyridine, rt, 30 min	MeO ₂ C (84)	443
X0-IIIOH	PDC (1.7 eq), CH ₂ Cl ₂		191

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)			
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO ₂ CCH ₂ OH	PCC, CH ₂ Cl ₂	MeO ₂ C	264
ОН	РСС (2.04 еq), NaOAc CH2Cl2, п, 1.5 h	(91)	444
сн <u>э</u> он	PCC, CH ₂ Cl ₂	CHO (75)	445
	PCC	" (78)	446
$O = \bigcup_{C_4H_9 - n}^{OH}$	РСС, СН ₂ Сl _{2.} п, 6 h	$O = \bigcup_{C_4H_9 \cdot n}^{O} (75)$	447
AcO.	CrO3•2Pyr (1.8eq) rt, 2 h	AcO. (85)	448
Aco 0	PCC (5.1 eq), CH ₂ Cl ₂ . 5 h	Ac0 0 (92)	449
AcO-	'n	Ac0 (71)	449
	PCC (4.2 eq), CH ₂ Cl _{2.} 2.5 h	Ac0 0 (81)	449
	PCC (4.2 eq), $CH_2CI_2$ , 30 mir	$A_{ACO} = O $ (90)	449
ООО	РСС (2.0 сq). CH ₂ Cl ₂ п, 1.5 h	(98) (98)	450
HOH ₂ C O AcO OAc	PCC (1.0 eq). Celite® 50°, 8 h	$OHC \xrightarrow{O} -OMe$ $AcO \xrightarrow{O} OAc$ $()$	451
O O CH2OH	PCC, 20°, 1 h	О О СНО (60)	452
N ₃ HO' O O	PDC (2.0 сq), 4 Å mol. sieves CH ₂ Cl ₂ , п, 72 h	$N_3 \longrightarrow O$ $OMe$ $O \longrightarrow O$ (89)	453
EtO ₂ C	PCC (1.5 eq), $CH_2CI_2$ rt, 3 h	EtO ₂ C, N. (75)	455

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
	DMAPCC (6.0 eq) CH ₂ Cl ₂ , 15 h	CHO (88)	43
	PCC, SiO ₂ , ultrasound	" (72)	64
HO	CrO ₃ •2Pyr	O (50)	87
OH	PCC		457
СН2ОН	PCC (2.5 eq), CH ₂ Cl ₂ 45 min	, CHO (61)	204
СН2ОН	PCC, CH ₂ Cl ₂	CHO (89)	458
	РСС (1.5 еq), CH ₂ Cl ₂ п, 2 h		459
	PCC (2.5 eq), $AI_2O_3$ hexane, 6 h		137
OH Pr-i	РСС (1.5 еq), CH ₂ Cl ₂ гt, 2 h	$= \underbrace{ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ $	460
H H	PCC (1.5 eq), NaOAc		461
OH	PCC	()	462
-он	CrO ₃ •2Руг (6.0 еq) CH ₂ Cl ₂ , rt, 25 min	<b>(85)</b>	463
С	PCC, SiO ₂ , ultrasound	(81)	64
0 CH ₂ OH	PCC (1.5 eq), rt, 1.5 h	0 CHO (79)	464
CH ₂ OH	PCC	CHO (60)	465
O CH2OH	PDC (1.1 eq), CH ₂ Cl ₂ rt, 19 h	0 ()	466
CH ₂ OH	PCC (2.5 cq), NaOAc CH ₂ Cl ₂ , dioxane (1:1)	СНО (53)	467

	23 P.2	Deadaatta and Vielda (6)	Dati
Substrate	Conditions	Product(s) and Held(s) (%)	Kels
HO, CH ₂ OH	PCC (1.5 eq). CH ₂ Cl ₂ 20 min	ноСпо (70)	468
но — СН ₂ ОН	PCC (1.5 eq). CH ₂ Cl ₂ 2 h	НО — СНО (85)	469
но	РСС (1.5 eq), NaOAc CH ₂ Cl ₂ , п, 3 h	но	470
ОН ОН	CrO3•2Pyr, rt. 18 h		471
ОНОН	PCC, CH ₂ Cl ₂ , 6 h	0 (31)	439
, OH , OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ rt, 15 min	Q (45)	472
MeO ₂ C., CH ₂ OH	PCC. CH ₂ Cl ₂	MeO ₂ C,	264
MeO ₂ C	PCC (1.52 eq), NaOAc Celite [®] , CH ₂ Cl ₂ , π. 5 h	MeO ₂ C, (63)	475
O OH	PCC	0 0 (75)	476
CH ₂ OH	PCC, CH ₂ Cl ₂	CHO (81)	178
СН2ОН	PCC (1.5 eq), $CH_2Cl_2$	()	477
CH2OH	CrO _{3*} 2Pyr (6.0 eq) CH ₂ Cl ₂ , п, 30 min	СНО (67)	478
Me2N HQ		(70) Me ₂ N O	479
HO CHN OME	PCC, CH ₂ Cl ₂ 3 Å mol. sieves	O MeOCHN OMe ()	480
	PCC, CH ₂ Cl ₂	" (84)	275
	РСС (3.0 еq), 3 Å mol. sieve CH ₂ Cl ₂ , п, 14 h	rs " (58)	481
MeOCHN OMe HO TO T	PCC, CH ₂ Cl ₂ 3 Å mol. sieves	MeOCHN OMe 0 (87)	482
	PCC (3.0 eq), 3 Å mol. sieve CH2Cl2, 14 h	²⁵ " (87)	483

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
	PCC (2.25 eq) 3 Å mol. sieves CH ₃ Cl ₃ . 24 h	$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$	155
ОН	PCC, CH ₂ Cl ₂	(59)	278
OH	PCC (1.5 eq). $CH_2Cl_2$ rt, 15 min	<b>O</b> (71)	484
)OH	РСС		485
	PCC (3.0 eq), $AI_2O_3$ hexane, 4 h	——————————————————————————————————————	137
	PCC (2.0 eq), NaOAc CH ₂ Cl ₂ , 25°	" (82)	14
	PDC (3.5 eq), DMF 25°, 0.9 h	————————————————————(83)	35
	PCC, NaOAc		486
	РСС (1.0 еq), NaOAc CH ₂ Cl ₂ , 4 h		487
CH ₂ OH	РСС (1.5 eq), п, 1.5 h	(91) CHO	488
ОН	PCC (2.1 eq), CH ₂ Cl ₂ 2 h	(79)	367
<i>t</i> -Bu—OH	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 1-2 h	<i>t</i> -Bu-(97)	14
OH Pr-i	PCC (2.5 eq), Al ₂ O ₃ hexane, 2.5 h	$- ^{O} - Pr - i \qquad (94)$	137
CH ₂ OH	PCC (1.5 eq), $CII_2CI_2$	CHO (80)	284
CH ₂ OH OH	PCC, NaOAc, CH ₂ Cl ₂ , rt	CHO O ()	489
CH ₂ OH	PCC	СНО (—)	164
CH2OH	PCC (1.5 cq), rt, 2 h	CHO (88) CO ₂ Me	490
Aco	PCC	AcO CHO (86)	491
	PCC (1.5 eq), 3 Å mol. siev 25°, 2 h	cs " (81)	492

VIDATIONS WITH	OYOCHROMIUM(VI)AMIN	JE REAGENTS (Continued)
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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
CH2OH	PCC, NaOAc, CH ₂ Cl ₂	$\begin{array}{c} O \\ O \\ O \\ O \\ Pr-i \end{array} $ (76)	493
CH ₂ OH	РСС (1.5 сq), NaOAc п, 2 h	$\bigvee_{O}^{O} Pr-i$ (73)	494
CH ₂ OH	CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , 0°, 30 min	CHO (50)	495
СН2ОН	PCC, CH ₂ Cl ₂ , rt	СНО (93)	496
OH COM	PCC		376
1ОН	PCC, CH ₂ Cl ₂ 4 Å mol. sieves	ICHO (76)	497
~~~~~ОН	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 1-2 h	(92)	14
	PCC (2.5 eq), Al_2O_3 hexane, 2.5 h	$- \underbrace{- CHO}_{Pr-i} \qquad (80)$	137
CH ₂ OH	PDC. 0°	CHO ()	498
TMS OH	PCC (1.5 eq), rt, 2 h	TMS 0 (51)	499
TBDMSO CH ₂ OH	PCC, CH_2CI_2	TBDMSO CHO (85)	500
C ₁₁ MeO		МеО	
MeO ₂ C	PDC (3.0 eq), CHCl ₃ reflux, 3 h	McO ₂ C (54)	412
CH ₂ OH	PDC, DMF	$\mathcal{L} - \mathbf{BuO} \xrightarrow{NH}_{O} \mathcal{L} O_2 H $ (66)	378
	PCC, CH ₂ Cl ₂ , n	BnO (68)	454
CO ₂ Me CH ₂ OH	РСС	CO ₂ Me CHO ()	474
CII2OH	N	()	501
Вr О О О О О СH2OH	PCC, SiO ₂ , ultrasound	Br O CHO (94)	64

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
BzOCH2OH	DMAPCC (1.5 eq) CH ₂ Cl ₂ , 24 h	Bz0 CHO (75)	43
MeO ₂ C S OH	CrO ₃ •2Pyr (1.3 eq) CH ₂ Cl ₂ , 15 min	MeO ₂ C S (55)	502
OH	CrO ₃ •2Pyr (8.0 eq) CH ₂ Cl ₂ , 3 h	(92)	503
$Ph \rightarrow N \rightarrow N$ $N \geq N$ CH_2OH	РСС (1.5 еq), CH ₂ Cl ₂ п, 2 h	$Ph \not \sim N $ (50) N $\approx N$ CHO	504
СН2ОН	РСС (1.2 еq), СН ₂ СІ ₂ п, 2 h	(48)	505
СН2ОН	РСС (5.0 еq), SiO ₂ СН ₂ Сl ₂ , rt, 10 h	(52)	391
1	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 22 h	· (50)	391
CH ₂ OH	PCC (5.0 cq), SiO ₂ CH ₂ Cl ₂ , rt, 8 h	(68)	391
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 15 h	" (65)	391
CH2OH	PDC (5.0 eq), Celite [®] CH₂Cl₂, 25°, 24 h	(70)	391
BzO OH	PCC, CH ₂ Cl ₂ , rt, 2 h	BzO(70)	506
OMe CH2OH	РСС (5.0 еq). SiO ₂ СH ₂ Cl ₂ , п. 11 h	OMe O (69)	391
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 20 h		391
McO	PCC (5.0 eq), SiO ₂ CH ₂ Cl ₂ , 25°, 8 h	MeO (71)	391
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 15 h	" (76)	391
MeO CH20H	PCC (5.0 cq), SiO ₂ CH ₂ Cl ₂ , 25°, 8 h	MeO (70)	391
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 14 h	" (70)	391
BzOOH	РСС (1.5 еq), CH ₂ Cl ₂ п. 2.5 h	BzO CHO (60)	157
Рһ,	PCC (1.5 eq). CH ₂ Cl ₂ 20°. 3 h	Ph 0 — 0 (72)	165

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
С S O O H	PCC, SiO ₂ , ultrasound	$ \underbrace{ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	507
H H H CO ₂ Me	СгОз•2Руг	H = O (73)	508
,CH ₂ OH O MeO	PCC (1.6 eq). CH ₂ Cl ₂ rt, 1 h	$ \begin{array}{c} $	509
CO ₂ Me OH	PCC (1.3 eq),CH ₂ Cl ₂ 0°, 5 h	\sim	145
OH N CO ₂ Me	PCC, NaOAc	O N CO ₂ Me (75)	510
MeO MeO	РСС (1.5 еq), п, 18 h	MeO Br (77)	511
CH2OH	PCC (3.0 eq), CH ₂ Cl ₂	CHO (90)	238
С	PCC	(98)	512
ОН	РСС (1.14 еq), CH ₂ Cl ₂ rt, 1.5 h	СНО (57)	513
BnO	PCC (1.5 eq), NaOAc rt, 1.5 h	BnO CHO (58)	514
	PCC	" (70)	515
O CH-OH	CrO ₃ •2Pyr		516
HO CH ₂ OH	PDC (7.6 eq), DMF rt, 18 h		409
СН2ОН	CrO3•2Pyr	CHO ()	517
MeO OH	PCC, 3 Å mol. sieves CH ₂ Cl ₂ , rt, 15 min	MeO ()	518
ОН	PCC		519
CH ₂ OH	PCC (2.0 eq), NaOAc Celite [®] , CH ₂ Cl ₂ , rt, 2 h	OAc CHO (74)	520

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PCC	$ \begin{array}{c} $	522
Aco H H	РСС (1.5 еq), п, 2 h	$\begin{array}{c} H \\ 0 \\ H \\ AcO \end{array} $ (15)	523
HO $ -$	PCC (1.42 eq), CH ₂ Cl ₂ 0°, 1.5 h	$OHC \xrightarrow{CO_2Me}_{MeO_2C} \xrightarrow{CO_2Me}_{CO_2Me} $ (80)	524
CH ₂ OH H Br	РСС (1.5eq), CH ₂ Cl ₂ п, 2 h	CHO H Br (95)	525
СН2ОН	CrO3•2Pyr, CH ₂ Cl ₂ 23°, 1 h	(86)	526
OH OH	PCC	(25)	424
OH OH	PCC (3.0 eq), CH ₂ Cl ₂	(90)	238
— — — — — — — — — — — — — — — — — — —	PCC (1.5 eq), NaOAc rt, 2 h		527
CH2OH	PCC (1.8 eq), CH ₂ Cl ₂ , rt	()	431
CH2OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1.5 h	СНО (96)	257
ОН СН2ОН	CrO ₃ •2Pyr	CHO (45)	528
CO ₂ Me CH ₂ OH	PCC	CO ₂ Me CHO ()	529
OMe CH ₂ OH	PCC, CH ₂ Cl ₂ , rt	OMe CHO (88)	530
MeO OMe OH	PCC	MeO O O (75)	531
OT OH	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , 30 min	$\mathcal{O}_{\mathbf{v}}^{\mathbf{v}}$ ()	532

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
О	РСС (7.0 ед), CH ₂ Cl ₂ п, 2 h	(85)	533
HO' O' O'	PCC, 3 Å mol. sieves CH ₂ Cl ₂ , rt, 10 h		534
	PCC (2.0 eq), CH ₂ Cl ₂ rt, 16 h		535
OH	PDC (4.0 eq), CH ₂ Cl ₂ rt, 16 h	" (59)	535
Me ^{-N} H OH	PCC	Me^{-N} (16)	536
	PCC (1.5 eq), CH ₂ Cl ₂ rt, 48 h		537
	PCC (3.5 eq), CH ₂ Cl ₂ rt, 1 h	~ 0	538
HO _{rt} N-CO ₂ Et	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	0 (93)	455
Me CH ₂ OH	PCC or PDC or CrO3•2Pyr	Me N CHO (0)	539
ОН	PCC, CH ₂ Cl ₂ rt, 1 h	0 (41)	540
СН2ОН	PCC (1.2 eq) CH ₂ Cl ₂ , 25°	(75)	541
ОН	CrO ₃ •2Pyr (3.6 eq) CH ₂ Cl ₂ , rt, 24 h	(85)	190
ОН	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , 20°, 5 h	O (75)	542
) () () () () () () () () () () () () ()	РСС (1.5 eq), NaOAc CH ₂ Cl ₂ , rt, 2 h	(97)	543
ОН	PCC (1.68 eq)	(89)	544
H OH	PCC, NaOAc, CH ₂ Cl ₂		545

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
H H H	PCC (1.1 eq), CH ₂ Cl ₂ , 3 h	(84) H	546
CH2OH	PCC (2.0 eq.). CH ₂ Cl ₂ rt, 3 h	о СНО (97)	547
MeO ⁴⁰ CH ₂ OH	CrO ₃ •2Pyr (7.0 eq) CH ₂ Cl ₂ , 3 h	MeO ^{rn} (90)	548
TBDMSO	PCC	TBDMSO	442
CH ₂ OH	PDC (1.5 eq.). DMF 0°. 2 h	(85)	549
CH ₂ OH O	PCC, CH ₂ Cl ₂	CHO 0 0 (72)	178
	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 15 min		550
ОН	PCC (2.0 eq), CH ₂ Cl ₂ 1.5 h		551
ОН	PCC (1.25 eq), Al ₂ O ₃ CH ₂ Cl ₂ , 6 h		551
	PCC (3.0 eq), rt, 2 h	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	552
о стран	РСС (1.5 eq), п, 1.5 h		553
OH OH	CrO ₃ •2Pyr		554
	CrO ₃ •2Pyr	OAc OH OH ()	92
MeO OMe	PDC (1.5 eq), 3 Å mol. sieve CH ₂ Cl ₂ , rt, 1 h	s O O (93)	334
CH ₂ OH CO ₂ Et	РСС, CH ₂ Cl ₂ , п, 8 h	CHO (85)	555
ОН	CrO₃•2Pyr (6.0 eq) rt, 15 h	(93)	556

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	OH	PCC (2.1 eq) CH ₂ Cl ₂ , 2 h	(84)	367
	.CH2OH	PCC (5.0 eq), CH ₂ Cl ₂ 0°, 3 h		557
	S S OH	PDC (7.0 eq), DMF 0°, 11 h	S S (85)	559
	ОН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 15 min	0 0 0 0 (95)	560
	CH ₂ OH	PCC, SiO ₂ , ultrasound	ОСНО (73)	64
	NO ₂ OH	РСС (2.25 eq), 3 Å mol. sieves CH ₂ Cl ₂ , п, 24 h	NO ₂ (86)	155
	S TMS CH ₂ OH	PCC, CH ₂ Cl ₂ 25°, 2-3 h	S CHO (60)	563
	TBDMSO	PCC, SiO ₂ , ultrasound	TBDMSO CHO (55)	64
	CO ₂ Me O O O Me	CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , rt, 1 h	CO ₂ Me O O O Me (95)	521
C ₁₂	O CH ₂ OH	CrO ₃ •2Pyr (8.0 eq) CH ₂ Cl ₂ , 45 min	0 (60)	575
	OH OH	CrO ₃ •2Pyr	(82)	558
	O OH	PCC, CH_2Cl_2 , 3 h		564
		PCC (2.0 eq) CH ₂ Cl ₂ , 1 h	$ \begin{array}{c} 0 & Me \\ N & N \\ 0 & N \end{array} $ (84)	565
	Br CH ₂ OH	PCC (1.6 eq), SiO ₂ CH ₂ Cl _{2,} 6 h	Br CHO (98)	566
	O OH O NO ₂ CO ₂ Me	PCC	$ \bigvee_{O}^{O} \bigvee_{NO_2}^{O} \bigvee_{CO_2Me} $ (80)	397

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
O, OH	CrO ₃ •2Руг (6.0 еq) CH ₂ Cl ₂ , 20 min	(89)	567
McO-V-N-CH2OH	РСС (1.0 еq) СН ₂ Сl ₂ , п, 1 h	MeO – N CHO O (76)	568
ОН	РСС (1.5 eq) CH ₂ Cl ₂ , п, 15 min	СНО (90)	569
CH ₂ OH	PCC (5.0 eq), SiO ₂ CH ₂ Cl ₂ , 25°, 9 h	0 (60)	391
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 18 h	" (63)	391
CH ₂ OH	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 25 h	(80)	391
OH OH	РСС (2.0 eq) СН ₂ Сl ₂ , rt, 4 h		288
о-ОН	PCC (1.5 eq), Na ₂ CO ₃ CH ₂ Cl ₂ , 0°, 30 min	0-(87)	570
MeO CH ₂ OH	РСС (1.5 сq), SiO ₂ CH ₂ Cl ₂ , 25°, 7 h	MeO. (69)	391
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 12 h	" (68)	391
MeO	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 24 h	MeO (79)	391
CH ₂ OH MeO	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 14 h	0 MeO (60)	391
ОН	РСС (1.5 сq) СН ₂ Сl ₂ , rt, 1 h	(80) CHO	571
	РСС (1.0 еq) СН ₂ СІ ₂ , п, 4 h	(30)	572

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)				
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
H H H H	PCC, CH ₂ Cl ₂	$ \begin{array}{c} 0 \\ H \\ H \\ H \\ 0 \end{array} $ (30)	573	
BzO	РСС (1.5 еq) СН ₂ Сl ₂ , п, 2.5 h	BzO CHO (59)	157	
CO ₂ Et	РСС (1.6 еq) СН ₂ Сl ₂ , п, 4 h	CHO (55) CO ₂ Et	574	
MeO MeO	PCC (5.0 eq), SiO ₂ CH ₂ Cl ₂ , 25°, 6 h	MeO (72)	391	
	PDC (5.0 eq), Celite [®] CH ₂ Cl ₂ , 25°, 13 h	" (70)	391	
OMe OH OMe	РСС (1.5 еq) СН ₂ Сl ₂ , п, 7 h	OMe OMe OMe (46)	576	
HO HO	PCC (1.5 eq), Celite® CH ₂ Cl ₂ , rt, 7.5 h	(72) 0	577	
OH SO ₂ C ₆ H ₅	PCC, NaOAc, Celite® CH ₂ Cl ₂	0 (74) SO ₂ C ₆ H ₅	578	
HOH ₂ C OMe	РСС (2.0 еq), CH ₂ Cl ₂ гт. 3 h	OHC OMe OMe OMe (89)	579	
OCH ₂ OAc	PCC (2.0 eq), (CH ₂ Cl) ₂ 80°, 17 h	$O_{CH_2OAc} (80)$	30	
	PDC, DMF	$D_3C \xrightarrow{D} CHO$ (42)	580	
Ph N CH ₂ OH	PDC, CrO ₃ •2Pyr	Ph N CHO (0)	581	
HO	РDС (1.5 еq) CH ₂ Cl ₂ , п, 4 h	(89)	582	
OH	PCC, NaOAc CH ₂ Cl ₂ , 25°	(89)	584	
BnO. OH	PCC	BnO CHO (66)	529	

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OH OBn	РСС (2.2 еq) СН ₂ Сl ₂ , rt, 1.5 h	OBn (82)	586
MeO ₂ C	PDC (3 eq). CHCl ₃ reflux, 24 h	MeO_2C (80)	412
	CrO3•2Pyr (6.0 eq) CH ₂ Cl ₂		587
MeO H	РСС (1.5 еq), CH ₂ Cl ₂ п, 1 h	MeO H (100)	588
MeO ₂ C OH	PCC (2.5 eq), CH ₂ Cl ₂ rt, 2 h	MeO ₂ C O H (87)	429
O WOH	PCC, CH ₂ Cl ₂	0 0 0 (70)	589
AcO AcO //OH	PCC, n, 2 h	AcO (40)	590
HO HO HO H	PDC (3.0 eq) 3 Å mol. sieves CH ₂ Cl ₂ , 20°, 2.5 h	$O \xrightarrow{H} O \xrightarrow{Br} (70)$	591
OH N Me	PCC (1.71 eq), NaOAc rt, 1.5 h	Me (60)	592
CH20H	PCC (2.0 eq)	(77) CHO	593
CH ₂ OH	PCC (3.0 eq), CH ₂ Cl ₂	CHO (90)	238
)он	PCC		424
, , , , , , , , , ,	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min	CHO (55)	595

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН	РDС (1.6 еq) DMF, п, 6 h	O (76)	255
CH2OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 15 min	CHO (83)	596
H, OH	PCC (1.5 eq), NaOAc CH ₂ Cl ₂	()	597
P ^r OH	РСС (1.7 еq), п, 1 h	(84)	598
HO OH	PCC		599
OH OH	PDC	(85)	600
СН2ОН	CrO ₃ •2Pyr, CH ₂ Cl ₂	Сно (—)	601
O H H	PCC		602
O H .CH2OH	PDC (3.4 eq), DMF rt, 12 h	(72)	603
CT ₂ OH	PCC	СТО (-)	604
CH ₂ OH	PDC (3.5 eq), DMF rt, 16 h	CHO (82)	605
CH2OH	PCC	О СНО О (42)	606
	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 25°, 10 h	$ \underbrace{ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	607
CONMe ₂ CO ₂ Me CH ₂ OH	РСС, CH ₂ Cl ₂ п. 4 h	CONMe ₂ CO ₂ Me (71) CHO	608

OXID	ATIONS WITH OXOCHROMIUM(VI	AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	РСС (3.8 еq), 3 Å mol. sieves CH ₂ Cl ₂ , rt, 24 h		609
	PDC (7.0 eq), Ac ₂ O, DMF CH ₂ Cl ₂ , reflux, 2 h		41
	РСС (3.8 eq), 3 Å mol. sieves CH ₂ Cl ₂ , п, 2 h	" (95)	610
	PCC (3.0 eq), benzene reflux, 3 h	$\begin{array}{c} & & \\$	135
O CH ₂ OH O O O O	PDC (7.0 eq), Ac ₂ O, DMF CH ₂ Cl ₂ , reflux, 2 h	о СНО 0 СНО 0 (71) 0 0 (71)	41
	РСС (5.0 eq) CH ₂ Cl ₂ , rt, 5 h	" (75)	611
N H OH	PCC, CH ₂ Cl ₂	(89)	612
CH2OH	PCC	$ \begin{array}{c} & & \\ & & $	613
CH ₂ OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 15 min	CHO (88)	614
CH ₂ OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 20 min	CHO (93)	615
CH ₂ OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 15 min	(94)	616, 617
n-C ₈ H ₁₇ OH CHBr ₂	PCC (1.5 eq) CH ₂ Cl ₂ , π, 4 h	0 n-C ₈ H ₁₇ (23)	618
H CH ₂ OH	CrO ₃ •2Pyr, CH ₂ Cl ₂	H CHO H J OAc	619
O OH	PDC (1.65 eq), Celite® rt, 24 h		620
CH ₂ OH	CrO ₃ •2Pyr (5.0 eq) CH ₂ Cl ₂ , rt, 4 h	CHO (42)	621

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	<i>t</i> -BuO U U O	РСС (1.15 еq) СН ₂ Сl ₂ , rt, 2 h	<i>t</i> -BuO (20)	256
	ОН	PCC, CH ₂ Cl ₂	(89)	622
	OMe OMe OH	PDC (1.5 eq), 3 Å mol. sieves CH ₂ Cl ₂ , Ac ₂ O	O O O O O O O O O O O O O O O O O O O	334
	MeHN CH2OH	PCC (2.0 eq), rt, 3 h	CHO (52)	623
	O O N Me	РСС	$\bigvee_{\substack{N\\ Me}}^{O} \bigvee_{\substack{N\\ Me}}^{O} (68)$	624
	~~~~ _{ОН}	PCC	CHO ()	625
	OH OH	РСС (3.8 еq) СН ₂ Сl ₂ , п, 1.5 h	O (81)	626
	OH TMS	PCC		627
	OMe OH	PCC (1.6 cq), 3 Å mol. sieves CH ₂ Cl ₂	0 0 0 (61)	551
	Br	PDC	Br CHO ()	628
	$t-BuO \xrightarrow{O}_{H} \underbrace{N}_{C_4H_9-n} \xrightarrow{CH_2OH}_{C_4H_9-n}$	PCC (1.49 eq) CH ₂ Cl ₂ , 23°, 4 h	$h-BuO \xrightarrow{O}_{H} \underbrace{N}_{C_4H_9-n} CHO $ (64)	629
	ОН	PCC	СНО (—)	630
	OH			630
C ₁₃	EtO ₂ C-V H H CH ₂ OH	CrO3•2Pyr (8.0 eq)	$EtO_2C$ () H CHO	635
	OH i-Pr	CrO ₃ •2Pyr	0 ) <i>i</i> -Pr	664
	Сосон	PCC (1.5 eq), rt		684
	OH Ph Ph	PCC (1.5 eq) CH ₂ Cl ₂ , 25°, 1-2 h	Ph (100)	14
		PCC (1.0 eq) CH ₂ Cl ₂ , rt, 4 h	" (55)	52

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS.

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OMe CH ₂ OH	РСС (1.625 еq) СН ₂ СІ ₂ , гt, 3 h	OMe CHO (76)	358
HO HO	PCC, CH ₂ Cl ₂	(72)	536
OAc	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2 h	OAc (86)	561
СН₂ОН	РСС (3.0 еq) CH ₂ Cl ₂ , rt, 45 min	СНО (75)	583
OH C	CrO3•2Pyr		585
И	PCC (1.5 eq), CH ₂ Cl ₂ , 2 h	СНО (78)	594
О СH ₂ OH	РСС (3.2 еq) CH ₂ Cl ₂ , п, 3.5 h	О СНО (92) О	631
O N O O O O H	PCC (7.0 eq), NaOAc	$( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) \\ ( ) $	632
OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, 2 h	(90)	633
O CH ₂ OH	PCC (4.0 eq) DMF, rt, 9 h	(36)	636
OH	PCC (1.5 eq), CH ₂ Cl ₂ π, 15 min	(50)	637
OH OH	PCC (2.0 eq), CH ₂ Cl ₂ rt, 21 h	0 (87)	288
NC. OH	PCC (1.5 eq), CH ₂ Cl ₂	NC, 0, (98)	638

OXIDATIONS WITH	OXOCHROMIUM(VI)AMINE REAGENTS (Continued)
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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HO MeO N COMe	CrO ₃ •2Pyr	MeO (79)	639
O OH O N CO ₂ Me	PCC	$\bigcup_{\substack{O \\ H}} O \\ O \\ H \\ O \\ H \\ O \\ O \\ H \\ O \\ O \\$	640
CO ₂ Et S CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, overnight	S CO ₂ Et (73)	641
ОН	CrO3•2Pyr (7.0 eq) rt, 24 h	(96)	642
CH ₂ OH	PCC, CH ₂ Cl ₂ , rt	CHO ()	643
CH ₂ OH	РСС, СН ₂ Сl ₂ , п, 2 h	(97) СНО	644
OH O	PCC (1.5 eq), Na ₂ CO ₃ CH ₂ Cl ₂ , 0°, 30 min	(83)	570
OH O	РСС (2.0 еq), CH ₂ Cl ₂ rt, 12 h	(83)	288
ОТОН	PCC (1.5 eq), $CH_2Cl_2$ 25°, 8 h	CHO (68)	645
CH ₂ OH MeO	PDC (5.0 cq), Celite [®] CH ₂ Cl ₂ , 25°, 22 h	MeO (68)	391
BzO OH	PCC, CH ₂ Cl ₂	BzO (79)	646
OMe OMe CH ₂ OH	CrO ₃ •2Pyr	OMe () OMe CHO	647
HO O O SO ₂ Ph	PCC	O O SO ₂ Ph ()	578
	РСС (4.0 сq), NaOAc CH ₂ Cl ₂ , п, 3 h	$U = \bigcup_{0}^{CHO} \bigcup_{F} \bigcup_{(75)}^{(75)}$	649
CH ₂ OH	PCC (3.0 eq), $CH_2Cl_2$	CHO (90)	238

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HO		0	
	PCC (1.5 eq), $CH_2Cl_2$ rt, 30 min	()	650
CO ₂ Me CH ₂ OH	РСС (1.5 еq), CH ₂ Cl ₂ п, 1 h	CO ₂ Me (90)	651
	PCC, $CH_2Cl_2$ , rt, 2 h	0=(97)	652
1	PCC, CH ₂ Cl ₂ , rt, 4 h	(73)	653
HO	u	0 (14)	653
MeO ₂ C	PCC (4.0 eq), NaOAc rt, 20 h		656
CO ₂ Me	РСС (4.0 еq), NaOAc CH ₂ Cl ₂ , п, 2 h	(99) CO ₂ Me	657
CH ₂ OH	CrO3•2Pyr (5.0 eq) CH2Cl2, 5 min	(90)	658
O O O	РСС (1.1 еq), CH ₂ Cl ₂ п, 3 h		659
$O = \bigcup_{MeO_2C} H OH$	PDC (1.5 eq), DMF rt, 18 h	$O = \bigvee_{MeO_2C}^{H} \bigvee_{(61)}^{O}$	660
$O = O = O + C_4 H_{9^{-}n}$	РСС, CH ₂ Cl ₂ , гt, 8 h	$ \begin{array}{c} E_{t}O_{2}C & O \\ O = & O \\ O = & O \\ C_{4}H_{9}-n \end{array} $ (58)	447
MeO OH OH OH OH OH	PDC	$MeO \rightarrow OMe \\ O \rightarrow OH \\ OMe $ (60)	661
$ \begin{array}{c} CH_2OH \\ H \\ H \\ H \\ CO_2Et \end{array} $	PCC (1.6 eq), CH ₂ Cl ₂ rt, 3 h	(58)	144
HN, HN, OH	PCC, CH ₂ Cl ₂		662

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ј-Рт ОН	PCC (2.0 eq), 4 Å mol. sieves CH ₂ Cl ₂ , 30°, 1 h HO ⁵⁷	(45) Pr- <i>i</i>	663
ОН	PDC (1.5 eq), $CH_2Cl_2$ rt, 4 h	(89)	582
	PDC (3.3 eq), CH ₂ Cl ₂ , 20 h	CHO (74)	665
$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	PCC (2.57 eq.), NaOAc	$C_8H_{17}-n \qquad (34)$	666
СН2ОН	PCC (1.5 eq), $CH_2Cl_2$ n, 2 h	сно ()	667
мер	PCC, DMF, CH ₂ Cl ₂		668
OH NEO	PCC (2.0 eq), 4 Å mol. sieves CH ₂ Cl ₂ , rt, 4 h		669
ОН	PCC (2.0 eq), 4 Å mol. sieves Cl1 ₂ Cl ₂ , π, 4 h	(70)	669
O O OH	PCC (1.5 eq), rt, 2 h	(98)	670
O CH ₂ OH	СгО3•2Руг (6.0 еq) СН ₂ Сl ₂ , г, 15 min	O CHO (80)	671
O O H	" (		8
Cox H	PCC (3.0 eq), NaOAc CH ₂ Cl ₂ , 8 h	0 $H$ $(74)$	672
O O U U O OH	РСС (5.0 eq), CH ₂ Cl ₂ п, 6 h		673
о сн ₂ он	CrO ₃ •2Pyr, CH ₂ Cl ₂	СНО (—)	674

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HO O ₂ CBu- <i>t</i>	PDC (1.4 eq), CH ₂ Cl ₂ 48 h	OEt $O$	675
CO ₂ Et	CrO3•2Pyr (12.5 еq) CH2Cl2, rt, 15 min	$O_{0}^{\text{CO}_{2}\text{Et}} $ (72)	676
CO ₂ Me V OH	PCC, CH ₂ Cl ₂ reflux, 4 h	$O_{0}^{\text{CO}_{2}\text{Me}} O_{0}^{\text{CO}_{2}\text{Me}} O_{0}^{\text{CO}_{2}Me$	202
	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1.5 h	$O = \underbrace{O - \underbrace{O}_{NO_2}}^{O} O $ (64)	677
O- O- Pr-i	PCC, CH ₂ Cl ₂ , rt, 3 h	$\bigvee_{0}^{0} \bigvee_{0}^{-} \bigvee_{0}^{Pr-i} \qquad (83)$	678
OH H H	СгО3•НМРА	(95)	679
CO ₂ Me CH ₂ OH	CrO ₃ •2Pyr	CO ₂ Me OCHO (71)	680
O CH2OH CO2Me	PDC	O ₁ SCHO CO ₂ Me (0)	681
CO ₂ Bu- <i>t</i>	PCC (3.0 eq), 3 Å mol. sieves, CH ₂ Cl ₂ , π	$\bigvee_{0}^{0} \bigvee_{CO_2 Bu-t}^{0} $ (65)	682
MeO ₂ COH	PCC (2.5 eq), CH ₂ Cl ₂ rt, 1 h	MeO ₂ C (83)	683
TBDMSO.	PCC, SiO ₂ , ultrasound	TBDMSO (61)	64
OH TMS OMe	PCC, CH ₂ Cl ₂	OMe (65) TMS OMe	685
OH TIPSO	PCC, CH ₂ Cl ₂ 3 Å mol. sieves	TIPSO (75)	686
CO ₂ Me	CrO ₃ •2Pyr (6.0 cq) CH ₂ Cl ₂ , 20 min	$\sim CHO$ $CO_2Me$ $(92)$	728
ОН	PCC (5.0 eq), CH ₂ Cl ₂ 23°, 1.5 h	· · · · · · · · · · · · · · · · · · ·	801

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

OXIDATIONS	ITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)	
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OXIDATI	ONS WITH OXOCHROMIUM(	VI)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
K S CH-OH	PDC. CH ₃ Cl ₃ . 24 h	(68)	634
OH H CO ₂ Me MeO ₂ C	PCC, CH ₂ Cl ₂ , 20°, 16 h	$ \begin{array}{c} 0 \\ H \\ CO_2Me \end{array} $ (30) $ \begin{array}{c} (30) \\ (30) \end{array} $	648
BnO-CH2OH	DMAPCC. (6.0 eq) CH ₂ Cl ₂ , π, 15 h	BnO CHO (88)	43
H CH ₂ OH N CO ₂ Et	РСС (1.6 еq), СН ₂ Сl ₂ гт, 1 h	(86)	144
F OH	PCC (1.5 eq), CH ₂ Cl ₂ , 8 h	F 0 (92)	251
ОСОСОН	РСС (2.0 еq), NaOAc CH ₂ Cl ₂ . п, 4 h		543
NHCO ₂ Bn CH ₂ OH	$CrO_3 \bullet 2Pyr (10.0 eq)$ $Celite^{(0)}, CH_2Cl_2,$	NIICO ₂ Bn (67)	562
OAc	CrO3•2Pyr (32.0 eq) reflux, 26 h	OAc (41)	654
OH OH	PCC (1.8 eq), CH ₂ Cl ₂ , rt		655
$\bigcup_{O}^{O} CO_2 Me$	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1 h	$ \begin{array}{c} 0 \\ V \\ V \\ O \\ O \\ \end{array} $ $ \begin{array}{c} CO_{2}Me \\ CHO \\ (34) \end{array} $	687
MeO HN N OH	PCC	$ \begin{array}{c}                                     $	688
BzO	PCC (1.5 eq), NaOAc CH ₂ Cl ₂	BzO (58)	689
HO HO	PCC, CH ₂ Cl ₂ , DMSO	(93)	690
	PCC (2.0 eq), CH ₂ Cl ₂ 25°, 6 h	$ \begin{array}{c}         O \\         Ph \\         H \\         H \\         N \\         N \\         O \\         (86)         $	691
OXIDA	TIONS WITH OXOCHROMIUM(	VI)AMINE REAGENTS (Continued)	
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SPh OH	Conditions	Product(s) and Yield(s) (%)	Refs.
	PCC (1.5 eq), CH ₂ Cl ₂ rt. 2 h	(92)	256
O C OH	РСС (1.5 еq), 3 Å mol. sieve CH ₂ Cl ₂ , rt, 1 h		692
MeO O CH ₂ OH	PCC, Celite [®] , CH ₂ Cl ₂ 20°, 2 h	MeO (86) E:Z ~ 4:1 CHO	693
OH H O H OH	PCC		694
O Pr-i	CrO ₃ •2Pyr	O = O = O = O = O $Pr - i = O = O = O$ $()$	695
OH OXO	PCC (1.5 eq), $C_6H_6$ reflux, 3 h		696
	PDC (1.5 eq), DMF, rt, 4 h	O = O = O O O O O O O O O O O O O O O O	697
OH N-Me	PCC	()	698
CH ₂ OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ , 25°	(95)	323
ОН	CrO ₃ •2Pyr, CH ₂ Cl ₂ rt, 10 min	(96)	642
OH O	PCC (1.5 eq), Na ₂ CO ₃ CH ₂ Cl ₂ , 30 min	(85)	570
O OH	РСС (1.7 еq), п, 3 h	0 (75)	699
CH ₂ OH	CrO ₃ •2Pyr	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ $	701
AcO OH OMe	PCC (1.52 eq)	AcO O O Me (73)	702

DATIONS WIT	I OXOCHROMII	IM(VI)AMINE F	<b>REAGENTS</b> (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PCC, NaOAc, CH ₂ Cl ₂		703
	PCC, 3 Å mol. sieves, 3 h		65
Ph CH ₂ OH r-Bu NH O	PDC, DMF	$\begin{array}{c} Ph \\ \hline CO_2H \\ \hline H \\ O \end{array} ()$	378
$\langle CO_2Me$ $GO_2Me$ H $GO_2Me$ H O H	CrO3•2Pyr (8.0 eq) rt, 1 h	$\begin{pmatrix} CO_2Me \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	704
OMc	PCC (2.0 eq), CH ₂ Cl ₂ 24 h	CO ₂ Me (46)	705
OH	PCC		706
MeO CH ₂ OH	PCC (1.5 eq), rt, 1.5 h	MeO CHO (66)	707
CH ₂ OH	PCC, CH ₂ Cl ₂ , 23°	CHO (92)	708
	PCC (1.8 eq), 3 Å mol. sieves, CH ₂ Cl ₂ , π, 30 min		709
O CH ₂ OH	PCC, CH ₂ Cl ₂	O CHO ()	710
MeO MeO Pr- <i>i</i> CH ₂ OH	CrO3•2Pyr (8.0 eq) CH ₂ Cl ₂ , rt, 30 min	MeO MeO Pr- <i>i</i> (83)	711
	PCC (3.0 eq), NaOAc CH ₂ Cl ₂ , 0°, 3 h	CHO (84) O H	712
омом	PCC (1.5 eq), 3 Å mol. sieves. rt. 2.5 h	омом (75)	713

OXIDATIONS	WITH OXO	OCHROMIUM	(VDAMINE	<b>REAGENTS</b> (Continue	d)
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Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
O. H OH H	CrO3•2Pyr, CH2Cl2 rt, 30 min	O $H$ $O$ $(82)$ $H$	714
O OH OHC O	PCC	$ \begin{array}{c} 0 \\ H \\ O \\ O \\ H \\ O \end{array} $ (73)	715
	CrO ₃ •2Руг (10.0 еq) CH ₂ Cl ₂ . гг, 3 h	O CONMe ₂ (63)	342
	DMAPCC (10.0 eq) CH ₂ Cl ₂ , 3 h	O CONMe ₂ (65)	342
MeO ₂ C Me-N CH ₂ OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 0°, 1.5 h	Me - N (-)	717
СН2ОН	PCC (1.53 eq), CH ₂ Cl ₂	(90) CHO	718
i-Pr	PCC (1.3 eq), 4 Å mol. sieves, CH ₂ Cl ₂ , 30°, 1 h	(65)	663
i-Pr. OH	PCC, pyridine	<i>i</i> -Pr. 0 (75)	719
OH Pr- <i>i</i>	PCC, NaOAc, CH ₂ Cl ₂	O Pr- <i>i</i> (72)	720
OH OH	PCC, 22°, 1.5 h	(85)	721
H H OH	CrO3•2Pyr (6.0 еq) CH ₂ Cl ₂ , п, 10 min		722
HOH ₂ C Pr- <i>i</i>	CrO3•2Pyr (6.0 eq) 20 min	OHC , Pr- <i>i</i> (100)	723
i-Pr OH	PCC (1.5 eq), 4 Å mol. sieves, CH ₂ Cl ₂ , 30°, 1 h	i-Pr O (75)	663
H H H	PCC, CH ₂ Cl ₂ 20°, 0.5 h		724

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН	PCC, NaOAc, CH ₂ Cl ₂		725
ОН	PCC, CH ₂ Cl ₂	(86)	726
<i>i-Pr</i> OH	PCC (4.2 eq), 4 Å mol. sieves, CH ₂ Cl ₂ . 0°, 30 min	0 (60)	663
HOH ₂ C H H H	PCC, CH ₂ Cl ₂ , Celite [®] , rt	CHO H O H (57)	262
HQ HQ HQ	PCC, CH ₂ Cl ₂ , rt, 2 h		727
CH ₂ OH	CrO3•2Pyr (8.0 eq) rt, 15 min	CHO (91)	729
O CH ₂ OH	PCC (3.0 eq), CH ₂ Cl ₂ 2 h	О СНО (89)	730
OH OH	PCC (6.0 eq), CH ₂ Cl ₂ rt, 2 h		731
MeO	PCC (2.0 eq), CH ₂ Cl ₂ 25°, 1 h	MeO _m O H O H (92)	732
ОН	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min		733
	CrO3•2Pyr (2.0 eq) 0.5-1 h		734
оорон	PCC (3.0 eq), NaOAc CH ₂ Cl ₂ , 5°-rt, 6 h	о о о о о о о о о о о о о о	735
С С С С С С С С С С С С С С С С С С С	CrO ₃ •2Pyr (4.3 eq) CH ₂ Cl ₂ , 30 min		736

		VI)AMINE REAGEN IS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Kets.
<i>t</i> -BuO ₂ C <i>t</i> -BuO ₂ C	РСС (2.0 еq), CH ₂ Cl ₂ п, 12 h	$r-BuO_2C$ $r-BuO_2C$ $N$ $O$ (81)	738
OAc OTBDMS	PCC (1.5 eq), CH ₂ Cl ₂ rt, 30 min	CHO OAc ON TBDMS	739
Br CH ₂ OH	PCC (1.5 eq), rt, 1 h	$Br \longrightarrow Pr{-i} $ (88)	740
OH OH	PCC		741, 742
i-Pr	PDC (2.1 eq), CH ₂ Cl ₂ 30°, 1 h	i.Pr' (50)	663
HOH ₂ C CH ₂ OH	CrO3•2Pyr (5.0 eq) BaO, 5°, 3 h	OHC CHO (75)	743
r-Bu OH Bu-t	PCC (2.4 eq)	HO Bu- $t$ (85)	103
CH ₂ OH	РСС (3.0 еq), NaOAc 4 Å mol. sieves CH2Cl2. гг, 25 min	CHO (70)	744
H ₂ CH ₂ OH		H, CHO (70)	744
	PCC (2.0 eq), CH ₂ Cl ₂ , 20°		745
MOMO. H OH	PDC (2.0 eq.), DMF, 0°, 3 h	момо. (90)	746
Pr- <i>i</i> CO ₂ Bu- <i>t</i>	PDC, DMF, 0°	$\int_{\text{Pr-}i}^{\text{O}} CO_2 \text{Bu-}i $ (89)	747
NHCO ₂ Bu- <i>t</i>	PDC (3.0 eq), DMF, 10 h	(10)	748

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
ОН	PCC (1.5 eq), NaOAc CH ₂ Cl ₂	CHO (80)	749
∩=∕OH	PCC (1.44 eq), CH ₂ Cl ₂ rt, 2 h	СНО (79)	750
CH ₂ OH	PCC (2.8 eq), NaOAc CH ₂ Cl ₂	CHO (98)	751
TBDMS H H CH ₂ OH	РDC (5.0 еq), DMF п, 15 h	TBDMS $H$ $H$ $CO_2H$ (91) O	752
OH OMe H H OMe O TBDMS	РСС (1.5 eq), NaOAc CH ₂ Cl ₂ , п, 6 h	O OMe H H OMe (63) O TBDMS	826
TBDMSO	PDC (1.5 eq), DMF 25°, 19 h	TBDMSO (94)	819
TMS	PDC (1.5 eq), CH ₂ Cl ₂ rt, 94 h	0 TMS (75)	1038
i-Pr	CrO3•2Pyr (6.0 eq) CH2Cl2, 15 min	<i>i</i> -Pr (91)	348
C ₁₅ OH	PCC (1.5 eq). CH ₂ Cl ₂ 25°, 2.5 h	(46)	772
CH ₂ OH	PCC (3.0 eq), NaOAc 3 Å mol. sieves	CHO (76)	815
Н СНО	СгО ₃ •2Руг, гt. 24 h	H CO ₂ H (61)	700
$H \rightarrow H \rightarrow$	PDC, CH ₂ Cl ₂ , rt. 6 h	$H \rightarrow H \rightarrow$	716
HO	PDC		737
CH ₂ OH	РСС (2.0 еq), п, 1.5 h	CHO (86)	753

Substrate	Conditions	Product(s) and Yield(s) (%)	Pefc
	PCC (2.5 eq), CH ₂ Cl ₂ π, 4 h	О (76)	754
	CrO3•2Pyr (7.6 eq)	CHO O=√O−OBz (−)	755
HO OH	PCC (1.5 eq), Celite [®] rt, 26 h	$ \begin{array}{c} CO_2Ph \\ N \\ O \swarrow & O \\ \end{array} $ (56)	756
	PVPCC, CH ₂ Cl ₂ , rt, 7 d	HO HO HO K K K K K K K K K K K K K K K K	756
OH N H N Mc	PCC	$ \begin{array}{c}                                     $	757
онсон	CrO ₃ •2Pyr (6.0 eq) rt, 15 min	OHC OHC OHC OHC OHC OHC OHC OHC OHC OHC	758
MeO ₂ C	PDC (2.0 eq), CH ₂ Cl ₂ , 7 d	MeO ₂ C (48)	759
O S N CO2Bn CH2OH	РDC (1.2 еq), CH ₂ Cl ₂ п, 36 h.	0, 0 S, N, CO ₂ Bn (98)	760
HO N-CO ₂ Bn	РСС (1.5 еq), CH ₂ Cl ₂ т, 2 h	0 (63)	761
Me N S OH	PCC (2.7 eq), NaOAc 20°, 17 h	S O (42)	762
BH ₃ OH Ph	PCC, CH ₂ Cl ₂	$\begin{array}{c} BH_3 & O \\ Ph - P \\ Ph \end{array} $ (72)	763
BnO HO O	PCC (3.5 eq), C ₆ H ₆ reflux, 1.5 h		135
Ph O OH MeO OMe	PCC (4.0 eq), 40°, 3 h	$\begin{array}{c} Ph & O \\ O \\ MeO \\ O \\$	22
$Ph \xrightarrow{O} OMc$ HO OMe HO OMe	PCC (4.0 eq), CH ₂ Cl ₂ , 40°	Ph O OMe (68)	22
O H H	РСС (2.0 еq). CH ₂ Cl ₂ . п. 5 h		764

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
O H OH	РСС, СН ₂ СІ <u>2</u> , п. 3 h		765
MOMO'	PCC	о	766
CH2OH	PCC	СНО (—)	767
он	PCC, CH ₂ Cl ₂		768
И СОН СОД	PCC (2.1 eq), CH ₂ Cl ₂ 20°, 1.5 h		769
HO Pr- <i>i</i>	РСС (1.5 eq), CH ₂ Cl ₂ п, 2 h	HO Pr- <i>i</i> (40)	770
HO H	PCC		771
Aco	PCC (3.0 eq), DMSO	Ac0 (26)	773
O O CH ₂ OH	РСС (1.5 еq), NaOAc CH ₂ Cl ₂ , rt, 2 h	о сно (64)	774
	CrO ₃ •2Pyr (7.0 eq) CH ₂ Cl ₂ , п, 30 min	TsO (93)	776
ОН	PCC, CH ₂ Cl ₂		777
Cl Br	PCC (2.0 eq). $CH_2Cl_2$	Cl Br' ()	778
CH2OH	DMAPCC (4.5 eq) CH ₂ Cl ₂ , 2 h	CHO (26)	43

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₂ OH	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , rt, 3 h	CHO (89)	779
CH ₂ OH	РDС (1.5 еq), CH ₂ Cl ₂ , 20 h	CHO (67)	780
OH	PCC (1.5 eq), rt, 2 h	(73)	782
A	PCC, CH ₂ Cl ₂		783
ОН	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	" (85)	784
OH	CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , 6 min	(90)	785
CH2OH OMe	PCC (4.0 eq), CH ₂ Cl ₂ 0°, 16 h	CHO () OMe	786
HO Pr CH2OH	PCC (3.0 eq), CH ₂ Cl ₂ rt, 2 h	о <i>i</i> -Pr (79)	787
i-Pr OAc	CrO ₃ •3,5-DMP (6.0 eq) CH ₂ Cl ₂ , 30°, 30 h	$O = \bigcup_{i \in \mathbf{Pr}} (73)$	663
HO Pr-i	PCC (3.0 eq), NaOAc CH ₂ Cl ₂	0 0 Pr- <i>i</i> (91)	788
HOH ₂ C CH ₂ OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ , 6 h	OHC CH ₂ OH CHO ()	789
HOLOTO	РСС (1.5 еq), CH ₂ Cl ₂ п, 24 h		791
ОН	PDC, CH ₂ Cl ₂ , 72 h	<u>о</u> ()	784
OAc H	PDC (3.0 eq), CH ₂ Cl ₂ rt, 10 h	ОАс " (95) Н 20	785
ОН И ИНИ	PCC, NaOAc, CH ₂ Cl ₂ , 1 h		792

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OH OH O H CO ₂ Et	PCC, CH ₂ Cl ₂ . 25°	$ \begin{array}{c} 0 \\ H \\ O \\ CO_2Et \end{array} $ (51)	793
O CH2OH CO2Me	PCC	CHO CO ₂ Me	794
	PCC, CH ₂ Cl ₂ , rt		795
OMe OH CO ₂ Me OMe	PDC	(-)	796
ОН	CrO ₃ •2Pyr	(81)	87
OH	РСС, NaOAc, CH ₂ Cl ₂ 16 h	(51) CHO	797
CH2OH	PDC (1.5 eq), CH2Cl2 rt, 15 h	CHO (60)	798
	CrO,*2Pyr (6.0 сq) CH ₂ Cl ₂ , п, 15 min		8
i-Pr	CrO3•2Pyr (6.0 eq) rt, 15 min	i-Pr (91)	799
HO	РСС (1.3 еq), п, 4 h	(72)	800
OH Pr-i	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , rt, 15 min	$O \xrightarrow{(-)} Pr_{i}$	8
CH ₂ OH	CrO3•2Pyr, CH2Cl2 23°, 8 h	CHO (90)	106
HO	РСС (4.0 eq), CH ₂ Cl ₂ rt, 1.5 h		18
	"	" (6.2)	802

OXIDAT	IONS WITH UXOCHROMIUM	(VI)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
CH2OH CH2OH	PCC (1.71 eq), CH ₂ Cl ₂ rt, 25 min	(72)	780
OH OH	CrO3•2Pyr (6.0 eq) CH2Cl2, rt, 15 min		803
OH CO ₂ Me	CrO ₃ •2Pyr (5.0 cq) rt, 15 min	(82) CO ₂ Me	804
	PCC, Al ₂ O ₃ 3 Å mol. sieves		805
CH ₂ OH CH ₂ OH	PDC (3.6 eq), DMF 20°, 9 h	CO ₂ H (61)	806
OH OH	РСС (6.0 еq), NaOAc CH ₂ Cl ₂ , 11 h		807
OH OH H	CrO3•2Pyr (6.0 eq) CH2Cl2, rt, 15 min	(85)	8
TBDMSO 0=0-UH	PCC, NaOAc, CH ₂ Cl ₂	$\begin{array}{c} \text{TBDMSO} \\ 0 \\ 0 \\ 0 \end{array} \begin{array}{c} 0 \\ 0 \end{array} \begin{array}{c} 0 \\ 0 \end{array} $ (48)	808
CH2OH	PCC (2.0 eq), NaOAc 25°, 2.5 h	CHO (98)	810
i-Pr	CrO ₃ •2Pyr	i-Pr (76)	811
NHCO ₂ Bu-r CH ₂ OH	PDC	NHCO ₂ Bu-r CO ₂ H ()	812
CH ₂ OH	CrO3•2Pyr (6.4 eq), CH2Cl2, rt, 5 h	CHO (85)	813
CH ₂ OH	PCC (1.5 eq), rt, 15 h	CHO ()	813
CH ₂ OH	СгО ₃ •2Руг (8.0 еq) СН ₂ Сl ₂ , гt, 10 min	(61) CHO	814

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
УОН О	PDC, DMF, rt, 24 h		816
HO H H H H H H H H H H H H H H H H H H	CrO3•2Pyr (2.0 eq) CH ₂ Cl ₂ , 5 min		817
$\sum_{i-Pr'}^{CH_2OH} OH$	PCC		818
	PCC (2.0 eq), 3 Å mol. sieves 20°, 8 h		820
CH ₂ OH	PCC (1.33 eq). $CH_2Cl_2$ 0°, 3 h	CHO (75)	821
о п-С ₁₀ Н ₂₁ ОН	PCC (2.5 eq), NaOAc CH ₂ Cl ₂ , rt, 2 h	о n-С ₁₀ Н ₂₁ Сно (98)	822
	PCC	" (99)	823
CH ₂ OH OTBDMS	РDС (1.5 eq), 3 Å mol. sieves CH ₂ Cl ₂ . п. 2 h	CHO OTBDMS (74)	824
TBDMSO	РСС (2.0 еq), NaOAc CH ₂ Cl ₂ , п, 2 h	TBDMSO (82)	825
TBDMSO	PCC (1.5 eq), CH ₂ Cl ₂		827
(n-Bu) ₃ Sn CH ₂ OH	PCC	(n-Bu) ₃ Sn CHO (55)	828
O ₂ N N CO ₂ Bu- <i>t</i> H CH ₂ OH	РСС (1.5 еq), NaOAc CH ₂ Cl ₂ , 2 h	(62)	888
СН2ОН	PCC	()	934
O= O- O- CH2OH	CrO ₃ •2Pyr (6.0 eq) 0°, 2h	$O = \underbrace{\bigcirc}_{O^-} \underbrace{\bigcirc}_{OBz} (48)$	1072
C ₁₆			
OBn CH ₂ OH	PCC (1.5 eq), Celite [®] CH ₂ Cl ₂ , rt, 3 h	OBn (77) CHO	345
	PCC, CH ₂ Cl ₂ , 45°, 3 d	TBDMSO (80) OBn	454

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph NHTs CH ₂ OH	PCC (3.0 eq), CH ₂ Cl ₂ 25°, 3.5 h	Ph NHTs (75) CHO	1054
OH O	PCC (6.8 eq), CH ₂ Cl ₂ , 1 h		775
СН2ОН	PCC, CH ₂ Cl ₂	(87) CHO	781
CO ₂ Me	PCC, NaOAc, 3 Å mol. sieves, CH ₂ Cl ₂	CO ₂ Me ()	790
Br	PDC (4.2 eq), DMF, rt, 3 h	0 Br (74.5)	829
CH ₂ OH	PCC	()	830
OH N CN	PDC (1.1 eq), CH ₂ Cl ₂ 20°, 18 h	(45)	831
O OH O OMe	РСС (2.5 еq), CH ₂ Cl ₂ п, 4 h	O O O H O Me O Me (74)	754
HO HO HO HO	PCC (1.1 eq), rt, 6 h	HO $O$ $OH$ $(-)$ $OH$ $(-)$ $OH$ $(-)$ $OH$ $(-)$	832
Ph CH ₂ OH Ph CH ₂ OH	PCC, CH ₂ Cl ₂	$\begin{array}{c} Ph \\ Ph \\ Ph \end{array} \rightarrow \begin{array}{c} O \\ Ph \\ Ph \end{array} \rightarrow \begin{array}{c} Ph \\ Ph \\ Ph \end{array} \rightarrow \begin{array}{c} O \\ Ph \\ Ph \end{array} (99-100)$	833, 834
но н	PCC (2.0 eq), CH ₂ Cl ₂ rt, 2.5 h		835
PhO-P-O-CH ₂ OH	РСС (1.5 еq), NaOAc CH ₂ Cl ₂ , 3 h	$\begin{array}{c} 0 \\ HO - P \\ O \\ PhO \end{array} (-) \\ PhO \end{array} (-)$	836
OH N Me	PCC (2.3 eq), NaOAc CH ₂ Cl ₂ , 20°, 16 h	(16)	831
BzO CH ₂ OH	PCC (3.0 eq), CH ₂ Cl ₂ rt, 3 h	BzO CHO (50)	837

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	РСС (8.0 еq), CH ₂ Cl ₂ п, 20 h		838
Bn NCH2OH	PDC	Bn N ()	839
EtO ₂ C-N Ph	PCC (1.5 eq), CH ₂ Cl ₂ rt, 3 h	$EtO_2C \xrightarrow{N} \qquad (58)$	455
HO	PCC, CH ₂ Cl ₂ , 25°, 2.5 h	0 H (66)	772
Ts CH ₂ OH	РСС (7.0 еq), Celite [®] CH ₂ Cl ₂ , rt, 1.7 h	Ts CHO (69)	345
BnO OH	CrO ₃ •2Pyr		841
Ŭ	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 2 h	" (30)	842
OH H BnO O	PCC, NaOAc	$BnO \xrightarrow{O}_{O} + O_{O}_{O} + O_{O}_{O} $ (83)	843
OBn HO O O	PDC (5.0 cq), NaOAc rt, 2 h	OBn 0 0 (80)	844
$\bigcup_{CO_2Me}^{OH} C_6H_{11}-c$	PCC, NaOAc	$\bigcup_{\substack{N\\CO_2Me}} O$ (58)	510
CH ₂ OH	PDC (2.0 eq), DMF, 0°, 2 h	CHO (73)	348
осто	PDC (27.0 eq), DMF, π, 4 h	СО ₂ Н 0 (18)	845
OH CH ₂ OPh	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 10 h	O CH ₂ OPh (72)	846
OBn OH	PCC (2.0 cq), CH2Cl2 rt, 1 h	OBn (63)	847
BnO OH	PCC (1.12 eq), NaOAc CH ₂ Cl ₂ , 4 h	BnO O  (46)	849
MeO O O Me	PCC (1.5 eq), 3 Å mol. sieves, DMF	MeO O O O Me	850

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
он он момо	PCC, CH ₂ Cl ₂ , rt. 4 h	MOMO ()	851
HO	CrO ₃ •2Pyr, CH ₂ Cl ₂ , 8°	$HO CO_2Mc$ $HO CHO$ $(91)$	852
Ph CH ₂ OH NHCO ₂ Bu-7	PDC, DMF	Ph CO ₂ H (—) NHCO ₂ Bu-r	378
AcO NHCOMe AcO H H H OH OH	PCC, PDC	$AcO \qquad H \qquad (0)$	854
Ph TMS	CrO ₃ •2Pyr, CH ₂ Cl ₂ 0°, 40 min	Ph (78)	855
PhS OH	РСС (1.5 eq), п, 2 h	PhS (75)	856
СН2ОН	РСС (1.7 еq), СН ₂ Сl ₂ п, 2 h	CHO (97)	848
O OH	СгО ₃ •2Руг (22.0 еq) СН ₂ СІ ₂ . 0°, 6 h		857
H H CH2OH	PDC (3.0 eq), 4 Å mol. sieves, CH ₂ Cl ₂ , 23°, 30 min	CHO (82)	858
S H OH	РСС (2.3 еq), NaOAc CH ₂ Cl ₂ , п, 3 h	(98)	859
OH OH H	CrO ₃ •2Pyr (10.0 eq) CH ₂ Cl ₂ , 16 h	OT OAc H (66)	860
OH OH H	РСС (2.05 еq), NaOAc CH ₂ Cl ₂ , п, 3 h		861
OH OH	PCC, CH ₂ Cl ₂ , 25°	OAc ()	862

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
OEt H O H CH ₂ OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ , rt	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} $	714
CH2OH	PCC (1.5 eq), 20°, 3 h.	(78)	863
CH2OH	PCC (1.5 eq), NaOAc CH ₂ Cl ₂ , rt, 2 h	(86) CHO	864
СН2ОН	PCC, 1 h	(70)	865
$HO \underbrace{C_6H_{11}-c}_{C_6H_{11}-c}OH$	PDC (6.0 eq), 3.5 d	$O \xrightarrow{C_6H_{11}-c} O $	866
HO	РСС (1.7 сq), NaOAc CH ₂ Cl ₂ , rt, 1 h	OTBDMS (100)	867
OMs OH	CrO ₃ •2Pyr, CH ₂ Cl ₂	OMs (92)	870
CH ₂ OH	РСС (1.4 еq), CH ₂ Cl ₂ п, 2 h	(84)	750
СН2ОН	PCC (1.5 cq), NaOAc CH ₂ Cl ₂ , rt	(81) CHO	749
OTBDMS	PDC	OTBDMS (80)	601
OTBDMS HO	PDC (2.0 eq), CH ₂ Cl ₂ 0°, 10 h	OTBDMS O H (97)	871
OTBDMS HO	PDC (1.5 eq), CH ₂ Cl ₂ 0°, 4 h	OTBDMS (98)	871
	PDC (1.5 eq), CH ₂ Cl ₂ rt, overnight		871

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OTBDMS	PCC (2.85 eq), NaOAc CH ₂ Cl ₂ , 45 min	OTBDMS (83)	872
CH ₂ OH	PCC (1.5 eq), CH ₂ Cl ₂ rt, 1.5 h	CHO (88)	873
OH Contraction of the second s	РСС (1.3 eq), CH ₂ Cl ₂ rt, 3 h	0 (83)	874
CH ₂ OH	CrO ₃ •2Pyr (6.6 eq) CH ₂ Cl ₂ , rt, 15 min	CHO (88)	885
r-BuO H	PCC, $CH_2Cl_2$ , $\pi$ , 2 h	r-BuO H	935
SO ₂ Ph HO	CrO3•2Pyr, rt, 4 h	$ \begin{array}{c} SO_2Ph \\ O \\ \end{array} $ (90)	654
CH ₂ OH O	PCC, CH ₂ Cl ₂ , rt	CHO 0 (75)	840
H OHC H CHO	РDС (5.0 eq), DMF, rt, 48 h	(31)	848
C ₁₇			
$EtO_2C$ $NH$ $EtO_2C$ $CO_2Et$	CrO3•2Pyr	$EtO_2C$ $NH$ $CO_2Et$ $CO_2Et$ $(65)$	853
OH CO ₂ Me	PDC, CH ₂ Cl ₂	(90)	869
OH	PDC, CH ₂ Cl ₂	CHO ()	875

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
NC D D OH	PDC (4.4 eq.), DMF, rt, 3 h	NC $D D O $ $(87)$	829
Ph Ph	CrO ₃ •2Pyr (15.0 eq) CH ₂ Cl ₂	Ph (84) Ph	876
	PCC (2.0 eq), CH ₂ Cl ₂ rt, 3 h	(93)	877
CH ₂ OH Ph	CrO ₃ •2Pyr, CH ₂ Cl ₂ rt, 30 min	CHO Ph (87)	878
OH NCO ₂ Bn CO ₂ Me	РСС (1.5 eq), CH ₂ Cl ₂ rt, 1 h	$O = \begin{pmatrix} NCO_2Bn \\ CO_2Me \end{pmatrix}$ ()	879
AcN H OH	РСС (1.0 еq), CH ₂ Cl ₂ rt, 4 h	$AcN \xrightarrow{H}_{H} (77)$	880
$H$ $CH_2OH$ H $OAc$	CrO3•2Pyr (6.0 eq) rt, 20 min	H $CHO$ (97)	882
CO ₂ Me CO ₂ Me	CrO ₃ •2Pyr	CO ₂ Me CO ₂ Me O (92)	771
OH NTs	PCC (1.15 eq) CH ₂ Cl ₂ , rt, 2 h	NTs (97)	883
OH BnO O	PCC (2.0 eq), NaOAc rt, 48 h	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	884
Ac0 OH	PDC, Celite [®] , CH ₂ Cl ₂ 45°, 18 h	Ac0 (75)	17
MeO CH2OH	PCC (1.4 eq), CH ₂ Cl ₂ 20°, 2 h	MeO (86)	886
MeO OMe	PCC. NaOAc. CH ₂ Cl ₂ rt, 7 d	$TsO \xrightarrow{OMe} (45)$	887

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
СН2ОН	PCC (2.0 eq), rt	(90)	238
HO	PCC (2.6 eq), rt. 3 h	OAc (94)	889
	PCC	$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$	890
١	PCC (3.0 eq), 3 Å mol. sieves CH ₂ Cl ₂ , 2.5 h	۱ ۳ (72)	891
	РСС (3.0 еq), CH ₂ Cl ₂ п, 4 h	$\begin{array}{c} \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ $	892
H CH2OH	CrO ₃ •2Руг (6.0 eq) CH ₂ Cl ₂ , п, 7 min	OAc H CHO (83)	722
OF OF	PCC (8.0 eq), NaOAc CH ₂ Cl ₂		894
OH OAc	CrO3•2Pyr (6.0 eq) CH2Cl2. rt, 1 h	$O \rightarrow O \rightarrow$	895
	PCC	H- H- H	896
CH ₂ OH	РСС (2.16 еq), CH ₂ Cl ₂ п, 3 h	$\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ $\downarrow$ CHO (50)	372
ОН	PCC, CH ₂ Cl ₂	(90)	897
r-BuCO ₂ HO r-BuCO ₂ OMe	РСС (3.0 сq), NaOAc 4 Å mol. sieves CH2Cl2, rt, 1 h	$t-BuCO_2$ $t-BuCO_2$ 0 OMe (76)	898

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HO HO <i>i</i> -BuCO ₂ OMe	РСС (2.8 сq.), NaOAc rt, 7 h	$\begin{array}{c} O_2 CBu-t \\ O \\ O \\ t-BuCO_2 \\ O Me \end{array} $ (60)	898
MOMO CH ₂ OH	PCC, CH ₂ Cl ₂	MOMO CHO H (66)	899
CH2OH	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 20°, 15 min.	(79)	900
Pr-i Br	PDC (2.0 eq), DMF 0°, 2 h	Pr- <i>i</i> Br (63)	348
CH ₂ OH	PCC	СНО (72)	902
'	и	" (70)	903
	PCC (1.5 eq), $CH_2Cl_2$ rt, 2 h	" (72)	904
	PCC (2.0 eq), $CH_2Cl_2$ rt, 1 h	" (70)	905
CH ₂ OH	РСС (1.5 еq), п, 1.5 h	CHO (63)	906
	PCC (2.16 eq), NaOAc rt, 1 h	" (57)	907
	PCC (1.48 eq), rt, 1.5 h	" (70)	908
CH ₂ OH CO ₂ Me	PCC	CHO ()	909
O OH	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 18 h	(98)	910
	CrO ₃ •2Pyr (6.0 eq) rt, 15 min		911
O OAc OH OH	РСС (1.45 еq), NaOAc п, 2.5 h	OAc O (81) OH	931
	PDC (7.0 eq), DMF 0°, 6 h	TBDMSO	976

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HOH ₂ C CH ₂ OH	PDC	OHC CHO Ph O Ph ()	298
N H CH2OH	PCC	()	881
MeO	CrO ₃ •2Pyr (12.0 eq)	MeO-()	901
CH ₂ OH	PCC	CHO ()	912
CH ₂ OH OMe	РСС (1.5 еq), CH ₂ Cl ₂ п, 2 h	CHO OMe (85)	913
O OH OH CH ₂ O OH O OH	H PCC	O OH CHO ()	914
PhS OH PhS PhS	РСС (2.0 еq), NaOAc п, 53 h	PhS (67)	915
OMe CH ₂ OH	РСС (2.0 еq), CH ₂ Cl ₂ rt, 1 h	OMe CHO (96) OMe	916
OMe CH ₂ OH	РСС (2.0 еq),СН ₂ Сl ₂ rt, 1 h	OMe CHO (96)	916
MeO-CO2Me	РСС (1.2 еq), CH ₂ Cl ₂ п, 2 h	MeO $O$ (15)	917
MeO NC HO	PCC, CH ₂ Cl ₂	McO NC (65)	918
Unit	"	" (—)	919
HO MeO NO	PCC (1.6 eq), CH ₂ Cl ₂ rt, 3 h	MeO MeO N O N O	920

OXIDATIO	ONS WITH OXOCHROMIUM	(VI)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	PCC (1.34 eq), $CH_2Cl_2$ 0°, 2 h	(90)	922
о тон	CrO _{3*} 2Pyr (10.0 eq) CH ₂ Cl ₂ , rt, 10 min		923
	PDC (3.0 eq), CH ₂ Cl ₂	OMe O O O O O O O O O O O O O O O O O O	924
ОСОН	PCC, NaOAc		925
MeO CH ₂ OH	PDC (1.5 cq), NaOAc	MeO OMe CHO (74)	926
HO	CrO3•2Pyr		927
	РСС (1.8 еq), CH ₂ Cl ₂ rt, 3 h		929
AcO CH ₂ OH AcO O	PCC, NaOAc, CH ₂ Cl ₂	$\begin{array}{c} AcO \\ \hline \\ \hline \\ \hline \\ \\ AcO \end{array} \begin{array}{c} CHO \\ \hline \\ \hline \\ \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	930
CH ₂ OH OBn	РСС (1.5 еq), NaOAc CH ₂ Cl ₂ , rt, 15 h	CHO OBn (80)	932
CH ₂ OH CO ₂ CH ₂ OPh	PCC (1.5 eq), NaOAc rt, 2 h	CHO (98) CO ₂ CH ₂ OPh	933
O OH	РСС, NaOAc, п, 25 h		936
CH ₂ OH	CrO ₃ •2Pyr, CH ₂ Cl ₂	CHO MeO ₂ C (69)	937
-CH ₂ OH OAc	CrO ₃ •2Pyr (10.0 cq) CH ₂ Cl ₂ . 6 min	OAc (87)	784

OXIDATIO	NS WITH OXOCHROMIUM	(VI)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HO OH	BPCC	HO OH ()	938
r-BuO2C	PCC (1.5 eq), rt, 2 h	<i>г</i> -ВиО ₂ С (73)	939
H H CO2Me CH2OH OMOM	CrO3•2Pyr (12.0 eq) CH ₂ Cl ₂ , 0°, 90 min	CO ₂ Me CHO OMOM (78)	940
MeO O H H	PDC, CH ₂ Cl ₂ , 20°, 4 h	MeO O H H (99)	941
CH ₂ OH	CrO3•2Pyr, 1.5 hr	(90) CHO	942
СН2ОН	PDC (2.0 eq), DMF 0°, 2 h	СНО (69)	348
<i>i</i> -Pr	CrO3•2Pyr, 5°, 15 min	i-Pr (97)	945
HO	PCC (2.7 eq), CH ₂ Cl ₂ rt, 3 h	HO, (93)	946
OH OH	PDC, DMF, rt, 4 h	$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$	947
O H CH ₂ OH	PCC, NaOAc, CH ₂ Cl ₂		948
B(Bu-s) ₂	PCC, CH ₂ Cl ₂ , 2 h	СНО (67)	950
CH2OH	PCC	(—)	951

OXIDA	TIONS WITH OXOCHROMIUM	I(V1)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OH H	CrO3•2Pyr, CH2Cl2 20 min	сно (69)	87
MeO ₂ C	CrO3•2Pyr(7.0eq) CH2Cl2, 15 min	MeO ₂ C (100)	893
BnO	PCC (2.0 eq)	BnO (79)	921
СНО	PDC, DMF, n, 4 h	CO ₂ H ()	925
AcO	PCC or PDC, CH ₂ Cl ₂ rt, 22 h	AcO (84)	928
HO-MAN OH	СгО3•2Руг		944
MeO ₂ C	PDC (6.0 eq), CH ₂ Cl ₂ 15 min	MeO ₂ C. (92)	949
Br CH ₂ OH	СгО ₃ •2Руг (6.0 еq) СН ₂ СІ ₂ , 1 h	CHO Br (84)	953
HO N CO ₂ Me	PCC (1.7 eq), NaOAc CH ₂ Cl ₂ , 25°, 1 h	Me CO ₂ Me (76)	954
HO N N	РСС (1.6 еq), NaOAc CH ₂ Cl ₂ , 25°, 1 h	(98)	954
Ph Ph Ph	CrO3•2Pyr (6.0 eq) CH ₂ Cl ₂ , 30 min	Ph Ph Ph Ph (80)	955
CH ₂ OH O	CrO ₃ •2Pyr (8.0 eq) CH ₂ Cl ₂ , 15 min	O O O O O O O O O O O O O O O (86)	956

OXIDATIONS	WITHOXO	CHROMIUM	VDAMINE I	REAGENTS	(Continued)
OVIDATION2	min OAO	CHROMIONI	A DUVINING I	NLAULNIS	(Commueu)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
СНуОН		СНО	
MeO-OMe MeO OMe	РСС (1.5 сq), CH ₂ Cl ₂ rt, 3 h	MeO-OMe (98) MeO OMe	957
CH ₂ OH O NHCOPh MeO	РСС (1.5 eq), NaOAc CH ₂ Cl ₂ , л, 1 h	NHCOPh (70)	958
BnO ₂ C CH ₂ OH BnO ₂ C	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min	BnO ₂ C CHO (69) BnO ₂ C NH (69)	959
MeO ₂ C OH H H NHCOPh	PCC (2.11 cq), CH ₂ Cl ₂ 25°, 1.5 h	$ \begin{array}{ccccccccc}  MeO_2C & O \\  \hline  & & \\  & & \\  & & \\  & H & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  & & \\  &$	961
HO O H OH	CrO ₃ •2Pyr	MeO H OH ()	962
HO HO OH OH OH	CrO3•2Pyr (10.0 eq) CH ₂ Cl ₂ , 1 h	MeO OH (71)	963
Ph CO ₂ H	PCC	Ph CO ₂ H ()	964
ОССОН	CrO ₃ •2Pyr (7.0 cq) 23°, 10 min		965
OH SO ₂ Ph	РСС (2.0 eq), CH ₂ Cl ₂ п, 8 h	(82)	966
HOH ₂ C 0 0	PCC		967
MeO H H H OH	PCC (2.0 eq), CH ₂ Cl ₂	MeO (86)	968
	PCC, NaOAc		969

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Me N OH O N O O Me O CH ₂ OH	PDC (6.65 eq), DMF π, 5 h	$Me \xrightarrow{N}_{O} O \xrightarrow{O}_{He} O \xrightarrow{O}_{O} O $	970
Me NO ₂ OH	PDC (1.1 eq), CH ₂ Cl ₂ rt, overnight	$Mc \qquad O \qquad NO_2 \qquad (83)$	641
но	CrO ₃ •2Pyr (4-6 eq) CH ₂ Cl ₂ , 10 min		971
но	"		971
но	CrO ₃ •2Pyr (8.0 eq) CH ₂ Cl ₂ , 22°, 30 min	0 (81)	972
OH Bu-t OBn	РСС (7.0 еq.), NaOAc п, 5.5 h	O Bu- <i>t</i> (71) OBn	942
	CrO ₃ •2Pyr (7.0 eq) CH ₂ Cl ₂ , 8 h	" (72)	942
HOM	DMAPCC (4.0 eq) CH ₂ Cl ₂ , 6 h	OH (44)	43
HO	DMAPCC (3.0 eq) CH ₂ Cl ₂ , 4 h	0 0 0 (49)	43
MeO ₂ C	PDC (1.5 eq), DMF 25°, 14 h	$MeO_2C$	973
MeO CH ₂ OH	PCC, CH ₂ Cl ₂ , rt	MeO (71) (71)	974
r-BuO AcO OMs	РСС (10.0 eq), CH ₂ Cl ₂ п, 20 h	r-Buo Aco OMs ()	975

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs
CH ₂ OH	PCC (4.0 eq), NaOAc 4 Å mol. sieves CH ₂ Cl ₂ , rt, 1 h	0, , , O, , CHO (65)	744
OTBDMS	PCC, CH ₂ Cl ₂ , rt, 40 min	(87)	977
, , , , , , , , , , , , , , , , , , , ,	PCC (2.5 eq), CH ₂ Cl ₂ rt, 40 min	″ (87) ∎ (9	978
HO N3 H	PCC (2.0 eq), NaOAc rt, 2 h	0 N3 H H (57)	1041
но	CrO3•2Pyr (4-6 eq) CH ₂ Cl ₂ , 10 min		971
r-Bu	PDC (1.0 eq) 3 Å mol. sieves HOAc, CH ₂ Cl ₂	II I-Bu- CHO H (75)	868
OH OH	PCC	(87)	943
HO H CH ₂ OH	PCC (4.64 eq), NaOAc EtOAc, 18 h	HO HH CHO (40)	960
	PCC		979
PhN N N O O OH	CrO ₃ •Pyr(6.0 eq) rt, 45 min	PhN N O O O O O O O O O O O O O (93)	980
O OH OH OH O OH	PCC	О ОН О ОН О ОН (67) ОН О ОН	981

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
но	PDC (3.0 eq.), DMF. 16 h	(88)	982
MeO CH ₂ OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ rt, 1 h	MeO CHO ()	983
OH O CH ₂ OH	CrO3•2Pyr, rt, 1 h	OH O CHO O CHO (26)	984
BnO OH	PCC (1.9 eq), $C_6H_6$ reflux, 5 h	BnO 0 (90) BnO 0	985
MeO CH ₂ OH CO ₂ Me	PCC (1.5 eq), 25°, 7 h	$MeO \qquad (95)$ $MeO \qquad (HO \qquad CO_2Me$	986
HO	PCC, SiO ₂ , CH ₂ Cl ₂ , 6 h		987
BH ₃ OH Ph-P Ph Ph	PCC, CH ₂ Cl ₂	$\begin{array}{c} BH_{3} & O \\ Ph \searrow P \\ Ph \end{array} \begin{array}{c} Ph \end{array} \begin{array}{c} Ph \\ Ph \end{array} \begin{array}{c} Ph \end{array} $ (78)	763
Ph O OH Ph OL MeO ₂ C	PCC (1.5 eq), CH ₂ Cl ₂ , 9 h	$\begin{array}{c} Ph & O \\ Ph & O \\ Ph & O \\ MeO_2C \end{array} $ (67)	988
Ph-OH BnO	PCC (2.5 eq), CH ₂ Cl ₂ , rt	Ph-(77) BnO-(77)	989
CH2OH	PCC, NaOAc, CH ₂ Cl ₂ rt, 30 min	CHO (24)	990
НО СНО	PCC (1.0 eq), CH ₂ Cl ₂ 0-25°, 1 h	СНО (50)	991
TBDPSO	PCC (1.6 eq), CH ₂ Cl ₂ 22-24°, 16 h	TBDPSO CHO (78)	992
O H OH O OBn	СгО ₃ •2Руг (6.0 еq) СН ₂ СІ ₂ , п, 15 min	OBn (94)	8

Substrate	Conditions	Produ	uct(s) and Yield(s) (%)	Refs.
O H O O H O O H	CrO ₃ •2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min		(88)	993
H OH OH	CrO ₃ •2Pyr, CH ₂ Cl ₂ , 15 min		(50)	994
HOH ₂ C H	PCC	OHC' H	= ()	995
HOH ₂ C H	CrO3 <b>•</b> 2Pyr (5.0 eq) CH ₂ Cl ₂ , 3 min	онс' н	(88)	996
HOH ₂ C'H	CrO3•2Pyr (20.0 eq) CH2Cl2, 1 min	OHC'H	()	997
OH O	PCC (2.0 eq), CH ₂ Cl ₂ , rt		, , , ()	998
HO	PCC, NaOAc, CH ₂ Cl ₂ 25°, 25 h		(80)	421
O O H H H CH ₂ OH	PDC (3.0 cq), 4 Å mol. sieves, CH ₂ Cl ₂ , 23°, 0.5 h	O H H H CHO	(80)	858
	CrO ₃ •2Pyr, CH ₂ Cl ₂ 23°, 30 min		(86)	999
H H CO ₂ Me OH	PCC (2.0 cq), CH ₂ Cl ₂ , 2 h	H O O	(90)	1000

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)				
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
OMe O- H	PCC, CH ₂ Cl ₂ , 25°, 2.5 h	$ \underbrace{ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$	(95) 1002	
HOH ₂ C	РСС (4.2 еq), 4 Å mol. sieves, CH ₂ Cl ₂ , п, 30 min	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	1003	
MsN H H H OH OO	CrO3•Pyr, rt, 19 h	$M_{SN} \xrightarrow{H} O_{H} O_{H} O_{H} (68)$	1004	
OH H	PCC, CH ₂ Cl ₂	OHC ** (40)	1005	
ОН	PCC, CH ₂ Cl ₂ , 2 h	(86)	1006	
CH ₂ OH H CH ₂ OH	CrO3•2Pyr, rt, 3 h	O H (59)	1007	
OAc 	PDC, DMF, 25°	OAc CHO ()	1008	
HO O O O O HO O HO O BDMS	PCC (1.5 eq), CH ₂ Cl ₂ rt, 15 min	O O O O H OTBDMS (60)	1009	
CH ₂ OH	PCC (4.0 eq), KOAc rt, 15 min	CHO (52)	1010	
HO HOO OTBDMS	PDC (3.0 eq), DMF, 18 h	OTBDMS OTBDMS H	1011	
MeO ₂ C OTBDMS	PCC	MeO ₂ C OTBDMS (45)	1012	



Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
O OH CO ₂ Me O OH OH	PCC (3.0 eq), $CH_2Cl_2$ $\pi$ , 3 h	$ \begin{array}{c} O & OH \\ \hline O & OH \\ \hline O & OH \\ O & OH \\ \end{array} $ (82)	1022
$O = \bigcup_{H} H + \bigcup_{Ar} CH_2OH$ $Ar = 4 - biphenylyl$	CrO ₃ 2Pyr	$O = \underbrace{\bigcirc}_{H} \underbrace{\bigcirc}_{H} \underbrace{\bigcirc}_{Ar} O = O \qquad (-)$	1023
	14	" (90)	418
$O = \bigvee_{H} \begin{array}{c} CH_2OH \\ - O \\ H \end{array} = O \\ Ar \\ - O \\ Ar = 4-biphenylyl \\ CH_2OH \\ - CH_2$	CrO ₃ •2Pyr (9.0 eq), Celite [®] CH ₂ Cl ₂ , 24 h	$O = \begin{pmatrix} H & CHO \\ N & H & -O \\ H & H & Ar \end{pmatrix} = O $ (99)	1024
	PCC		1025
OMe OMe OH O O	PCC (2.0 eq), CH ₂ Cl ₂	OMe OMe  OMe OMe  O  O  O  O  O  O  O  O  O  O	1026
OMe OH OMe O O	·	$OMe \\ OMe \\ OMe \\ O \\ $	1026
Ph OH Ph	РСС (1.3 еq), NaOAc CH ₂ Cl ₂ , rt, 4 h	Ph O (87) Ph	543
BnO OMe CH ₂ OH OBn	PCC (1.5 eq), NaOAc Celite [®] , CH ₂ Cl ₂ , 2 h	BnO OMe CHO (77) OBn	1027
Ph to OH OH BnO OMe	PCC (4.0 eq), CH ₂ Cl ₂ , 40°	$\begin{array}{c} Ph & O \\ O \\ BnO \\ O \\$	22
CO ₂ Bn HN CO ₂ Bn CO ₂ Bn	PCC (1.5 eq), CH ₂ Cl ₂ , 2.5 h	$ \begin{array}{c} CO_2Bn \\ N \\ CO_2Bn \end{array} $ (46)	581
	PCC	$MeO \qquad CHO \qquad 0 \qquad (68)$ $MeO \qquad Me = N \qquad 0 \qquad (68)$	1028
HOH ₂ C MeO OBn	СгО3•2Руг (4.0 еq) СН ₂ СІ ₂	OHC OF Ph MeO OBn (99)	1029

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph ^{OH}	PCC	$Ph^{S=0}$ (85)	1030
Bn N N Bn	PCC (1.5 eq), 4 Å mol. sieves, rt, 15 h	Bn N Bn (100)	1031
BnO ₂ CHN OH	РСС (10 еq),СН ₂ СІ ₂ rt, 1 h	$ \begin{array}{c} 0 & OH \\ 0 & H \\ 0 & H$	1032
HO HO H H H	PDC, CH ₂ Cl ₂ , 25°, 10 h	MeO (60)	1033
	РСС, CH ₂ Cl ₂ , п, 5 h	H O H OBn (89)	1034
BnO H H CH ₂ OH	PCC (2.0 eq), CH ₂ Cl ₂ rt, 1 h	$ \begin{array}{c} \text{BnQ} & H \\ \text{H} & O \\ \text{H} & O \\ \text{H} & O \\ \text{CHO} \end{array} $ (94)	1034
MeO ₂ C H H H C H C H ₂ O H	CrO3•2Pyr, CH2Cl2 0°, 1 h	(89)	1035
H OBn	CrO3•2Pyr (6.0 eq) CH2Cl2, rt, 15 min	OBn (99)	8
MeO i-Pr	PCC (1.54 eq), CH ₂ Cl ₂ rt, 1.5 h	MeO i-Pr H (78)	1036
MeO i-Pr	PCC (1.6 eq), CH ₂ Cl ₂ rt, 1.5 h	i-Pr $O$ (68)	1036
HO H H H CO ₂ Me	CrO ₃ •2Pyr	H CO ₂ Me (80)	1037
HO H H H CO ₂ Me	··	(61)	1037

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)				
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.	
HO	CrO ₃ •2Pyr (4-6 eq) CH ₂ Cl ₂ , 10 min		971	
CO ₂ Et	РСС	(70)	1039	
O OH OAc	СгО3•2Руг (5.0 еq) СН ₂ Сl ₂ , гt, 6 h	O O O O H O Ac (71)	1040	
MeO ₂ C H OH	PCC (1.7 eq), CH ₂ Cl ₂ , 2 h	$MeO_2C \xrightarrow{H}_{H} O_{CO_2Me} O $ (90)	1000	
но	CrO3•2Pyr (4-6 eq) CH ₂ Cl ₂ , 10 min		971	
HOH ₂ C	РСС (4.0 eq) 4 Å mol. sieves CH ₂ Cl ₂ , rt, 30 min	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ CO_2 \\ Et \end{array} $ (82)	1003	
O O O H CO ₂ Me	РСС (4.7 еq) 4 Å mol. sieves СН ₂ Сl ₂ , г, 1 h	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	1003	
СН2ОН	PCC (1.4 eq). CH ₂ Cl ₂ 3 h	СНО (67)	1043	
HOTEDMS	PCC	O H OTBDMS (91)	1044	
	PCC, CH ₂ Cl ₂	" (91)	1045	
CH ₂ OH OTBDMS	PCC	CHO OTBDMS (79)	771	
OH OMe	PDC (3.0 eq), CH ₂ Cl ₂ rt, 24 h	OMe (100)	1046	



OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)					
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
OH Ph	CrO ₃ •2Pyr	Ph ()	1051		
$O = \bigvee_{\substack{N \\ Bn}}^{Bn} \bigcup_{s} S$	PCC (10 eq), CH ₂ Cl ₂ 1.5 h	$0 = \bigvee_{\substack{N \\ Bn}}^{Bn} \int_{S}^{CHO} S $ (38)	1055		
HO F O	PDC (2.0 eq), DMF 3.2 h	O SCH ₂ Cl O F (74)	1056		
	CrO ₃ •2Pyr, CH ₂ Cl ₂		1057		
PhS OH OH	PCC (1.5 eq), Celite® CH ₂ Cl ₂	PhS OMe (74)	1058		
HOCH ₂ H H H H H	PCC (1.5 eq), CH ₂ Cl ₂ rt, 45 min	H (45)	1059		
	PCC, NaOAc, CH ₂ Cl ₂ , rt		1060		
HO	РСС (1.5 еq), NaOAc CH ₂ Cl ₂ , п, 3 h	0 (45)	1061		
OAc OH	PCC, NaOAc, CH ₂ Cl ₂		1063		
OH OH	PCC	AcO (85)	1064		
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.		
-------------------------------------------------------------------	-----------------------------------------------------------------------------	--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	-------		
	CrO ₃ •2Pyr	other of the other of the other of the other oth	1065		
,	CrO ₃ •2Pyr, rt 15 min	" (—)	1066		
OTs H OH i-Pr' H	PCC (2.0 eq), CH ₂ Cl ₂ rt, 2 h	$ \begin{array}{c}                                     $	1067		
HO	CrO ₃ •2Pyr (4-6 eq) CH ₂ Cl ₂ , 10 min		971		
O OH OH CO ₂ Et	РСС (5.0 eq), 4 Å mol sieves, CH ₂ Cl ₂ , п, 1 h	O $H$ $O$	1003		
HOH ₂ C O HOH ₂ C H	PCC, NaOAc, CH ₂ Cl ₂ , rt		1069		
CH ₂ OH	PCC (2.0 eq), NaOAc CH ₂ Cl ₂ , 4 h	CHO (95)	1070		
CH ₂ OH	CrO3•2Pyr (6.0 eq) rt, 15 min	$C_{15}H_{31}-n$ (84) OH	1071		
THPO OH O	PCC (1.5 eq), NaOAc CH ₂ Cl _{2,} 2 h	THPO O O O	1073		
	CrO ₃ •2Pyr	TBDMSO O H OMs (96)	1074		
OTBDMS C ₅ H ₁₁ -n CH ₂ OH	PCC, CH ₂ Cl ₂	$CHO OTBDMS (85) C_5H_{11}-n$	1075		
HO HO HO	PCC, CH ₂ Cl ₂ 3 h	OHC $(60)$	1076		
TMS HO TMS HO CH ₂ OH	PCC, CH ₂ Cl ₂ 15 h	TMS MeO TMS O TMS O (75)	1077		

## OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

OXIDATIO	NS WITH OXOCHROMIUM(	VI)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{23}$ $MeO$ $CH_2OH$ $CO_2Me$	PCC (2.2 eq), CH ₂ Cl ₂ , 3 h	$MeO \xrightarrow{O} O O O O O O O O O O O O O O O O O O $	1053
	PCC, NaOAc CH ₂ Cl ₂ , 4 h	·· ()	1054
PhO PhO PhO Ph Ph	PDC (1.5 eq), CH ₂ Cl ₂ 30 min	$\begin{array}{c} H & H \\ PhO \\ \hline \\ O \\ \hline \\ O \\ \hline \\ Ph \\ \end{array} \begin{array}{c} H \\ Ph \\ \hline \\ O \\ \hline \\ Ph \end{array} (-)$	1078
AcO CH2OH	PCC	Aco ()	1079
$\begin{array}{c} PhO_2S \\ Bn \\ Bn \\ CH_2OH \end{array}$	PCC (1.5 eq), CH ₂ Cl ₂ 25°, 3 h	$\begin{array}{c} PhO_2S & \\ & N \\ & Bn \end{array} \begin{array}{c} Bn \\ CHO \end{array} $ (75)	1080
$Ar$ $OH$ $OT_{s}$ $Ar = \rho - MeOC_{6}H_{4}$	CrO3•2Pyr, CH2Cl2 rt, 15 min	Ar O OTs (93)	1081
HO BNO O	PCC (2.8 eq), CH ₂ Cl ₂ 20°, 24 h	OBn H O BnO $O$ (90)	1082
Ph ₂ PO	PCC, CH ₂ Cl ₂	Ph ₂ PO (60)	1083
OH OTBDPS	PCC, NaOAc	OTBDPS (92)	1084
OH CO ₂ Me BnO	PCC (1.5 eq), 25°, 2 h	OH CO ₂ Me (95) BnO CHO	1085
HO Ph SO ₂ Ph OTMS	CrO3•2Pyr	O SO ₂ Ph ()	1086
AcO CH ₂ OH	РСС (1.5 eq), NaOAc п, 3 h	AcO CHO (50)	1087

OXIDATIC	ONS WITH OXOCHROMIUM	VI)AMINE REAGENTS (Continued)	
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
HO HO CO ₂ Me MeO ₂ C H	PCC, CH ₂ Cl ₂ , 25°	$MeO_2C$ $MeO_2C$ $H$ $(80)$	1088
HO HO O	РСС. СН ₂ Сl _{2.} п. 3 h	OAc OH OH (83)	1089
O O O CH ₂ OH OBn	PCC (1.5 eq), CH ₂ Cl ₂ rt, 30 min	CHO (100)	1090
CH ₂ OH	CrO3•2Pyr (6.0 eq) CH ₂ Cl ₂ , 15 min	CHO (-)	1091
BnO OTBDMS HO OH	РСС (5 еq), Celite [®] , NaOAc Florisil, CH ₂ Cl ₂ , rt, 1.5 h	$BnO \rightarrow O \rightarrow$	1092
CH ₂ OH OTBDMS C ₂₄	РСС (2.0 еq), NaOAc п, 2.5 h	OTBDMS (94-96)	1093, 1094
HO O HO HO	PCC (3.0 eq), CH ₂ Cl ₂ reflux, 24 h	HO + IO +	809
	PDC (1 eq), CH ₂ Cl ₂ 38°, 5 h		1062
MeO N NO2 BnO _{HO}	PDC (1.5 eq), CH ₂ Cl ₂ 30 h	MeO NO2 BnO O ()	1095
O-OH Ph Ph	РСС (1.5 еq), NaOAc CH ₂ Cl ₂ , п, 2.5 h	Ph Ph (23)	1096
Ph ₃ SnOH	PCC	Ph ₃ Sn ()	1097

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
CH ₂ OH BnO O BnO OAc	PCC	$ \begin{array}{c} CHO\\BnO\\BnO\\OAc \end{array} (-) $	1098
	CrO ₃ •2Pyr (9.0 eq) CH ₂ Cl ₂ , rt, 47 h	момо 0 H 0 (59) момо 0 (59)	1099
Ph o O H	РDC (2.5 eq), CH ₂ Cl ₂ п, 216 h	Ph $O$ $(20)$	1100
O O O O O O O O O O O O O O O O O O O	РСС (1.7 еq), CH ₂ Cl ₂ гт, 1 h		1101
	PCC (60 eq), CH ₂ Cl ₂ 25°, 4 h	H- H- OMe (68)	1102
O O O OMe O CH ₂ OH	PCC, NaOAc	O O O O O O O O O O O O O O O O O O O	1103
OTS OH	PDC, CH ₂ Cl ₂ 4 Å mol. sieves, 25°, 6 h	OTS OMOM (90)	1104
CH ₂ OH SPh	PDC (2.0 eq), DMF 0°, 2 h	CHO SPh (82)	348
СТССОН	РСС		1105
TBDMSO OH	PCC, Celite [®]	TBDMS0, 0 (95)	1048

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

	Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C ₂₅	Ph CH ₂ OH	PCC (2.0 eq), CH ₂ Cl ₂ 2 h	Ph Ph Ph CHO (82)	1106
		РСС	$ \begin{array}{c} OMe & O \\ OH & O \\ OH & O \\ BnO & O \end{array} $ (90)	1107
	Ph Ph CH ₂ OH	PCC (1.16 eq), CH ₂ Cl ₂ rt, 15 min	Ph $OBu-r$ (89) CHO $CHO$	1108
	Aco	PCC (1.52 eq), CH ₂ Cl ₂ rt		1109
	TBDPSO	PCC (3.0 eq) 3 Å mol. sieves	TBDPSO $0$ (89)	1110
	CO ₂ Me OTBDPS CH ₂ OH	PDC (5.0 eq), DMF	$CO_2Me OTBDPS (100)$	1112
	HO. $H$	PCC (1.1 eq), rt, 32 h	$ \begin{array}{c}                                     $	1113
	CH ₂ OH CH ₂ OH CH ₂ OH	PCC, CH ₂ Cl ₂ , rt	CH ₂ OH CHO CHO ()	1114
	HO CO ₂ H	CrO3•2Pyr (6.08 eq) CH2Cl2. 3 h	$CO_2H$ (40)	322
	HO. CO ₂ Me	PCC (1.5 eq), rt, 1 h	0 CO ₂ Me (84)	194
	MeO ₂ C OH	PCC (1.6 eq), 1.5 hr		1116

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
OBn OH	PDC, CH ₂ Cl ₂ 3 Å mol. sieves, 25°	OBn (73)	1104
HQ CO ₂ Me TMSO OH	СтО3•2Руг	CO ₂ Me ()	1117
O CH ₂ OH O OTBDMS	PCC (2.0 eq), CH ₂ Cl ₂ rt, 3 h	O CHO (91)	1118
HOH ₂ C MeO ₂ C AcO AcO AcO OAc	PCC (4.0 eq), NaOAc Celite [®] , rt, 1 h	$ \begin{array}{c}                                     $	1111
O MOMO HO	PCC, CH ₂ Cl ₂	OBn (79) MOMO CHO	1115

OXIDATIONS WITH OXOCHROMIUM(VI)AMINE REAGENTS (Continued)

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## References

- Sisler, H. H.; Bush, J. D.; Accountius, O. E. J. Am. Chem. Soc., 1948, 70, 3827.
- Sisler, H. H.; Ming, W. C. L.; Metter, E.; Hurley, F. R. J. Am. Chem. Soc., 1953, 75, 446.
- 3. Sisler, H. H.; El-Jadir, N.; Busch, D. H. J. Inorg. Nuc. Chem., 1961, **16**, 257.
- Poos, G. I.; Arth, G. E.; Beyler, R. E.; Sarrett, L. H. J. Am. Chem. Soc., 1953, **75**, 422.
- 5. Holum, J. R. J. Org. Chem., 1961, 26, 4814.
- 6. Cornforth, R. H.; Cornforth, J. W.; Popjak, G. Tetrahedron, 1962, **18**, 1351.
- 7. Collins, J. C.; Hess, W. W.; Frank, F. J. Tetrahedron Lett., 1968, 3363.
- 8. Ratcliffe, R.; Rodehorst, R. J. Org. Chem., 1970, **35**, 4000.
- 9. Corey, E. J.; Fleet, G. W. J. Tetrahedron Lett., 1973, 45, 4499.
- Salmond, W. G.; Barta, M. A.; Havens, J. L. J. Org. Chem., 1978, 43, 2057.
- 11. Mancusco, A. J.; Swern, D. Synthesis, 1981, 165.
- 12. Pfitzner, K. E.; Moffatt, J. G. J. Am. Chem. Soc., 1965, 87, 5661.
- 13. Corey, E. J.; Kim, C. U. J. Org. Chem., 1973, 38, 1233.
- 14. Corey, E. J.; Suggs, J. W. Tetrahedron Lett., 1975, 2647.
- 15. Suggs, J. W., Ph. D. Dissertation, Harvard University, 1976, Chapter III.
- 16. Piancatelli, G.; Scettri, A.; D'Auria, M. Synthesis, 1982, 245.
- 17. Majetich, G.; Lowery, D.; Khetoni, V.; Song, J. S.; Hull, K.; Ringold, C. J. Org. Chem., 1991, **56**, 3988.
- 18. Mori, K.; Kato, M. Tetrahedron Lett., 1986, 27, 981.
- 19. Heathcock, C. H.; Mahaim, C.; Schlecht, M. F.; Utawanit, T. J. Org. Chem., 1984, **49**, 3264.
- 20. Corey, E. J.; Ensley, H. E.; Suggs, J. W. J. Org. Chem., 1976, 41, 380.
- 21a. Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*, Springer-Verlag, Berlin, 1984, 167.
- 21b. Freeman, F. Organic Synthesis by Oxidation with Metal Compounds, Mijs, W. J.; DeJonge, C. R. H. I., Eds. Plenum Press, New York; 1986, 41.
- Ley, S. V.; Madin, F. "Oxidation Adacent to Oxygen of Alcohols by Chromium Reagents", in *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I., Eds., Vol. 7, Pergammon, Oxford, 1993, 251.
- 21. Bissember, B. B.; Wightman, R. H. Carbohydr. Res., 1980, 81, 187.

- 22. Wada, E.; Okawara, M.; Nakai, T. J. Org. Chem., 1979, 44, 2952.
- Brown, H.; Kulkarni, S. U.; Rao, C. G.; Patil, V. D. Tetrahedron, 1986, 42, 5515.
- 24. Bonadies, F.; DiFabio, R.; Bonini, C. J. Org. Chem., 1984, 49, 1647.
- Wender, P. A.; Eissenstat, M. A.; Filosa, M. D. J. Am. Chem. Soc., 1979, 101, 2196.
- 26. Rangarajan, R.; Eisenbraun, E. J. J. Org. Chem., 1985, 50, 2435.
- 27. Rathore, R.; Saxena, N.; Chandrasekaran, S. Synth. Commun., 1986, 16, 1493.
- Aizpurua, J. M.; Juaristi, M.; Lecea, B.; Palomo, C. Tetrahedron, 1985, 41, 2903.
- 29. Rollin, P.; Sinay, P. Carbohydr. Res., 1981, 98, 139.
- 30. Piancatelli, G.; Scettri, A.; D'Auria, M. Tetrahedron, 1980, 36, 661.
- 31. Antonioletti, R.; D'Auria, M.; DeMico, A.; Piancatelli, G.; Scettri, A. Synthesis, 1984, 280.
- 32. Maloney, J. R.; Lyle, R. E.; Saavedra, J. E.; Lyle, G. Synthesis, 1978, 212.
- 33. Drabowics, J. Synthesis, 1980, 125.
- 34. Corey, E. J.; Schmidt, G. Tetrahedron Lett., 1979, 399.
- Liotta, D.; Brown, D.; Hoekstra, W.; Monahan, R. Tetrahedron Lett., 1987, 28, 1069.
- 36. Muzart, J.; N'ait Aijou, A. J. Mol. Catal., 1991, 66, 151.
- 37. Corey, E. J.; Schmidt, G. Tetrahedron Lett., 1980, 21, 731.
- 38. Chidambaram, N.; Chandrasekaran, S. J. Org. Chem., 1987, 52, 5048.
- Chidambaram, N.; Bhat, S.; Chandrasekaran, S. J. Org. Chem., 1992, 57, 5013.
- 40. Andersson, F.; Samuelsson, B. Carbohydr. Res., 1984, **129**, C1–C3.
- 41. Guziec, F. S., Jr.; Luzzio, F. A. Synthesis, 1980, 691.
- 42. Guziec, F. S., Jr.; Luzzio, F. A. J. Org. Chem., 1982, 47, 1787.
- 43. Davis, H. B.; Sheets, R. M.; Brannfors, J. M.; Paudler, W. W.; Gard, G. L. Heterocycles, 1983, **20**, 2029.
- 44. Davis, H. B.; Sheets, R. M.; Paudler, W. W.; Gard, G. L. Heterocycles, 1984, **22**, 2029.
- 45. Rao, C. S.; Deshmukh, A. A.; Thakor, M. R.; Srinivasan, P. S. Indian J. Chem., 1986, **25**, 324.
- 46. Santaniello, E.; Milani, F.; Casati, R. Synthesis, 1983, 749.
- 47. Acharya, S. P.; Rane, R. A. Synthesis, 1990, 127.
- 48. Corey, E. J.; Mehrotra, M. M. Tetrahedron Lett., 1985, 26, 2411.
- 49. Luzzio, F. A., Ph. D. Dissertation, Tufts University, 1982.

- 50. Akamanchi, K. G.; Iyer, L. G.; Meenakshi, R. Synth. Commun., 1991, **21**, 419.
- 51. Balasubramanian, K.; Prathiba, V. Indian J. Chem., 1986, 25B, 326.
- 52. Cossio, F. P.; Lopez, M. C.; Palomo, C. Tetrahedron, 1987, 43, 3963.
- 53. Santaniello, E.; Ferraboschi, P. Synth. Commun., 1980, 10, 75.
- 54. Firouzabadi, H.; Sardavian, A.; Gharibi, H. Synth. Commun., 1984, **14**, 89.
- 55. Kim, S.; Lhim, D. C. Bull. Chem. Soc. Jpn., 1986, 59, 3297.
- Chakraborty, T. K.; Chandrasekaran, S. Tetrahedron Lett., 1980, 21, 1583.
- 57. Bhattacharjee, M. N.; Chaudhuri, M. K.; Dasgupta, H. S.; Roy, N. Synthesis, 1982, 588.
- 58. Muzart, J. New J. Chem., 1989, 13, 9.
- 59. Cainelli, G.; Cardillo, G.; Orena, M.; Sandri, S. J. Am. Chem. Soc., 1976, 98, 6737.
- 60. Frechet, J. M. J.; Warnock, J.; Farrall, M. J. J. Org. Chem., 1978, **43**, 2618.
- Binns, F.; Hayes, R.; Ingham, S.; Saengchantara, Celite S. T.; Turner, R. W.; Wallace, T. W. Tetrahedron, 1992, 48, 515.
- 62. Corey, E. J.; Tramontano, A. J. Am. Chem. Soc., 1984, 106, 463.
- 63. Adams, L. L.; Luzzio, F. A. J. Org. Chem., 1989, 54, 5387.
- 64. Herscovici, J.; Antonakis, K. J. Chem Soc., Chem. Commun., 1980, 561.
- Choudary, B. M.; Prasad, A. D.; Swapna, V.; Valli, V. L. K.; Bhuma, V. Tetrahedron, 1992, 48, 953.
- 66. Parish, E. J.; Scott, A. D. J. Org. Chem., 1983, 48, 4766.
- 67. Corey, E. J.; Samuelsson, B. J. Org. Chem., 1984, 49, 4735.
- 68. O'Connor, B.; Just, G. Tetrahedron Lett., 1987, 28, 3235.
- Holloway, F.; Cohen, M.; Westheimer, F. H. J. Am. Chem. Soc., 1951, 73, 65.
- 70. Panigrahi, G. P.; Magapatro, D. D. Bull. Soc. Chim. Belg., 1981, 90, 927.
- 71. Banerji, K. K. J. Chem. Res. (M) 1978, 2561.
- 72. Dey, D.; Mahanti, M. K. J. Org. Chem., 1990, 55, 5848.
- 73. Banerji, K. K. J. Chem. Soc., Perkin Trans. 2, 1978, 639.
- 74. Bhattacharjee, M. N.; Chaudhuri, M. K.; Dasgupta, H. S. Bull. Chem. Soc. Jpn., 1984, **57**, 258.
- 75. Banerji, K. K. J. Org. Chem., 1988, 53, 2154.
- 76. Brown, H. C.; Rao, C. G.; Kulkarni, S. U. J. Org. Chem., 1979, 44, 2809.
- 77. Piers, E.; Worster, P. M. Can. J. Chem., 1977, 55, 733.
- 78. Hudlicky, M. Oxidation in Organic Chemistry, American Chemical

Society, Washington, D. C., 1990, 138.

- 79. Kwart, H.; Francis, P. S. J. Am. Chem. Soc., 1959, 81, 2116.
- 80. Peng, T. Y.; Rocek, J. J. Am. Chem. Soc., 1976, 98, 1026.
- Wiberg, K. B. Oxidation in Organic Chemistry; Academic Press, New York, 1965, Part A, 69.
- 82. Corey, E. J.; Boger, D. Tetrahedron Lett., 1978, 28, 2461.
- 83. Corey, E. J.; Ensley, H. E. J. Am. Chem. Soc., 1975, 97, 6908.
- 84. Babler, J. H.; Coghlan, M. J. Synth. Commun., 1976, 6, 469.
- 85. Dauben, W. G.; Michno, D. M. J. Org. Chem., 1977, 42, 682.
- 86. Sundararaman, P.; Herz, W. J. Org. Chem., 1977, 42, 813.
- Majetich, G.; Condon, S.; Hull, K.; Ahmad, S. Tetrahedron Lett., 1989, 30, 1033.
- 88. Luzzio, F. A.; Moore, W. J. J. Org. Chem., 1993, 58, 2966.
- 89. Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. J. Am. Chem. Soc., 1977, **99**, 3120.
- 90. Schlecht, M. F.; Kim, H.-J. Tetrahedron Lett., 1986, 27, 4889.
- 91. Walba, D. M.; Stoudt, G. S. Tetrahedron Lett., 1982, 23, 727.
- 92. Schlecht, M. F.; Kim, H.-J. J. Org. Chem., 1989, 54, 583.
- 93. Schlecht, M. F.; Kim, H.-J. Tetrahedron Lett., 1985, 26, 127.
- 94. Luzzio, F. A.; Guziec, F. S., Jr. Org. Prep. Proced. Int., 1988, 20, 533.
- 95. Muzart, J. Synthesis, 1993, 11.
- Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley-Interscience, New York, 1979, 7, 309.
- 97. Herscovici, J.; Egron, M.-J.; Antonakis, K. J. Chem Soc., Perkin Trans. 1, 1982, 1967.
- 98. Garegg, P. J.; Samuelsson, B. Carbohydr. Res., 1978, 67, 267.
- 99. Mancusco, A. J.; Huang, S.-L.; Swern, D. J. Org. Chem., 1978, **43**, 2480.
- 100. Moffatt, J. G. *Oxidation*, Augustine, R.; Trecker, D. J. Eds., Vol. **2**, Marcel Dekker, New York, 1.
- 101. Dess, D. B.; Martin, J. C. J. Org. Chem., 1983, 48, 4156.
- 102. Wolf, S.; Agosta, W. C. Can. J. Chem., 1984, 62, 2429.
- 103. Waddell, T. G.; Carter, A. D.; Miller, T. J.; Pagni, R. M. J. Org. Chem., 1992, 57, 381.
- 104. Walba, D. M.; Haltiwanger, R. C.; Wand, M. D.; Wilkes, M. C. Tetrahedron, 1981, **37**, 1663.
- 105. Corey, E. J.; Ha, D. C. Tetrahedron Lett., 1988, 29, 3171.
- 106. McDonald, F. E.; Towne, T. B. J. Am. Chem. Soc., 1994, **116**, 7921.

- 107. Fatiadi, A. J. Synthesis, 1976, 65.
- 108. Dauben, W. G.; Lorber, M.; Fullerton, D. S. J. Org. Chem., 1969, **34**, 3587.
- 109. Krysan, D. J.; Haight, A. R.; Lallaman, J. E.; Langridge, D. C.; Menzia, J. A.; Narayanan, B. A.; Pariza, R. J.; Reno, D. S.; Rockway, T. W.; Stuk, T. L.; Tien, J. H. Org. Prep. Proced. Int., 1993, **25**, 437.
- 110. Dess, D. B.; Martin, J. C. J. Am. Chem. Soc., 1991, **113**, 7277.
- 111. Marshall, J. A.; Bartley, G. S. J. Org. Chem., 1994, 59, 7169.
- 112. Marshall, J. A.; Beaudoin, S. J. Org. Chem., 1994, 59, 6614.
- 113. McWilliams, J. C.; Clardy, J. J. Am. Chem. Soc., 1994, 116, 8378.
- 114. DeVoss, J. J.; Hangeland, J. J.; Townsend, C. A. J. Org. Chem., 1994, **59**, 2715.
- 115. Spino, C.; Liu, G.; Tu, N.; Girard, S. J. Org. Chem., 1994, **59**, 5596.
- 116. Roush, W. R.; Wada, C. J. Am. Chem. Soc., 1994, **116**, 2151.
- 117. Shair, M. D.; Yoon, T.; Danishefsky, S. J. J. Org. Chem., 1994, 59, 3755.
- 118. Linderman, R. J.; Jamois, E. A.; Tennyson, S. D. J. Org. Chem., 1994, **59**, 957.
- 119. Kigoshi, H.; Ojika, M.; Ishigaki, T.; Suenaga, K.; Mutou, T.; Sakakura, A.; Ogawa, T.; Yamada, K. J. Am. Chem. Soc., 1994, **116**, 7443.
- 120. Kusmich, D.; Wu, S. C.; Ha, D.-C.; Lee, C.-S.; Ramesh, S.; Atarashi, S.; Choi, J.-K.; Hart, D. J. J. Am. Chem. Soc., 1994, **116**, 6943.
- 121. Fieser, M.; *Reagents for Organic Synthesis*; Wiley-Interscience, New York, 1994; **17**, 271.
- 122. Muzart, J. Chem. Rev., 1992, 92, 113.
- 123. Muzart, J. Tetrahedron Lett., 1987, 28, 2133.
- 124. Kanemoto, S.; Oshima, K.; Matsubara, S.; Takai, K.; Nozaki, H. Tetrahedron Lett., 1983, **24**, 3185.
- 125. Corey, E. J.; Barrette, E.-P.; Magriotis, P. A. Tetrahedron Lett., 1985, **26**, 5855.
- 126. Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. J. Chem Soc., Chem. Commun., 1987, 1625.
- 127. Griffith, W. P.; Ley, S. V. Aldrichimica Acta, 1990, 23, 13.
- 128. Wetterhahn, K. E.; Cupo, D. Y. Cancer. Res., 1985, 45, 1146.
- 129. *Prudent Practices for Disposal of Chemicals from Laboratories*; National Academy Press, Washington, D. C., 1983, 83.
- 130. Ratcliffe, R. W. *Organic Synthesis*; John Wiley and Sons, New York, 1976, **55**, 84.
- 131. Singh, R. P.; Subba Rao, H. N.; Dev, S. Tetrahedron, 1979, **35**, 1789.
- 132. Huang, X.; Chan, C.-C. Synthesis, 1982, 1091.

- 133. Bohlmann, F.; Rotard, W. Liebigs Ann. Chem., 1982, 1216.
- 134. Hollenberg, D. H.; Klein, R. S.; Fox, J. J. Carbohydr. Res., 1978, **67**, 491.
- 135. Wilen, S. H.; Shen, D.; Licata, J. M.; Baldwin, E.; Russell, C. S Heterocycles 1984, 22, 1747.
- 136. Cheng, Y. S.; Liu, W. L.; Chen, S. Synthesis, 1980, 223.
- 137. LaLonde, R. T.; Perakyla, H.; Hayes, M. P. J. Org. Chem., 1990, **55**, 2847.
- 138. Baraldi, R. G.; Simoni, D.; Moroder, F.; Manfredini, S.; Mucchi., ; Vecchia, F. D.; Orsolini, P. J. Heterocycl. Chem., 1982, **19**, 557.
- 139. Schneider, M. P.; Goldbach, M. J. Am. Chem. Soc., 1980, 102, 6114.
- 140. Coates, R. M.; Hutchins, C. W. J. Org. Chem., 1979, 44, 4742.
- 141. Joshi, H. H.; Mamdapur, V.; Chadha, M. S. J. Chem Soc., Perkin Trans. 1, 1979, 2346.
- 142. Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. J. Org. Chem., 1987, **52**, 3708.
- 143. Witiak, D. T.; Tomita, K.; Patch, R. J.; Enna, S. J. J. Med. Chem., 1981, **24**, 788.
- 144. Garst, M. E.; Bonfiglio, J. M.; Grudoski, D. A.; Marks, J. J. Org. Chem., 1980, **45**, 2307.
- 145. Cane, D. E.; Iyengar, R.; Shiao, M. S. J. Am. Chem. Soc., 1981, **103**, 914.
- 146. Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. J. Org. Chem., 1986, **51**, 432.
- 147. Subramanian, C. S.; Thomas, P. J.; Mamdapur, V. R.; Chadha, M. S. J. Chem Soc., Perkin Trans. 1, 1979, 2346.
- 148. Schroeder, C.; Wolf, S.; Agosta, W. C. J. Am. Chem. Soc., 1987, **109**, 5491.
- 149. Wu, P. L.; Wang, S. W. J. Org. Chem., 1994, 59, 622.
- 150. Schüll, V.; Hopf, H. Tetrahedron Lett., 1981, 22, 3439.
- 151. Hart, D. J.; Yang, T. K. J. Org. Chem., 1985, 50, 235.
- 152. Szekeres, D. P.; Deleris, G.; Picard, J. P.; Pillot, J. P.; Calas, R. Tetrahedron Lett., 1980, **71**, 4267.
- 153. Wilt, J.; Aznavoorian, P. M. J. Org. Chem., 1978, 43, 1285.
- 154. Rosini, G.; Ballini, R. Synthesis, 1983, 543.
- 155. Brown, H. C.; Bhat, K. S.; Randal, R. S. J. Org. Chem., 1989, 54, 1570.
- 156. Stetter, H.; Leinen, H. T. Chem. Ber., 1983, 116, 254.
- 157. Hine, J.; Green, L. R.; Meng, P. C.; Thiagarajan, V. J. Org. Chem., 1976, 41, 3343.

- 158. Wirth D.; Fischer-Lui, I.; Boland, Icheln, D.; Runge, T.; König, W. A.; Phillips, J.; Clayton, M. Helv. Chim. Acta., 1992, **75**, 734.
- 159. Spurlock, L. A.; Fayter, R. G. Jr. J. Am. Chem. Soc., 1972, 94, 2707.
- 160. Dappen, M. S.; Pelliciari, R.; Natalini, B.; Monahan, J. B.; Chiorri, C.; Cordi, A. A. J. Med. Chem., 1991, **34**, 161.
- Bischofberger, N.; Waldmann, H.; Saito, T.; Simon, E. S.; Lees, W.; Bednarski, M. D.; Whitesides, G. M. J. Org. Chem., 1988, 53, 3457.
- 162. Schwarz, W.; Trautman, W.; Musso, H. Chem. Ber., 1981, 114, 990.
- 163. Bourgeois, M. J.; Maillard, B.; Montaudon, E. Tetrahedron, 1986, **42**, 5309.
- 164. Haslegrave, J. A.; Jones, J. B. J. Am. Chem. Soc., 1982, 104, 4666.
- 165. Nair, V.; Jahnke, T. S. Tetrahedron, 1987, 4257.
- 166. Lee, J. J.; Dewick, P. M.; Gorst-Allman, C. P.; Spreafico, F.; Kowal, C.; Chang, C.; McInnes, A. G.; Walter, J. A.; Keller, P. J.; Floss, H. G. J. Am. Chem. Soc., 1987, **109**, 5426.
- 167. Corey, E. J.; Shirahama, H.; Yamamoto, H.; Terashima, S.; Venkatswarlu, A.; Schaaf, T. K. J. Chem. Soc., 1971, 93, 1490.
- 168. Herdewijn, P.; Claes, P. J.; Vanderhaeghe, H. J. Med. Chem., 1986, **29**, 661.
- 169. Huckstep, M.; Taylor, R. K.; Caton, M. P. Synthesis, 1982, 881.
- 170. Ferraboschi, P.; Canevotti, R.; Grisenti, P.; Santoniello, E. J. Chem Soc., Perkin Trans. 1, 1987, 2301.
- 171. Carballeira, N.; Thompson, J. E.; Ayanoglu, E.; Djerassi, C. J. Org. Chem., 1986, **51**, 2751.
- 172. Crow, W. D.; Osawa, T.; Platz, K. M.; Sutherland, D. S. Aust. J. Chem., 1976, **29**, 2525.
- 173. Desrut, M.; Kergomard, A.; Renard, M. F.; Veschambre, H. Tetrahedron, 1981, **37**, 3825.
- 174. Jensen, U.; Schafer, H. J. Chem. Ber., 1981, 114, 292.
- 175. Jung, M. E.; Gaede, B. Tetrahedron, 1979, 35, 621.
- 176. Trigo, G. G.; Munoz, E. M.; Hurtado, E. L. J. Heterocycl. Chem., 1984, **21**, 1479.
- 177. Wu, T. C.; Mareda, J.; Gupta, Y. M.; Houk, K. N. J. Am. Chem. Soc., 1983, **105**, 6996.
- 178. Bravo, P.; Resnati, G.; Viani, F. Gazz. Chim. Ital., 1987, 117, 747.
- 179. Kirmse, W.; Prolingheuer, E. C. Chem. Ber., 1980, 113, 104.
- 180. Goering, H. L.; Kantner, S. S.; Seitz, E. P., Jr. J. Org. Chem., 1985, **50**, 5495.
- 181. Prugh, J. D.; Hartman, G. D.; Mallorga, P. F.; McKeever, B. M.; Michelson, S. R.; Murcko, M. A.; Schwam, H.; Smith, R. L.; Sodney, J.

M.; Springer, J. P.; Sugrue, M. F. J. Med. Chem., 1991, 34, 1805.

- 182. Acheson, R. M.; Lee, G. C. M. J. Chem Soc., Perkin Trans. 1, 1987, 2321.
- 183. Ardakani, M. A.; Smalley, R. K.; Smith, R. H. J. Chem Soc., Perkin Trans. 1, 1983, 2501.
- 184. Kieslich, W.; Kurreck, H. J. Am. Chem. Soc., 1984, 106, 4328.
- 185. Banwell, M. G. J. Chem Soc., Chem. Commun., 1982, 847.
- 186. Looker, J. H.; Cliffton, M. D. J. Heterocycl. Chem., 1986, 23, 225.
- 187. Sampath, V.; Schore, N. J. Org. Chem., 1983, 48, 4882.
- 188. Schippers, P. H.; Van der Ploeg, J. P. M.; Dekkers, H. P. M.; J. Am. Chem. Soc., 1983, **105**, 84.
- 189. Yadav, J. S.; Patil, D. G.; Krishna, R. R.; Chawla, H.; Dev, S. Tetrahedron, 1982, 38, 1003.
- 190. Oberhauser, T.; Bodenteich, M.; Faber, K.; Penn, G.; Griengl, H. Tetrahedron, 1987, **43**, 3931.
- 191. Burke, S. D.; Magnin, D. R.; Oplinger, J. A.; Baker, J. P.; Abdelmagid, A. Tetrahedron Lett., 1984, 25, 19.
- 192. Greene, A. E.; Deprés, J. P.; Meana, M. C.; Crabbé, P. Tetrahedron Lett., 1976, **41**, 3755.
- 193. Deprés, J. P.; Greene, A. E.; Crabbé, P. Tetrahedron, 1981, 37, 621.
- 194. Luef, W.; Vogeli, U. C.; Keese, R. Helv. Chim. Acta, 1983, 66, 2729.
- 195. Camenzind, H.; Krebs, E. P.; Keese, R. Helv. Chim. Acta, 1982, 2042.
- 196. Matsuo, T.; Mori, K.; Matsui, M. Tetrahedron Lett., 1976, 23, 1979.
- 197. DeVos, M. J.; Krief, A. Tetrahedron Lett., 1979, 21, 1891.
- 198. Shea, K. J.; Burke, L. D. J. Org. Chem., 1988, **53**, 318.
- 199. Matlin, A. K.; Wolff, S.; Agosta, W. C. Tetrahedron Lett., 1983, 24, 2961.
- 200. Oare, D. A.; Henderson, M. A.; Sanner, M. A.; Heathcock, C. H. J. Org. Chem., 1990, 55, 132.
- 201. Barrett, A. G. M.; Carr, R. A. E.; Attwood, S. V.; Richardson, G.; Walshe, N. D. A. J. Org. Chem., 1986, **51**, 4840.
- 202. Oppolzer, W.; Siles, S.; Snowden, R. L.; Bakker, B. H.; Petrzilka, M. Tetrahedron, 1985, **41**, 3497.
- 203. Boland, W.; Jaenicke, L. Chem. Ber., 1977, 110, 1823.
- 204. Kermse, W.; Streu, J. J. Org. Chem., 1985, 50, 4187.
- 205. Kakushima, M.; Allain, L.; Dickinson, R. R.; White, D. S.; Valenta, Z. Can. J. Chem., 1979, **57**, 3354.
- 206. Larcheveque, M.; Debal, A. Synth. Commun., 1980, 10, 49.
- 207. Jones, T. H.; Franko, J. B.; Blum, M. S.; Fales, H. M. Tetrahedron Lett., 1980, **21**, 789.

- 208. Vig, O. P.; Sharma, M. L.; Gauba, R. Indian J. Chem., 1985, 24B, 313.
- 209. Thompson, W. J.; Buhr, C. A.; J. Org. Chem., 1983, 48, 2769.
- 210. Birnbaum, J. E.; Cervoni, P.; Chan, P.; Chen, S. L.; Floyd, M. B.; Grudzinskas, C. V.; Weiss, M. J. Dessy, F.; J. Med. Chem., 1982, 25, 492.
- 211. Sum, F. W.; Weiler, L. J. Org. Chem., 1979, 44, 1012.
- 212. Lord, M. D.; Negri, J. T.; Paquette, L. A. J. Org. Chem., 1995, 60, 191.
- 213. Takemura, T.; Jones, J. B. J. Org. Chem., 1983, 48, 791.
- 214. Ogawa, T.; Takasaka, N.; Matsui, M. Carbohydr. Res., 1978, 60, C4.
- 215. Hanessian, S.; Demailly, G.; Chapleur, Y.; Leger, S. J. Chem Soc., Chem. Commun., 1981, 1125.
- 216. Bosone, E.; Farina, P.; Guazzi, G.; Innocenti S.; Marrotta, V. Synthesis, 1983, 942.
- 217. DeLaszlo, S. E.; Williard, P. G. J. Am. Chem. Soc., 1985, 107, 199.
- 218. Overman, L. E.; LeSuisse, D.; Hashimoto, M. J. Am. Chem. Soc., 1983, 105, 5373.
- 219. Bates, H. A.; Farina, J.; Tong, M. J. Org. Chem., 1986, **51**, 2637.
- 220. Tsuzuki, K.; Nakajima, Y.; Watanabe, T. Tetrahedron Lett., 1978, **11**, 989.
- 221. Botteghi, C.; Soccolini, F. Synthesis, 1985, 592.
- 222. Klein, L. L. Synth. Commun., 1986, 16, 431.
- 223. Meyers, A. I.; Lawson, J. P.; Walker, D. G.; Linderman, R. J. J. Org. Chem., 1986, **51**, 5111.
- 224. Bulat, J. A.; Liu, H. J. Can. J. Chem., 1976, 54, 3869.
- 225. Joshi, N. N.; Mamdapur, V. R.; Chadha, M. S. Indian J. Chem., 1984, **23B**, 577.
- 226. Mori, K.; Ikunaka, M. Tetrahedron, 1987, 43, 45.
- 227. Just, G.; Potvin, P.; Hakimelahi, G. H. Can. J. Chem., 1980, 58, 2780.
- 228. Kirmse, W.; Loosen, K.; Prolingheuer, E. C. Chem. Ber., 1980, 113, 129.
- 229. Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. J. Org. Chem., 1980, 45, 1066.
- 230. Schaefer, T.; Penner, G. H.; Wildman, T. A.; Peeling, J. Can. J. Chem., 1985, **63**, 2256.
- 231. Phillips, B. T.; Hartman, G. D. J. Heterocycl. Chem., 1986, 23, 897.
- 232. Meinwald, J.; Putzig, D. E. J. Org. Chem., 1970, 35, 1891.
- 233. Johnson, W. M. P.; Holan, G. Aust. J. Chem, 1981, 34, 2355.
- 234. Mata, E. G.; Setti, E. L., Mascaretti, O. A.; Boggio, S. B.; Roveri, O. A. J. Chem Soc., Perkin Trans. 1, 1988, 1551.
- 235. Echter, T.; Meier, H. Chem. Ber., 1985, **118**, 182.

- 236. Pirillo, D.; Gazzaniga, A.; Traverso, G. J. Chem. Res., 1983, O133.
- 237. Boland, W.; Jaenicke, L. J. Org. Chem., 1979, 44, 4819.
- 238. Gilbert, J. C.; Smith, K. R. J. Org. Chem., 1976, 41, 3883.
- 239. Nakazaki, M.; Naemura, K.; Kondo, Y. J. Org. Chem., 1976, 41, 1229.
- Davis, D. P.; Borchardt, R. T.; Grunewald, G. L. J. Med. Chem., 1981, 24, 12.
- 241. Nakazaki, M.; Naemura, K.; Kondo, Y. J. Org. Chem., 1979, 44, 16.
- 242. Lightner, D. A.; Gawronski, J. K.; Bouman, T. D. J. Am. Chem. Soc., 1980, **102**, 5749.
- 243. Pfoertner, K. H.; Zell, R. Helv. Chim. Acta, 1980, 63, 645.
- 244. Macco, A. A.; deBrouwer, R. J.; Buck, H. M. J. Org. Chem., 1977, **42**, 3196.
- 245. Macco, A. A.; Driessen-Engels, J. M. G.; Pennings M. L. M.; deHaan, J. W.; Buck, H. M. J. Chem Soc., Chem. Commun., 1978, 1103.
- 246. Adam, W.; Bakker, B. H.; Tetrahedron Lett., 1979, 43, 4171.
- 247. Corey, E. J.; Snider, B. B. J. Org. Chem., 1974, 39, 256.
- 248. Furneaux, R. H.; Gainsford, G. J.; Shafizadeh, F.; Stevenson, T. T. Carbohydr. Res., 1986, **146**, 113.
- 249. Malacria, M.; Roumestant, M. L. Tetrahedron, 1977, 33, 2813.
- 250. Nijhuis, W.; Verbrom, W.; El-Fadl, A.; Harkema, S.; Renhoudt, D. M. J. Org. Chem., 1989, **54**, 199.
- 251. Wender, P. A.; Hilleman, G. L.; Szymonifka, M. J. Tetrahedron Lett., 1980, **21**, 2205.
- 252. Simons, S. S. Jr.; J. Am. Chem. Soc., 1974, 96, 6492.
- 253. Lease, T. G.; Shea, K. J.; J. Am. Chem. Soc., 1993, **115**, 2248.
- 254. Zaidleweicz, M. Synthesis, 1988, 701.
- 255. Block, E.; Wall, A. J. Org. Chem., 1987, 52, 809.
- 256. Takeuchi, K.; Kitagawa, I.; Akiyama, F.; Shibata, T.; Kato, M.; Okamoto, K. Synthesis, 1987, 613.
- 257. Kirmse, W.; Streu, J. Synthesis, 1983, 994.
- 258. Pyne, S. G.; Bloem, P.; Chapman, S. L.; Dixon, C. E.; Griffith, R. J. Org. Chem., 1990, **55**, 1086.
- 259. Danishefsky, S.; Funk, R. L.; Kerwin, J. F. Jr. J. Am. Chem. Soc., 1980, 102, 6889.
- 260. Roberts, M. R.; Parsons, W. H.; Schlessinger, R. H. J. Org. Chem., 1978, **43**, 3970.
- 261. Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stowe, K. Tetrahedron, 1981, **37**, 4371.
- 262. Sevrin, M.; Hevesi, L.; Krief, A. Tetrahedron Lett., 1976, 43, 3915.

- 263. Devos, M. J.; Denis, J. M.; Krief, A. Tetrahedron Lett., 1978, 21, 1847.
- 264. Jakovac, I. J.; Goodbrand, H. B.; Lok, K. P.; Jones, J. B. J. Am. Chem. Soc., 1982, **104**, 4659.
- 265. Soucy, P.; Ho, T. L.; Deslongchamps, P. Can. J. Chem., 1972, 50, 2048.
- 266. Lee, J.; Snyder, J. K. J. Org. Chem., 1990, 55, 4995.
- 267. Hirsch, J. A.; True, V. C. J. Org. Chem., 1986, 51, 2218.
- 268. Corey, E. J.; Park, H.; Barton, A.; Nii, Y. Tetrahedron Lett., 1980, **21**, 4243.
- 269. Corey, E. J.; Albright, J. O.; Barton, A. E.; Hashimoto, S. J. Am. Chem. Soc., 1980, **102**, 1436.
- 270. Gagnieu, G.; Grouiller, A. Carbohydr. Res., 1980, 84, 61.
- 271. Hicks, D. R.; Fraser-Reid, B. J. Chem Soc., Chem. Commun., 1976, 869.
- 272. Norlander, J. E.; Owor, P. O.; Cabral, D. J.; Haky, J. E. J. Am. Chem. Soc., 1982, **104**, 201.
- 273. Parry, R. J.; Trainor, D. A. J. Am. Chem. Soc., 1978, 100, 5244.
- 274. Brimacombe, J. S.; Rahman, K. J. Chem Soc., Perkin Trans. 1, 1985, 1073.
- 275. Anderson, R. J. J. Am. Chem. Soc., 1970, 92, 4978.
- 276. Walchii, P. C. Eugster, C. H. Helv. Chim. Acta, 1978, 61, 885.
- 277. Jones, T. H.; Blum, M. S.; Fales, H. M. Tetrahedron Lett., 1979, **12**, 1031.
- 278. Ashby, E. C.; Argyropoulos, J. M. J. Org. Chem., 1985, 50, 3274.
- 279. Ashby, E. C.; Deshpande, A. K. J. Org. Chem., 1994, 59, 3798.
- 280. Dollinger, M.; Henning, W.; Kirmse, W. Chem. Ber., 1982, 115, 2309.
- 281. Piers, E.; Wong, T.; Ellis, K. A. Can. J. Chem., 1992, 70, 2058.
- 282. Barton, D. H. R.; Boivin, J. Gastiger, M.; Morzycki, J.; Hay-Motherwell, R. S.; Motherwell, W. B.; Ozbalik, N.; Scwartzentruber, K. M. J. Chem Soc., Perkin Trans. 1, 1986, 947.
- 283. Vincek, W. C.; Aldrich, C. S.; Borchardt, R. T.; Grunewald, G. L. J. Med. Chem., 1981, **24**, 7.
- 284. Jones, J. B.; Takemura, T. Can. J. Chem., 1982, 60, 2950.
- 285. Epstein, R.; LeGoff, N. Tetrahedron Lett., 1981, 22, 1965.
- 286. Corey, E. J.; Enders, D. Tetrahedron Lett., 1976, 1, 11.
- 287. Kachinsky, J. L. C.; Salomon, R. G. J. Org. Chem., 1986, 51, 1393.
- 288. Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Spitzer, W. A. J. Am. Chem. Soc., 1970, **92**, 1786.
- 289. Meniczyki, R.; Malanga, C.; Lordicci, L.; Peconioso, A. J. Chem. Res., 1983, 124.

- 290. Bell, T. W.; Cheng, P. G.; Newcomb, M.; Cram, D. J. J. Am. Chem. Soc., 1982, **104**, 5185.
- 291. Trost, B. M.; Verhoeven, T. R. J. Am. Chem. Soc., 1980, 102, 4743.
- 292. Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. Tetrahedron, 1984, **40**, 2239.
- 293. Hayashi, H.; Nakanishi, K.; Brandon, C.; Marmur, J. J. Am. Chem. Soc., 1973, **95**, 8749
- 294. Bal, S. A.; Marfat, A.; Helquist, P. J. Org. Chem., 1982, 47, 5045.
- 295. Kozluk, T., Cottier, L.; Descotes, G. Tetrahedron, 1981, 37, 1875.
- 296. Maskill, H. J. Chem Soc., Perkin Trans. 1, 1987, 1739.
- 297. Christopfel, W. C.; Miller, L. L. J. Org. Chem., 1986, 51, 4169.
- 298. Salaun, J.; Fadel, A.; Conia, J. M. Tetrahedron Lett., 1979, 16, 1429.
- 299. Brimacombe, J. S.; Rahman, K. M. M.; J. Chem Soc., Perkin Trans. 1, 1985, 1067.
- 300. Monneret, C.; Conveur, C.; Huu, Q. K. Carbohydr. Res., 1978, 65, 35.
- 301. Trost, B. M.; Lautens, M. J. Am. Chem. Soc., 1987, 109, 1469.
- 302. Brosch, D.; Kirmse, W. J. Org. Chem., 1993, 58, 1118.
- 303. Parry, R. J.; Rao, H. S. P.; Mueller, J. J. Am. Chem. Soc., 1982, 104, 339.
- 304. Casey, C. P.; Cyr, C. R. J. Am. Chem. Soc., 1973, 95, 2240.
- 305. Heathcock, C. H.; Lampe, J. J. Org. Chem., 1983, 48, 4330.
- 306. Wilson, S. R.; Zucker, P. A. J. Org. Chem., 1988, 53, 4682.
- 307. Barner, R.; Schmid, M. Helv. Chim. Acta, 1979, 62, 2384.
- 308. Lowe, J. D.; Turnbull, K. J. Heterocycl. Chem., 1986, 23, 125.
- 309. Ziegler, F. E.; Fowler, K. W.; Sinha, N. D. Tetrahedron Lett., 1978, 2767.
- 310. Berens, G.; Kaplan, F.; Rimerman, R.; Roberts, B. W.; Wissner, A. J. Am. Chem. Soc., 1975, **97**, 7076.
- 311. Newman-Evans, R. H.; Simon, R. J.; Carpenter, B. K. J. Org. Chem, 1990, **55**, 695.
- 312. Coates, R. M.; Kirkpatrick, J. C. J. Am. Chem. Soc., 1970, 92, 4883.
- 313. Bradbury, R. H.; Gilchrist, T. L.; Reese, C. W. J. Chem Soc., Perkin Trans. 1, 1981, 3234.
- 314. Cooke, M. P. Jr.; Widener, R. K. J. Org. Chem, 1987, **52**, 1381.
- 315. Baker, R.; Sims, R. J. J. Chem Soc., Perkin Trans. 1, 1981, 3087.
- 316. Biethan, H.; Fauth, W.; Musso, H. Chem. Ber., 1977, **110**, 3636.
- 317. Schaefer, T.; Penner, G. H.; Davie, K. J.; Sebastian, R. Can. J. Chem., 1985, **63**, 777.
- 318. Callant, P.; Storme, P.; Van der Eycken, E.; Vandewalle, M. Tetrahedron Lett., 1983, **24**, 5797.

- 319. Ryono, D. E.; Loudon, G. M. J. Am. Chem. Soc., 1976, 98, 1889.
- 320. Durrant, G.; Green, R. H.; Lambeth, P. F.; Lester, M. G.; Taylor, N. R. J. Chem Soc., Perkin Trans. 1, 1983, 2211.
- 321. Schwartz, S.; Weber, G.; Depner, J.; Schaumann, J.; Schick, H.; Welzel, H. P. Tetrahedron, 1982, 38, 1261.
- 322. Brinkmeyer, R. S. Tetrahedron Lett., 1979, 3, 207.
- 323. Shea, K. J.; Wise, S. Tetrahedron Lett., 1979, 12, 1011.
- 324. Shea, K. J.; Wise, S.; Burke, L. D.; Davis, P. D.; Gilman, J. W.; Greely, A. C. J. Am. Chem. Soc., 1982, **104**, 5708.
- 325. Paul, G. C., Gajewski, J. J. J. Org. Chem., 1992, 57, 1970.
- 326. Sato, T.; Gotoh, Y.; Watanabe, M.; Fujisawa, T. Chem. Lett., 1983, 1533.
- 327. Harding, K. E.; Strickland, J. B.; Pommerville, J. J. Org. Chem, 1988, 53, 4877.
- 328. Dauben, W. G.; Kellogg, M. S. J. Am. Chem. Soc., 1980, **102**, 4456.
- 329. Detty, M. R.; Paquette, L. A. J. Am. Chem. Soc., 1977, 99, 821.
- 330. Kraus, G. A.; Frazier, K. J. Org. Chem, 1980, 45, 2579.
- 331. Bruzknor, C.; Reissig, H. Liebig. Ann. Chem., 1988, 465.
- 332. Salaun, J.; Almirantis, Y. Tetrahedron, 1983, 2421.
- 333. Tamura, V.; Annoura, H.; Kondo, H.; Fuji, M.; Yoshida, T.; Fujioka, H. Chem. Pharm. Bull., 1987, **35**, 2305.
- 334. Isobe, M.; Iio, H.; Kawai, T.; Goto, T. Tetrahedron Lett., 1977, 8, 703.
- 335. lio, H.; Isobe, M.; Kawai, T.; Goto, T. Tetrahedron, 1979, 35, 941.
- 336. Mori, K.; Watanabe, H.; Yanagi, K.; Minobe, M. Tetrahedron, 1985, **41**, 3663.
- 337. Fraser-Reid, B.; Walker, D. L.; Tam, S. Y.-K., Holden, N. L. Can. J. Chem., 1973, **51**, 3950.
- 338. Weidman, H.; Rauter, A. P. Liebigs Ann. Chem., 1982, 2231.
- 339. Just, G.; Reader, G.; Chaland-Faure, B. Can. J. Chem., 1976, 54, 849.
- 340. Lightner, D. A.; Crist, B. V. Tetrahedron, 1985, 41, 3021.
- 341. Jakubowski, A. A.; Guziec, F. S.; Sugiura, M.; Tam, C. C.; Tshler, M.; Omura, S. J. Org. Chem, 1982, 47, 1221.
- 342. Boekman, R. K. Jr.; Thomas, E. W. J. Am. Chem. Soc., 1977, 99, 2806.
- 343. Boekman, R. K. Jr.; Thomas, E. W. J. Am. Chem. Soc., 1978, 101, 987.
- 344. Kurth, M. J.; O'Brien, M. J.; Hope, H.; Yanuck, M. J. Org. Chem, 1985, **50**, 2626.
- 345. Oppolzer, W.; Snowden, R. L. Helv. Chim. Acta., 1981, 64, 2592.
- Naf-Muller, R.; Pickerhagen, W.; Willhalm, B. Helv. Chim. Acta, 1981, 64, 1424.

- 347. Parker, K. A.; Iqbal, T. J. Org. Chem, 1987, 52, 4369.
- 348. Crandall, J. K.; Rambo, E. J. Org. Chem, 1990, 55, 5929.
- 349. Gassman, P. G.; Williams, E. A.; Williams, F. J. J. Am. Chem. Soc., 1971, **93**, 5199.
- 350. Wiberg, K. B.; Nakahira, T. J. Am. Chem. Soc., 1971, 93, 5193.
- 351. Shea, K. J.; Greely, A. C.; Nguyen, S.; Beauchamp, P. D.; Aue, D. H., Witzeman, J. S. J. Am. Chem. Soc., 1986, **108**, 5901.
- 352. Taber, D. F.; Amedio, J. C. Jr.; Raman, K. J. Org. Chem, 1988, **53**, 2984.
- 353. Deslongchamps, P.; Lamothe, S.; Lin, H. S. Can. J. Chem., 1984, **62**, 2395.
- 354. Xu, Y.; Roughton, A. L.; Plante, R.; Goldstein, S.; Deslongchamps, P. Can. J. Chem., 1993, **71**, 1152.
- 355. Lightner, D. A.; Gawronski, J. K.; Bouman, T. D. J. Am. Chem. Soc., 1980, **102**, 1983.
- 356. Smith, A. B.; Thompson, A. S. J. Org. Chem, 1984, 49, 1469.
- 357. Cane, D. E.; Thomas, P. J. J. Am. Chem. Soc., 1984, 106, 5295.
- 358. Gillard, F.; Heissler, D.; Riehl, J. J. J. Chem Soc., Perkin Trans. 1, 1988, 2291.
- 359. Mori, K.; Uematzu, T.; Watanabe, H.; Yanagi, K.; Minobe, M. Tetrahedron Lett., 1984, **25**, 3875.
- 360. Mori, K.; Uematzu, T.; Yanagi, K.; Minobe, M. Tetrahedron, 1985, **41**, 2751.
- 361. Brimacombe, J. S.; Hanna, R.; Tucker, L. Carbohydr. Res., 1985, **136**, 419.
- 362. Heathcock, C. H.; Von Geldern, T. W. Heterocycles, 1987, 25, 75.
- 363. Nachman, R.; Honel, M. Williams, T. M.; Halaskz, R. C.; Mosher, H. S. J. Org. Chem, 1986, **51**, 4802.
- 364. Johnson, W. S.; Chen, Y. Q.; Kellogg, M. S. J. Am. Chem. Soc., 1983, 105, 6653.
- 365. Little, R. D.; Carsoll, G. L.; Peterson, J. L. J. Am. Chem. Soc., 1983, 105, 928.
- 366. Sucrow, W.; Minas, H.; Stegemeyer, H.; Geschwinder, P.; Marawski, H. R.; Kruger, C. Chem. Ber., 1985, **118**, 3332.
- 367. Spencer, R. W.; Tam, T.; Thomas, E.; Robinson, V. J.; Krantz, A. J. Am. Chem. Soc., 1986, **108**, 5589.
- 368. Kaloustian, S. A.; Agosta, W. C. J. Org. Chem, 1981, 46, 4880.
- 369. Corey, E. J.; Yamamoto, H.; Herron, D. K.; Achiwa, K. J. Am. Chem. Soc., 1970, 92, 6635.
- 370. Kato, M.; Kageyama, M. Tonaka, R.; Kuwahara, K.; Yoshikoshi, A. J.

Org. Chem, 1975, 40, 1932.

- 371. Vig, O. P.; Sharma, M. L.; Nanda, R., Puri, S. K. Indian J. Chem., 1985, **24B**, 247.
- 372. Tsutsui, H.; Mitsunobu, O. Tetrahedron Lett., 1984, 25, 2159.
- 373. Pianetti, P.; Pougny, J. J. Carbohydr. Chem., 1988, 7, 811.
- 374. Roush, W. R.; Myers, A. G. J. Org. Chem, 1981, 46, 1511.
- 375. Jarosz, S.; Fraser-Reid, B. Tetrahedron Lett., 1981, 2533.
- 376. Berti, G.; Canedoli, S.; Crotti, P.; Macchia, F. J. Chem Soc., Perkin Trans. 1, 1984, 1183.
- 377. Alcón, M.; Canas, M.; Poch, M.; Moyano, A.; Perics, M. A.; Riera, A. Tetrahedron Lett., 1994, **35**, 1589.
- 378. DeGraw, J. I.; Rodin, J. O. J. Org. Chem., 1971, 36, 2902.
- 379. Lambert, J. B.; Salvador, L. A.; Stern, C. L. J. Org. Chem., 1993, **58**, 5428.
- Redlich, H.; Xiang, J.; Paulsen, H.; Francke, W. Tetrahedron Lett., 1981, 22, 5043.
- 381. Payard, M.; Couquelet, J. Synthesis, 1979, 889.
- 382. Pearson, J. R.; Porter, Q. N. Aust. J. Chem., 1991, 44, 1085.
- 383. Paquette, L. A.; Dunkin, I. R. J. Am. Chem. Soc., 1973, 95, 3067.
- 384. DeShong, P.; Dicken, C. M.; Staib, R. R.; Freyer, A. J.; Weinreb, S. M. J. Org. Chem., 1982, 47, 4397.
- 385. Semmelhack, M. F.; Zask, A. J. Am. Chem. Soc., 1983, 105, 2034.
- 386. Franz, J. A.; Alnajjar, M. S.; Barrows, R. D.; Kaisaki, D. L.; Camaioni, D. M.; Suleman, N. K. J. Org. Chem., 1986, **51**, 1446.
- 387. Baldwin, J. E.; Patapoff, T. W.; Burden, T. C. J. Am. Chem. Soc., 1984, 106, 1421.
- 388. Armstrong, R. J.; Brown, R. F. C.; Eastwood, F. W.; Romyn, M. E. Aust. J. Chem., 1979, **32**, 1767.
- 389. Zelechonok, Y.; Silverman, R. B. J. Org. Chem., 1992, 57, 1785.
- 390. Bijoy, P.; Subba Rao, G. S. R. Synth. Commun., 1993, 23, 2701.
- 391. Saengchantara, S. T.; Wallace, T. W. J. Chem Soc., Chem. Commun., 1986, 1592.
- 392. Oda, M.; Oikawa, H. Tetrahedron Lett., 1980, 21, 107.
- 393. Barrero, A. F.; Oltra, J. E.; Herrador, M. M.; Cabrera, E.; Sanchez, J. F.; Quílez, J. F.; Rojas, F. J.; Reyes, J. F. Tetrahedron 1993, 49, 141.
- 394. McCombie, S. W.; Metz, W. A. Tetrahedron Lett., 1987, 28, 383.
- 395. Finkelstein, J.; Holden, K. G.; Perchonock, C. D. Tetrahedron Lett., 1978, **19**, 1629.
- 396. Barreiro, E. J.; Costa, P. R.; Regina, P.; Borros, V. R.; Queiroz, W. M. J.

Chem. Res., 1982, 5, 102.

- 397. Chang, C. P.; Hsu, L. F.; Chang, N. C. J. Org. Chem., 1994, **59**, 1898.
- 398. Oda, M.; Oda, M.; Kitahara, Y. Tetrahedron Lett., 1976, 11, 839.
- 399. Muzart, J.; Riahi, A.; Pete, J. P. J. Organomet. Chem., 1985, 280, 269.
- 400. Paul, V. J.; McConnell, O. J.; Fenical, W. J. Org. Chem., 1980, 45, 3401.
- 401. Nordlander, J. E.; Haky, J. E. J. Org. Chem., 1980, 45, 4780.
- 402. Paquette, L. A.; McCreadie, T. J. Org. Chem., 1971, 36, 1402.
- 403. Wilder, P. Jr.; Portis, A. R. Jr.; Wright, G. W.; Shepherd, J. M. J. Org. Chem., 1974, **39**, 1636.
- 404. Grayson, J. I.; Warren, S. J. Chem Soc., Perkin Trans. 1, 1977, 2263.
- 405. Chenevert, R.; Thiboutot, S. Can. J. Chem., 1986, 64, 1599.
- 406. Amyes, T. L.; Jencks, W. P. J. Am. Chem. Soc., 1988, **110**, 3677.
- 407. Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L.; Smith, J.; Stauffer, R. J. Am. Chem. Soc., 1981, **103**, 6460.
- 408. Zhang, Q.; Mohan, R. M.; Cook, L.; Kasanis, S.; Peisach, D.; Foxman,
  B. M.; Snider, B. B. J. Org. Chem., 1993, 58, 7640.
- 409. Tokuda, M.; Satoh, S.; Suginome, H. J. Org. Chem., 1989, 54, 5608.
- 410. Crabbé, P.; Garcia, G. A.; Rius, C. J. Chem. Soc., Perkin Trans. 1, 1973, 811.
- 411. Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. J. Am. Chem. Soc., 1987, **109**, 3991.
- 412. Casas, R.; Ortuño, R. M. Tetrahedron Asym., 1992, 3, 1205.
- 413. Primeau, J. L.; Anderson, R. C.; Fraser-Reid, B. J. Am. Chem. Soc., 1983, **105**, 5874.
- 414. Gaoni, Y.; Tomazic, A.; Potgieter, E. J. Org. Chem., 1985, 50, 2943.
- 415. Witiak, D. T.; Kamat, P. L.; Allison, D. L. Liebowitz, S. M.; Glaser, R.; Holliday, J. E.; Moeschberger, M. L.; Schaller, J. P. J. Med. Chem., 1983, 26, 1679.
- 416. Corey, E. J.; Wein shenker, H. M.; Schaaf, T. K.; Huber, W. J. Am. Chem. Soc., 1969, **91**, 5671.
- 417. Caton, M. P. L. Tetrahedron, 1979, 35, 2705.
- 418. Chapdelaine, M. J.; Warwick, P. J.; Shaw, A. J. Org. Chem., 1989, **54**, 1218.
- 419. Ognyanov, V. I.; Datcheva, V. K.; Kyler, K. S. J. Am. Chem. Soc., 1991, **113**, 6992.
- 420. Deutsch, E. A.; Snider, B. B. Tetrahedron Lett., 1983, 24, 3701.
- 421. Fish, R. H.; Browne, L. E.; Wood, D. L.; Hendry, L. B. Tetrahedron Lett., 1979, **17**, 1465.
- 422. Bal, S. A.; Helquist, P. Tetrahedron Lett., 1981, 22, 3933.

- 423. Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. J. Am. Chem. Soc., 1986, **108**, 3385.
- 424. Boland, W.; Jaenicke, L.; Maller, D. G. Liebigs Ann. Chem., 1981, 2266.
- 425. Sarburg, H.; Mondon, A. Chem. Ber., 1981, 114, 118.
- 426. Maas, D. D.; Blagg, M.; Wiemer, D. F. J. Org. Chem., 1984, 49, 853.
- 427. Sethi, S. C.; Natu, A. D.; Wadia, M. S. Indian J. Chem., 1986, 25B, 248.
- 428. Roush, W. R.; Peseckis, S. M. J. Am. Chem. Soc., 1981, 103, 6696.
- 429. Oppolzer, W.; Snowden, R. L.; Briner, P. H. Helv. Chim. Acta, 1981, **64**, 2022.
- 430. Dauben, W. G.; Michno, D. M. J. Am. Chem. Soc., 1981, 103, 2284.
- 431. Marshall, J. A.; Greene, A. E. J. Org. Chem., 1971, 36, 2035.
- 432. Darby, N.; Lamb, M.; Money, T. Can. J. Chem., 1979, **57**, 742.
- 433. Spurlock, L. A.; Clark, K. P. J. Am. Chem. Soc., 1972, 94, 5349.
- 434. Sasaki, T.; Eguchi, S.; Ban, H. J. Org. Chem., 1983, 48, 4073.
- 435. Liu, H. J.; Chan, W. H. Can. J. Chem., 1982, 60, 1081.
- 436. Guillerm, D.; Boussac, G.; Lalande, J.; Lemaitre, P.; Lallemand, J. Y. Synth. Commun., 1981, **11**, 627.
- 437. Takacs, J. M.; Myoung, Y. C. Tetrahedron Lett., 1992, 33, 317.
- 438. Allen, M. S.; Darby, N.; Salisbury, P.; Sigurdson, E. R.; Money, T. Can. J. Chem., 1979, **47**, 733.
- 439. Carceller, E.; Garcia, M. L.; Moyano, A.; Serratosa, F. J. Chem Soc., Chem. Commun., 1984, 825.
- 440. Smith, A. B.; Malamas, M. S. J. Org. Chem., 1982, 47, 3442.
- 441. Asami, M. Tetrahedron Lett., 1985, 26, 5803.
- 442. Marshall, J. A.; Ellison, R. H. J. Org. Chem., 1975, 40, 2070.
- 443. Mori, K. Tetrahedron, 1978, 34, 915.
- 444. Mori, K.; Sasaki, M. Tetrahedron Lett., 1979, 15, 1329.
- 445. Mori, K.; Sasaki, M. Tetrahedron, 1980, 36, 2197.
- 446. Nubbemeyer, U. Synthesis, 1993, 1120.
- 447. Ganter, C.; Moser, J. F. Helv. Chim. Acta, 1971, 54, 2229.
- 448. Ishihara, J.; Tomita, K.; Tadano, K.; Ogawa, S. J. Org. Chem., 1992, **57**, 3789.
- 449. Lightner, D. A.; Crist, B. V.; Kalyanam, H.; May, L. M.; Jackman, D. E. J. Org. Chem., 1985, **50**, 3867.
- 450. Unger, F. M.; Stix, D.; Moderndorfer, E.; Hammerschmid, F. Carbohydr. Res., 1978, **67**, 349.
- 451. Tsuji, J.; Mandai, T. Tetrahedron Lett., 1978, 21, 1817.
- 452. Kefurt, K.; Kefurtora, Z. Jary, J. Coll. Czech. Chem. Commun., 1988, 53,

1795.

- 453. Steiner, O.; Tamm, C. Tetrahedron Lett., 1993, 34, 6729.
- 454. Krow, G. R.; Shaw, D. A.; Szczepanski, S.; Ramjit, H. Synth. Commun., 1984, **14**, 429.
- 455. Feiring, A. E.; Ciabattoni, J. J. Org. Chem., 1972, 37, 3784.
- 456. Wender, P. A.; Filosa, M. P. J. Org. Chem., 1976, 41, 3490.
- 457. Larock, R. C.; Oertle, K. Porter, G. F. J. Am. Chem. Soc., 1980, **102**, 190.
- 458. Meinwald, J.; Jones, T. H. J. Am. Chem. Soc., 1978, **100**, 1883.
- 459. Guella, G. Carazza, M.; Guerriero, A.; Pietra, F. Helv. Chim. Acta, 1984, 67, 1248.
- 460. Oppolzer, W.; Snowden, R. L.; Simmons, D. P. Helv. Chim. Acta, 1981, 64, 2002.
- 461. Bierl-Leonhardt, B. A.; Moreno, D. S.; Schwarz, M.; Fargerlund, J.; Plimmer, J. R. Tetrahedron Lett., 1981, **22**, 389.
- 462. Taylor, M. D.; Minaskanian, G.; Wimzarberg, K. H.; Santone, D.; Smith,A. B. J. Org. Chem., 1982, 47, 3960.
- 463. Matsuda, I.; Murata, S.; Izumi, Y. J. Org. Chem., 1980, 45, 237.
- 464. Morizawa, Y.; Oshima, K.; Nozaki, H. Tetrahedron Lett., 1982, 23, 2871.
- 465. Agami, C.; Platzer, N.; Puchot, C.; Sevestre, H. Tetrahedron, 1987, **43**, 1091.
- 466. Ruttimann, A.; Mayer, H. Helv. Chim. Acta, 1980, 63, 1456.
- 467. Kaiser, R.; Lamparsky, D. Helv. Chim. Acta, 1978, 61, 373.
- 468. Pellegata, R.; Ventura, P.; Villa, M.; Palmisano, G.; Lesma, G. Synth. Commun., 1985, **15**, 165.
- 469. McCormick, J. P.; Barton, D. L. Tetrahedron, 1978, 34, 325.
- 470. Wilson, C. W.; Shaw, D. E. J. Org. Chem., 1973, 38, 1684.
- 471. Marshall, J. A.; Hagan, C. P.; Flynn, G. A. J. Org. Chem., 1975, **40**, 1162.
- 472. Little, R. D.; Muller, G. W. J. Am. Chem. Soc., 1979, 101, 7129.
- 473. Jones, T. H.; Blum, M. S. Tetrahedron Lett., 1980, 21, 1701.
- 474. Kinney, W. A.; Coghlan, M. J.; Paquette, L. A. J. Am. Chem. Soc., 1985, **107**, 7352.
- 475. Stevens, R. V.; Lee, A. W. M. J. Chem Soc., Chem. Commun., 1982, 102.
- 476. Bengtsson, M.; Lilyefors, T.; Hansson, B. S. Bioorg. Chem., 1987, **15**, 409.
- 477. Mori, K.; Nakahara, Y.; Matsui, M. Tetrahedron, 1972, 28, 3217.
- 478. Lebel, N. A.; Ojha, N. D.; Menke, J. R. Newland, R. J. J. Org. Chem.,

1972, **37**, 2896.

- 479. Brimacombe, J. S.; Rahman, K. M. Carbohydr. Res., 1983, 113, C6.
- 480. Brimacombe, J. S.; Mengech, A. S.; Rahman, K. M.; Tucker, L. C. N. Carbohydr. Res., 1982, **110**, 207.
- 481. Brimacombe, J. S.; Hanna, R.; Tucker, L. C. N. Carbohydr. Res., 1982, **105**, C1.
- 482. Brimacombe, J. S.; Hanna, R.; Tucker, L. C. N. J. Chem Soc., Perkin Trans. 1, 1983, 2277.
- 483. Kutney, J. D.; McGrath, M. J.; Young, R. N.; Worth, B. R. Can. J. Chem., 1979, **57**, 3145.
- 484. Le Borgne, J. F.; Cuvigny, T.; Larcheveque, M.; Normant, H. Tetrahedron Lett., 1976, **17**, 1379.
- 485. Santaniello, E.; Manzocchi, A.; Biendi, P. A.; Secchi, C.; Simonic, T. J. Chem Soc., Chem. Commun., 1984, 803.
- 486. Mori, K.; Waku, M. Tetrahedron, 1984, 40, 305.
- 487. Schoenfelder, W.; Snatzke, G. Chem. Ber., 1980, 113, 1855.
- 488. Stork, G.; Shiner, C. S.; Winkler, J. D. J. Am. Chem. Soc., 1982, **104**, 310.
- 489. Gerlach, H.; Kunzler, P.; Oertle, K. Helv. Chim. Acta, 1978, 61, 1226.
- 490. Babler, J. H.; Coghlan, M. J. Tetrahedron Lett., 1979, 22, 1971.
- 491. Kann, N.; Rein, T.; Akermark, B.; Helquist, P. J. Org. Chem., 1990, **55**, 5312.
- 492. Kitahara, T.; Matsuoka, T.; Katayama, M.; Marumo, S.; Mori, K. Tetrahedron Lett., 1984, **25**, 4685.
- 493. Kitahara, T.; Kurata, H.; Matsuoka, T.; Mori, K. Tetrahedron, 1985, **41**, 5475.
- 494. Sauvé, G.; Schwartz, D. A.; Ruest, L.; Deslongchamps, P. Can. J. Chem., 1984, **62**, 2929.
- 495. Negri, D. D.; Kishi, Y. Tetrahedron Lett., 1987, 28, 1063.
- 496. Burger, A.; Clark, J. E.; Nishimoto, M.; Muerhoff, A. S.; Masters, B. S. S.; Ortiz de Montellano, P. R. J. Med. Chem., 1993, **36**, 1418.
- 497. Wilson, S. R.; Augelli-Szafran, C. E. Tetrahedron, 1988, 44, 3983.
- 498. Fristad, W. E.; Bailey, T. R.; Paquette, L. A. J. Org. Chem., 1980, **45**, 3028.
- 499. Roush, W. R.; Koyama, K. Tetrahedron Lett., 1992, **33**, 6227.
- 500. Smith, J. G.; Fogg, D. E.; Munday, I. J.; Sandborn, R. E.; Dibble, P. W. J. Org. Chem., 1988, **53**, 2942.
- 501. Tamaru, Y.; Yamada, Y.; Yoshida, Z. Tetrahedron, 1979, **35**, 329.
- 502. Bowers, K. G.; Mann, J.; Walsh, E. B.; Howarth, O. W. J. Chem Soc.,

Perkin Trans. 1, 1987, 1657.

- 503. Sato, E.; Kanaoka, Y.; Padwa, A. J. Org. Chem., 1982, 47, 4256.
- 504. Sharma, M. S. P.; Rao, G. S. Indian J. Chem., 1987, 26B, 257.
- 505. Bellassoued, M.; Dardoize, F.; Gandemar, M. J. Organomet. Chem., 1979, **177**, 35.
- 506. Carretero, J. C.; Dominguez, E. J. Org. Chem., 1992, 57, 3867.
- 507. Hutchinson, C. R.; Mattes, K. C.; Nakane, M.; Partridge, J. J.; Uskokovic, M. R. Helv. Chim. Acta, 1978, **61**, 1221.
- 508. Takeda, K.; Shibata, Y.; Sagawa, Y.; Urahata, M.; Funaki, K.; Hori, K.; Sasahara, H. Yoshii, E. J. Org. Chem., 1985, **50**, 4673.
- 509. Natsume, M.; Muratake, H. Tetrahedron Lett., 1979, 36, 3477.
- 510. Ziegler, F. E.; Chliwner, I.; Fowler, K. W.; Ranfer, S. J.; Kuo, S. J.; Sinha, N. D. J. Am. Chem. Soc., 1980, **102**, 790.
- 511. Kirmse, W.; Gunther, B. R.; Loosen, K. Chem. Ber., 1980, **113**, 2140.
- 512. Durman, J.; Elliot, J.; McElroy, A. B.; Warren, S. J. Chem Soc., Perkin Trans. 1, 1985, 1237.
- 513. Dawson, M. I.; Vasser, M. J. Org. Chem., 1977, 42, 2783.
- 514. Green, D. L. C.; Thompson, C. M. Tetrahedron Lett., 1991, 32, 5051.
- 515. Corey, E. J.; Carney, R. L. J. Am. Chem. Soc., 1971, 93, 7318.
- 516. Stork, G.; Kreft, A. F. III J. Am. Chem. Soc., 1977, 99, 3851.
- 517. Sugahorn, T.; Iwata, T.; Yamaoka, M. Takano, S. Tetrahedron, 1989, **30**, 1821.
- 518. Chastrette, M.; Axiotis, G. P. J. Organomet. Chem., 1981, 206, 139.
- 519. Snider, B. B.; Phillips, G. B.; Cordova, R. J. Org. Chem., 1983, 48, 3003.
- 520. Büchi, G.; Carlson, J. A.; Powell, J. E.; Tietze, L. F. J. Am. Chem. Soc., 1973, **95**, 340.
- 521. Grieco, P. A.; Yokoyama, Y.; Withers, G. P. Okuniewies, F. J.; Wang, C. L. J. J. Org. Chem., 1978, **43**, 4178.
- 522. Whitesell, J. K.; Matthews, R. S. J. Org. Chem., 1978, 43, 1650.
- 523. Brillon, D. Synth. Commun., 1986, 16, 291.
- 524. Coates, R. M.; Muskopf, J. W.; Senter, P. A. J. Org. Chem., 1985, **50**, 3541.
- 525. Suzuki, A.; Sono, S.; Itoh, M.; Brown, H. C.; Midland, M. J. Am. Chem. Soc., 1969, **91**, 4521.
- 526. Wawrzencyk, C.; Zabza, A. Tetrahedron, 1980, 36, 3091.
- 527. Corey, E. J.; Schulman, J. I. J. Am. Chem. Soc., 1970, 92, 5522.
- 528. Ackroyd, J.; Manro, A.; Scheinman, F.; Appleton, R. A.; Bantick, J. R. Tetrahedron Lett., 1983, **24**, 5139.
- 529. Schmidt, G.; Fukuyama, T.; Akasaka, K.; Kishi, Y. J. Am. Chem. Soc.,

1979, **101**, 259.

- 530. Jung, M. E.; Radcliffe, C. D. Tetrahedron Lett., 1980, 21, 4397.
- 531. Gottschalk, F. J.; Weyerstahyl, P. Chem. Ber., 1980, 113, 555.
- 532. Phaff, R. Bishofberger, N.; Matheis, P.; Petter, W.; Frei, B.; Jeger, O. Helv. Chim. Acta, 1985, **68**, 1204.
- 533. Tadano, K.; Miyazaki, M.; Ogawa, S.; Suami, T. J. Org. Chem., 1988, **53**, 1574.
- 534. Liu, D.; Caperelli, C. A. Synthesis 1991, 933.
- 535. Imanishi, T.; Yagi, N.; Hanaoka, M. Tetrahedron Lett., 1981, 22, 667.
- 536. Martin, S. F.; Austin, R. E.; Oalmann, C. J. Tetrahedron Lett., 1990, **31**, 4731.
- 537. Porter, N. A.; Ziegler, C. B.; Khouri, F. F.; Roberts, D. H. J. Org. Chem., 1985, **50**, 2252.
- 538. Dharanipragada, R.; Fodor, G. J. Chem Soc., Perkin Trans. 1, 1986, 545.
- 539. Yamada, K.; Tan, H.; Hirota, K. Tetrahedron Lett., 1980, 21, 4873.
- 540. Nicolaou, K. C.; Petasis, N. A.; Li, W. S.; Ladduwahetty, T.; Randall, J. L.; Webber, S. E.; Hernandez, P. E. J. Org. Chem., 1983, **48**, 5403.
- 541. Gurskii, M. E.; Baranin, S. V.; Lutsenko, A. I.; Mikhailov, B. M. J. Organomet. Chem., 1984, **270**, 17.
- 542. Baldwin, J. E.; Lusch, M. J. Tetrahedron, 1982, 38, 2939.
- 543. Apparu, M.; Barrelle, M. Tetrahedron, 1978, 34, 1817.
- 544. Piers, E.; Karunaratne, V. Can. J. Chem., 1984, 62, 629.
- 545. Middleton, S.; Stock, L. E. Aust. J. Chem., 1980, 33, 2467.
- 546. Duthaler, R. O.; Maienfisch, P. Helv. Chim. Acta, 1984, 67, 856.
- 547. Buchecker, R.; Hamm, P.; Eugster, C. H. Helv. Chim. Acta, 1974, **57**, 631.
- 548. Marshall, J. A.; Grote, J.; Audia, J. E. J. Am. Chem. Soc., 1987, **109**, 1186.
- 549. Kramer, A.; Pfander, H. Helv. Chim. Acta, 1984, 67, 21.
- 550. Cockerill, G. S.; Kocienski, P.; Treadgold, R. J. Chem Soc., Perkin Trans. 1, 1985, 2093.
- 551. Mancini, C.; Guella, G.; Pietra, F. Gazz. Chim. Ital., 1988, 118, 447.
- 552. Marshall, J. A.; Flynn, G. A. Synth. Commun., 1979, 9, 123.
- 553. Smith, A. B.; Thompson, A. S. J. Org. Chem., 1984, 49, 1471.
- 554. Kozikowski, A. P.; Park, P. J. Am. Chem. Soc., 1985, 107, 1763.
- 555. Chiang, Y. P.; Yang, S.; Heck, J. V.; Chabala, J. C.; Yang, M. N. J. Org. Chem., 1989, **54**, 5708.
- 556. Schulte-Elte, K. H.; Giersch, W.; Winter, B.; Pamingle, H.; Ohloff, G.

Helv. Chim. Acta, 1985, 68, 1961.

- 557. Ireland, R. E.; Dawson, M. I.; Bordner, J.; Dickerson, R. E. J. Am. Chem. Soc., 1970, **92**, 2568.
- 558. Shelly, K. P.; Weiler, L. Can. J. Chem., 1988, 66, 1359.
- 559. Brown, H. C.; Basavaiah, D.; Racherla, U. S. Synthesis, 1983, 886.
- 560. de Boggiato, M. V.; de Heluani, C. S.; de Fenik, I. J. S.; Catalan, C. J. Org. Chem., 1987, **52**, 1505.
- 561. Rittle, K. E.; Homnick, C. F.; Ponticello, G. S.; Evans, B. E. J. Org. Chem., 1982, **47**, 3016.
- 562. Anderson, N. H.; McCrae, D. A.; Grotjahn, D. M.; Gabbe, S. V.; Theodore, L. J.; Ippolito, R. M.; Sarkar, T. K. Tetrahedron, 1981, **37**, 4069.
- 563. Seeger, D. E.; Lanti, P. M.; Rossi, A. R.; Berson, J. A. J. Am. Chem. Soc., 1986, **108**, 1251.
- 564. Hayakawa, S.; Tamai, Y.; Yuasa, T.; Okamoto, M.; Ohta, S. Heterocycles, 1987, **26**, 1877.
- 565. Ozlu, Y.; Cladingboel, D. E.; Parsons, P. J. Tetrahedron, 1994, **50**, 2183.
- 566. Nakazaki, M.; Naemura, K. J. Org. Chem., 1977, 42, 2985.
- 567. Silverman, R. B.; Ding, C. Z. J. Am. Chem. Soc., 1993, 115, 4571.
- 568. VanderWeerdt, A. J. A.; Cerfontain, H. Tetrahedron, 1981, 37, 2121.
- 569. Tanis, S. P.; Herrinton, P. M. J. Org. Chem., 1985, 50, 3988.
- 570. Walborsky, H. M.; Reddy, S. J. Org. Chem., 1988, 53, 4846.
- 571. Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. Tetrahedron, 1981, **37**, 4543.
- 572. Mehta, G.; Srikrishna, A. J. Chem Soc., Chem. Commun., 1982, 218.
- 573. Chuang, C. P.; Galluci, J. C.; Hart, D. J. J. Org. Chem., 1988, 53, 3210.
- 574. Viswanathan, N.; Balakrishnan, V.; von Philisbaum, W. Helv. Chim. Acta, 1975, **58**, 2026.
- 575. Arvidsson, L.; Hacksell, U.; Johansson, A. M.; Nilsson, J. G.; Lindberg, P.; Sanchez, D.; Wikstrom, H.; Svensson, K.; Hjorth, S.; Carlsson, A. J. Med. Chem., 1984, **27**, 45.
- 576. Schuda, P. F.; Ammon, H. L.; Heimann, M. R.; Bhattacharjee, S. J. Org. Chem., 1982, **47**, 3434.
- 577. Robin, S.; Huet, F. Tetrahedron Lett., 1993, 34, 2945.
- 578. Ireland, R. E.; Thompson, W. J. J. Org. Chem., 1979, 44, 3041.
- 579. Bengtsson, M.; Liljefors, T. Synthesis, 1988, 250.
- 580. Tice, C. M.; Ganem, B. J. Org. Chem., 1983, 48, 5048.
- 581. Liu, H.-J.; Wynn, H. Can. J. Chem., 1986, 64, 658.

- 582. Boland, W.; Jaenicke, L. Chem. Ber., 1978, 111, 3262.
- 583. Snowden, R. L.; Naf, R. Tetrahedron Lett., 1984, 25, 2877.
- 584. Mani, J.; Cho, J.-H.; Astik, R. R.; Stamm, E.; Bigler, P.; Meyer, V.; Keese, R. Helv. Chim. Acta, 1984, **67**, 1930.
- 585. Suami, T.; Tadano, K.; limura, Y.; Yokoo, H. J. Carbohydr. Chem., 1986, **5**, 1.
- 586. Weyerstahl, D.; Marschal-Weyerstahl, H.; Penninger, J.; Walter, L. Tetrahedron, 1987, **43**, 5287.
- 587. Kieczykowski, G. R.; Quesada, M. L.; Schlessinger, R. H. J. Am. Chem. Soc., 1980, **102**, 782.
- 588. Sueda, N.; Ohrui, H.; Kuzuhara, H. Tetrahedron Lett., 1979, 22, 2039.
- 589. Lesage, S.; Perlin, A. S. Can. J. Chem., 1978, 56, 2889.
- 590. Munroe, J. E. Ph. D. Dissertation, Harvard University, 1982.
- 591. Browne, E. J. Aust. J. Chem., 1984, 37, 367.
- 592. Morizawa, Y.; Kanakura, A.; Yamamoto, H.; Hiyama, T.; Nozaki, H. Bull. Chem. Soc. Jpn., 1984, 57, 1935.
- 593. Elliot, W. J.; Needleman, P.; Sprecher, H. J. Org. Chem., 1983, **48**, 5378.
- 594. Crawford, R. J.; Erman, W. F.; Broaldins, C. D. J. Am. Chem. Soc., 1972, **94**, 4298.
- 595. Solas, D.; Wolinsky, J. J. Org. Chem., 1983, 48, 1988.
- 596. Piers, E.; Gavai, A. V. J. Org. Chem., 1990, 55, 2380.
- 597. Turecek, F.; Hanus, V.; Sedmera, P.; Antropiusova, H.; Mach, K. Tetrahedron, 1979, **35**, 1463.
- 598. Bell, T. W.; Vargas, J. R.; Crispino, G. A. J. Org. Chem., 1989, 54, 1978.
- 599. Garcia-Grandos, A.; Molina, A.; Cabrera, E. Tetrahedron, 1986, 42, 81.
- 600. van Tamelen, E. E.; Anderson, R. J. J. Am. Chem. Soc., 1972, 94, 8225.
- 601. Ziegler, F. E.; Piwinski, J. J. J. Am. Chem. Soc., 1980, 102, 6577.
- 602. Vite, G. D.; Spencer, T. A. J. Org. Chem., 1988, 53, 2555.
- 603. Arigoni, D.; Cane, D. E.; Muller, B.; Tamm, C. Helv. Chim. Acta, 1973, 56, 2946.
- 604. Haynes, R. K.; Lambert, D. E.; Parafinink, K. A.; Schober, P. A.; Turner, S. G. Aust. J. Chem., 1987, 40, 273.
- 605. Ibuka, T.; Minakata, H.; Mitsui, Y.; Tabushi, E.; Taga, T.; Inubushi, Y. Chem. Lett., 1981, 1409.
- 606. Sun, W-C.; Ng, C-S.; Prestwich, G. D. J. Org. Chem., 1992, 57, 132.
- 607. Wakamatsu, T.; Hara, H.; Ban, Y. Tetrahedron Lett., 1979, 14, 1227.
- 608. Shing, T. K. M.; Gillhouley, J. G. Tetrahedron 1994, 50, 8685.
- 609. Tadano, K.; Imura, Y.; Suami, T. J. Carbohydr. Chem., 1986, 5, 411.

- 610. Lesage, S.; Perlin, A. S. Can. J. Chem., 1978, 56, 3117.
- 611. Hua, D. H.; Bharathi, S. M.; Robinson, P. D.; Tsujimoto, A. J. Org. Chem., 1990, **55**, 2128.
- 612. Imanishi, T.; Shin, H.; Yagi, H.; Aanaoka, M. Tetrahedron Lett., 1980, **21**, 3285.
- 613. Ireland, R. E.; Dawson, M. I.; Kowalski, C. J.; Lipinski, C. A.; Marshall, D. R.; Tilley, J. W.; Bordner, J.; Tons, B. L. J. Org. Chem., 1975, **40**, 973.
- 614. Ireland, R. E.; McKenzie, T. C.; Trust, R. I. J. Org. Chem., 1975, **40**, 1007.
- 615. Johnson, W. S.; Harbert, C. A.; Stipanovic, R. D. J. Am. Chem. Soc., 1968, **90**, 5279.
- 616. Johnson, W. S.; Harbert, C. A.; Ratcliffe, B. E.; Stipanovic, R. D. J. Am. Chem. Soc., 1976, **98**, 6188.
- 617. De Nys, R.; Coll, J. C.; Bowden, B. F. Aust. J. Chem., 1992, 45, 1625.
- 618. Boeckman, R. K. Jr.; Bruza, K. J.; Heinrich, G. R. J. Am. Chem. Soc., 1978, **100**, 7101.
- 619. Nakagawa, Y.; Stevens, R. V. J. Org. Chem., 1988, 53, 1871.
- 620. Barraclough, P.; Young, D. W. J. Chem Soc., Perkin Trans. 1, 1975, 264.
- 621. Piers, E.; Lau, C. K. Synth. Commun., 1977, 7, 495.
- 622. Takahashi, S.; Kusumi, T.; Sato, Y.; Inoue, Y.; Kakisawa, H. Bull. Chem. Soc. Jpn., 1981, 54, 1777.
- 623. Momose, T.; Kinoshita, M.; Imanishi, T. Heterocycles, 1979, 12, 243.
- 624. Patterson, J. W.; Pfister, J. R.; Wagner, P. J. J. Org. Chem., 1983, **48**, 2572.
- 625. Babler, J. H.; Invergo, B. J.; Sarussi, S. J. J. Org. Chem., 1980, **45**, 4241.
- 626. Wilson, S. R.; Price, M. F. J. Am. Chem. Soc., 1982, 104, 1124.
- 627. Bidd, H.; Kelly, D. J.; Ottley, P. M.; Paynter, O. I. Simmons, D. J.; Whiting, M. C. J. Chem Soc., Perkin Trans. 1, 1983, 1369.
- 628. Kalivretenos, A. G.; Nakanishi, K. J. Org. Chem., 1993, 58, 6596.
- 629. Tomioka, H.; Takai, K.; Oshima, K. Nozaki, H. Tetrahedron Lett., 1981, 22, 1605.
- 630. Wilson, R. M.; Wunderly, S. W.; Walsh, T. F.; Musser, A. K.; Outcalt, R.;
  Geiser, F.; Gee, S. K.; Brabender, Yerino, L. Jr.; Conrad, T. T.; Tharp,
  G. A. J. Am. Chem. Soc., 1982, **104**, 4429.
- 631. Williams, T. M.; Crumbie, R.; Mosher, H. S. J. Org. Chem., 1985, 50, 91.
- 632. Paddon-Row, M. H.; Lap, B. V.; Patney, H. K.; Warrener, R. H. Aust. J. Chem., 1980, **33**, 1493.
- 633. Terpstra, J. W.; Van Leusen, A. M. J. Org. Chem., 1986, 51, 230.

- 634. Ishii, H.; Murakami, Y. Tetrahedron, 1975, 31, 933.
- 635. Amlaiky, N.; Leclerc, G. Synthesis, 1982, 426.
- 636. Kelly, D. P.; Leslie, D. R.; Smith, B. D. J. Am. Chem. Soc., 1984, **106**, 687.
- 637. Elliot, J. D.; Choi, V. M. F.; Johnson, W. S. J. Org. Chem., 1983, **48**, 2295.
- 638. McLean, A.; Proctor, G. R. J. Chem Soc., Perkin Trans. 1, 1973, 1085.
- 639. Stachulski, A. V. Tetrahedron Lett., 1982, 23, 3789.
- 640. Venuti, M. C.; Jones, G. H.; Alvarez, R.; Bruno, J. J. Med. Chem., 1987, 30, 303.
- 641. McMurry, J. E.; Von Beroldingen, L. A. Tetrahedron, 1974, **30**, 2027.
- 642. Fukayama, T.; Akasaka, K.; Karanewsky, D. S.; Wang, C. J.; Schmid, G.; Kishi, Y. J. Am. Chem. Soc., 1979, **101**, 260.
- 643. Ingham, S.; Turner, R. W.; Wallace, T. W. J. Chem Soc., Chem. Commun., 1985, 1664.
- 644. Ziegler, F. E.; Klein, S. I.; Pati, U. K.; Wang, T. F. J. Am. Chem. Soc., 1985, **107**, 2730.
- 645. Ishiyama, J.; Maeda, S.; Takahashi, K.; Senda, Y.; Imaizumi, S. Bull. Chem. Soc. Jpn., 1987, **10**, 1721.
- 646. Dauben, W. G.; Cunningham, A. F. Jr. J. Org. Chem., 1983, 48, 2842.
- 647. Skaltsounis, A. L.; Michel, S.; Tilleguin, F.; Koch, M. Tetrahedron Lett., 1984, **25**, 2783.
- 648. Grieco, P. A.; Williams, F.; Sugahara, T. J. Org. Chem., 1979, 44, 2194.
- 649. Takeda, K.; Shimono, Y.; Yoshi, E. J. Am. Chem. Soc., 1983, 105, 563.
- 650. Marshall, J. A.; Wuts, P. G. M. J. Org. Chem., 1977, 42, 1794.
- 651. Niwa, H.; Yoshida, Y.; Hasegawa, T.; Yamada, K. Chem. Lett., 1985, 1687.
- 652. Niwa, H.; Yoshida, Y.; Hasegawa, T.; Yamada, K. Tetrahedron 1991, 47, 2155.
- 653. Hobbs, P. D.; Magnus, P. D. J. Am. Chem. Soc., 1976, 98, 4594.
- 654. Grieco, P. A.; Oguri, T.; Gilman, S.; DeTitta, G. T. J. Am. Chem. Soc., 1978, **100**, 1616.
- 655. Frei, B.; Weck, G.; Mullen, K.; Wolf, H. R.; Jeger, O. Helv. Chim. Acta, 1979, 62, 553.
- 656. Roush, W. R.; Hall, S. E. J. Am. Chem. Soc., 1981, 103, 5200.
- 657. Mercier, C.; Adams, A. R.; Deslongchamps, P. Can. J. Chem., 1972, **50**, 1882.
- 658. Mlinari'c-Majerski, K.; Vinkovi'c, M.; Fry, J. L. J. Org. Chem., 1994, **59**, 664.

- 659. Yates, P.; Bumell, D. J.; Freer, V. J.; Sawyer, J. F. Can. J. Chem., 1987, 65, 69.
- 660. Tixidre, A.; Alazard, J. P.; Thal, C. Tetrahedron Lett., 1983, 24, 3323.
- 661. Banerjee, A. K.; Caraballs, P. C.; Huntado, H. S.; Carrasco, M. C.; Rivas, C. Tetrahedron, 1981, **37**, 2749.
- 662. Mehta, G.; Krishnamurthy, N.; Karra, S. J. Am. Chem. Soc., 1991, **113**, 5765.
- 663. Piers, E.; Britton, R. W.; Keziere, R. J.; Smillie, R. D. Can. J. Chem., 1971, **49**, 2623.
- 664. Hutchinson, J. H.; Money, T.; Piper, S. E. Can. J. Chem., 1986, **64**, 1404.
- 665. Massy-Westropp, R. A.; Warren, R. F. O. Aust. J. Chem., 1984, 37, 1303.
- 666. Vite, G. D.; Spencer, T. A. J. Org. Chem., 1988, 53, 2560.
- 667. Wang, W. Y.; Reusch, W. Tetrahedron, 1988, 44, 1007.
- 668. Paquette, L. A.; Lanter, J. C.; Wang, H. L. J. Org. Chem., 1996, **61**, 1119.
- 669. Posner, G.; Babiak, K. A.; Loomis, G. L.; Frazee, W. J.; Mittal, R. D.; Karle, I. L. J. Am. Chem. Soc., 1980, **102**, 7498.
- 670. Becker, D.; Harel, Z.; Nagler, M.; Gillon, A. J. Org. Chem., 1982, **47**, 3297.
- 671. Tice, C. M.; Heathcock, C. H. J. Org. Chem., 1981, 46, 9.
- 672. Ohta, S.; Frei, B.; Jeger, O. Helv. Chim. Acta, 1982, 65, 2363.
- 673. Semmelhack, M. F.; Yamashita, A.; Tomesch, J. C.; Hrotsu, K. J. Am. Chem. Soc., 1978, **100**, 5567.
- 674. Prasad, J. S.; Clive, D. L. J.; daSilva, G. V. J. J. Org. Chem., 1986, **51**, 2717.
- 675. Schow, S. R.; Bloom, J. D.; Thompson, A. S.; Winzenberg, K. M.; Smith, A. B. III J. Am. Chem. Soc., 1986, **108**, 2662.
- 676. Aono, T.; Hesse, M. Helv. Chim. Acta, 1984, 67, 1448.
- 677. Randazzo, G.; Evidente, A.; Boccalette, A.; Rossi, C. Phytochemistry, 1981, **20**, 2177.
- 678. Banerjie, A. K.; Caraballo, P. C.; Hurtado, H. E.; Carrasco, M. C. Heterocycles, 1980, **14**, 315.
- 679. Thijs, L.; Egenberger, D. M.; Zwanenberg, B. Tetrahedron Lett., 1989, **30**, 2153.
- 680. Jones, D. H.; Kogan, T. P.; Newton, R. F. J. Chem Soc., Perkin Trans. 1, 1982, 1333.
- 681. Nakata, T.; Nagao, S.; Oishi, T. Tetrahedron Lett., 1985, 26, 75.
- 682. Cameron, A. G.; Knight, D. W. J. Chem Soc., Perkin Trans. 1, 1986,

161.

- 683. Beckwith, A. L. J.; Lawrence, T. J. Chem Soc., Perkin Trans. 1, 1979, 1535.
- 684. Boeckman, R. K.; Blum, D. M.; Arthur, S. D. J. Am. Chem. Soc., 1979, **101**, 5060.
- 685. Horner, L.; Mathias, J. J. Organomet. Chem., 1985, 282, 155.
- 686. Nagai, U., Sato, K. Tetrahedron Lett., 1985, 26, 647.
- 687. Reed, J. M.; Snieckus, V. Tetrahedron Lett., 1984, 25, 5505.
- 688. Noyori, R.; Sato, T.; Koayashi, H. Bull. Chem. Soc. Jpn., 1983, 56, 2661.
- 689. Manchand, A. P.; Earlywine, A. D. J. Org. Chem., 1984, 49, 1660.
- 690. Hua, D. H.; Bensoussan, D.; Bravo, A. A. J. Org. Chem., 1989, 54, 5379.
- 691. Hua, D. H.; Venkataraman, S. Tetrahedron Lett., 1985, 26, 3765.
- 692. Binns, F.; Hayes, R.; Ingham, S.; Saengchantara, S. T.; Turner, R. W.; Wallace, T. W. Tetrahedron 1992, **48**, 515.
- 693. Danishefsky, S.; Zamboni, R.; Kahn, M.; Etheredge, S. J. J. Org. Chem., 1980, **102**, 2097.
- 694. Koft, E. R.; Smith, A. B. III J. Am. Chem. Soc., 1982, 104, 5568.
- 695. Buchanan, J. G.; MacLean, K. A.; Wightman, R. H.; Paulsen, H. J. Chem Soc., Perkin Trans. 1, 1985, 1463.
- 696. Martin, S. F.; Davidson, S. K.; Puckette, T. A. J. Org. Chem., 1987, **52**, 1962.
- 697. Iddon, B.; Price, D.; Suschitzky, H.; Scopes, D. I. C. J. Chem Soc., Perkin Trans. 1, 1983, 2583.
- 698. Grieco, P. A.; Oguri, T.; Gilman, S. J. Am. Chem. Soc., 1980, **102**, 5886.
- 699. Colvin, E. W.; Malchenko, S.; Raphael, R. A.; Roberts, J. S. J. Chem Soc., Perkin Trans. 1, 1989, 1973.
- 700. Valverde, S.; Herradon, B.; Martin-Lomae, M. Tetrahedron Lett., 1985, **26**, 3731.
- 701. Danishefsky, S.; Schuda, P. F.; Massa, S.; Kato, K. J. Org. Chem., 1976, **41**, 3468.
- 702. Fronza, G.; Fuganti, C.; Grasselli, P.; Marinoni, G. Tetrahedron Lett., 1979, **40**, 3883.
- 703. Mann, J.; Thomas, A. J. Chem Soc., Perkin Trans. 1, 1986, 2287.
- 704. Roumesfant, M. L.; Carvallin, B.; Butrand, M. Bull. Soc. Chim. Fr., 1983, **II**, 309.
- 705. Hiyama, T.; Shinoda, M.; Nozaki, H. Tetrahedron Lett., 1979, 37, 3529.
- 706. Yamada, K.; Kyotani, Y.; Manabe, S.; Suzuki, M. Tetrahedron, 1979, **35**, 293.
- 707. Corey, E. J.; Tius, M. A.; Das, J. J. Am. Chem. Soc., 1980, 102, 7612.

- 708. Mehta, G.; Murthy, A. H.; Reddy, D. S.; Reddy, A. V. J. Am. Chem. Soc., 1986, **108**, 3443.
- 709. Masamune, S.; Imperiali, B.; Garvey, D. S. J. Am. Chem. Soc., 1982, **104**, 5528.
- 710. Johnson, W. S.; Shenvi, A. B.; Boots, S. G. Tetrahedron, 1982, **38**, 1397.
- 711. Torii, S.; Inokuchi, T.; Yamafuji, T. Bull. Chem. Soc. Jpn., 1979, **52**, 2640.
- 712. Kakiuchi, K.; Ue, M.; Nagashima, T.; Kinugawa, M.; Kubiro, K.; Tobe, Y.; Odaira, Y. Chem. Pharm. Bull., 1988, **36**, 542.
- 713. Georges, M.; Tam, T.; Fraser-Reid, B. J. Org. Chem., 1985, 50, 5747.
- 714. Kido, F.; Tooyama, Y.; Noda, Y.; Yoshikoshi, A. Chem. Lett., 1983, 881.
- 715. Martin, S. F.; Li, W. J. Org. Chem., 1989, 54, 265.
- 716. Zoretic, P. A.; Barcelos, F.; Jardin, J.; Bhakta, C. J. Org. Chem., 1980, **45**, 810.
- 717. Boland, W.; Jaenicke, L. Liebigs. Ann. Chem., 1981, 92.
- 718. Gigueu, R. J.; Hoffman, H. M. R. Tetrahedron Lett., 1981, 22, 5039.
- 719. Kitahara, T.; Mori, M.; Koseki, K.; Mori, K. Tetrahedron Lett., 1986, **27**, 1343.
- 720. Schlessinger, R. H.; Schultz, A. J. J. Org. Chem., 1983, 48, 407.
- 721. Uyehara, T.; Yamada, J.; Ogata, K.; Kato, T. Bull. Chem. Soc. Jpn., 1985, **58**, 211.
- 722. Piers, E.; Isenring, H. P. Can. J. Chem., 1977, 55, 1039.
- 723. Franck-Neuman, M.; Milsch, M.; LaCroix, E. Tetrahedron Lett., 1989, **30**, 3529.
- 724. McMurry, J. E.; Choy, W.; Tetrahedron Lett., 1980, 21, 2477.
- 725. Tobe, Y.; Yamashita, T.; Kakiuchi, K.; Odaira, Y. J. Chem Soc., Chem. Commun., 1985, 898.
- 726. Ireland, R. E.; Thomson, W. J.; Mandel, N. S.; Mandel, G. S. J. Org. Chem., 1979, **44**, 3583.
- 727. Henrick, C. A.; Schaub, F.; Siddall, J. B. J. Am. Chem. Soc., 1972, **94**, 5374.
- 728. Joshi, N. N.; Mamdapur, V. R.; Chada, M. S. Indian J. Chem., 1984, **23B**, 231.
- 729. Silverman, I. R.; Edington, C.; Elliott, J. D.; Johnson, W. S. J. Org. Chem., 1987, **52**, 180.
- 730. Gill, M.; Rickards, R. W. J. Chem Soc., Perkin Trans. 1, 1981, 599.
- 731. Hua, D. H.; Coulter, M. J.; Badejo, I. Tetrahedron Lett., 1987, 28, 5465.
- 732. Ireland, R. E.; Baldwin, S. W.; Welch, S. C. J. Am. Chem. Soc., 1972,

**94**, 2056.

- 733. Bosch, M. P.; Camps, F.; Coll, J.; Guerrero, A.; Tatsuoka, T.; Meinwald, J. J. Org. Chem., 1986, **51**, 773.
- 734. Torii, S.; Inokuchi, T.; Handa, K. Bull. Chem. Soc. Jpn., 1982, 55, 887.
- 735. Anderson, R. C.; Fraser-Reid, B. J. Org. Chem., 1985, 50, 4781.
- 736. Raucher, S.; Chi, K. W.; Hwang, K.; Burks, J. E. Jr. J. Org. Chem., 1986, **51**, 5503.
- 737. Olson, R. K.; Ramasamy, K.; Emery, T. J. Org. Chem., 1984, 49, 3527.
- 738. Buynak, J. D.; Rao, M. N.; Pajouhesh, H. Chandresekaran, R. V.; DeMeester, P.; Chu, S. C. J. Org. Chem., 1985, **50**, 4245.
- 739. Taber, D. F.; Korsmeyer, R. W. J. Org. Chem., 1978, 43, 4925.
- 740. Drtina, G. J.; Wiemer, D. F. Tetrahedron Lett., 1982, 23, 803.
- 741. Becilka, B. T.; Koerwitz, F. L.; Datina, G. J.; Baenziger, N. C.; Wiemer, D. F. J. Org. Chem., 1990, 55, 5613.
- 742. Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. L.; Faulkner, D. J.; Petersen, M. R. J. Am. Chem. Soc., 1970, **92**, 741.
- 743. Hamon, D. P. G.; Krippner, G. Y. J. Org. Chem., 1992, 57, 7109.
- 744. Montana, A. M.; Nicholas, K. M. J. Org. Chem., 1990, 55, 1569.
- 745. Ziegler, F. E.; Hwang, K.; Kadow, J. F.; Klein, S. I.; Pati, U. K.; Wang, T. F. J. Org. Chem., 1986, **51**, 4573.
- 746. Burke, S. D.; Armistead, D. M.; Schoenen, F. J.; Fevig, J. M. Tetrahedron, 1986, **42**, 2787.
- 747. Rajashekhar, B.; Kaiser, E. T. J. Org. Chem., 1985, 50, 5480.
- 748. Brown, H. C.; Basavaiah, D.; Bhat, M. G. J. Org. Chem., 1986, 51, 4518.
- 749. Bestman, H. J.; Kautarjiew, I.; Rosel, P.; Stransky, W.; Vostrowsky, O. Chem. Ber., 1978, **111**, 248.
- 750. Mori, K.; Sakai, T. Liebigs Ann. Chem., 1988, 13.
- 751. Kawabata, T.; Kimura, Y. Ito, Y.; Terashima, S.; Sasaki, A.; Sonajawa,M. Tetrahedron, 1988, 44, 2149.
- 752. Padwa, A.; Ku, H.; Mazzu, A. J. Org. Chem., 1978, 43, 381.
- 753. Krohn, K. Liebigs Ann. Chem., 1981, 2285.
- 754. Cooper, E. L.; Yankee, E. W. J. Am. Chem. Soc., 1974, 96, 5876.
- 755. Cloudsdale, I. S.; Kluge, A. F.; McClure, N. L. J. Org. Chem., 1982, **47**, 919.
- 756. Martinez, S. J.; Dalton, L.; Joule, J. A. Tetrahedron, 1984, 40, 3339.
- 757. Wei, R.; Schnoes, H. K.; Hart, P. A.; Strong, F. M. Tetrahedron, 1975, **31**, 109.
- 758. Bruckner, C.; Suchland, B.; Ressig, H. Liebig. Ann. Chem., 1988, 471.
- 759. Joyce, R. P.; Gainor, J. A.; Weinreb, S. M. J. Org. Chem., 1987, 52,
- 760. Krow, G. R.; Johnson, C. Synthesis, 1979, 50.
- 761. Browne, E. J. Aust. J. Chem., 1985, 38, 765.
- 762. Pellon, P. Tetrahedron Lett., 1992, 33, 4451.
- 763. Tada, M.; Sugimoto, Y.; Takahashi, T. Bull. Chem. Soc. Jpn., 1980, **53**, 2966.
- 764. Fujimoto, Y.; Miura, H.; Shimizu, T.; Tatsuno, T. Tetrahedron Lett., 1980, **21**, 3409.
- 765. Kieczykowski, G. R.; Schlessinger, R. H. J. Am. Chem. Soc., 1978, **100**, 1938.
- 766. Kaiser, R.; Lampersky, D. Helv. Chim. Acta, 1983, 66, 1843.
- 767. Marshall, J. A.; Konicek, T. R.; Flynn, K. F. J. Am. Chem. Soc., 1980, 102, 3287.
- 768. Masaki, Y.; Hashimoto, K.; Sakuma, K.; Kaji, K. J. Chem Soc., Perkin Trans. 1, 1984, 1289.
- 769. Bowden, B. F.; Coll, J. C.; Engelhardt, L. M.; Tapiolas, D. M.; White, A. H. Aust. J. Chem., 1986, **39**, 103.
- 770. Tanis, S. P.; Nakanishi, K. J. Am. Chem. Soc., 1979, 101, 4398.
- 771. Chatterjee, S. K.; Bhattacharya, S.; Raychanduri, S.; Chatterjee, A. Indian, J. Chem., 1986, **25B**, 1191.
- 772. Becker, E.; Albrecht, R.; Bernhard, K.; Leuenberger, H. W.; Mayer, H.; Müller, R. K.; Schuep, W.; Wagner, H. P. Helv. Chim. Acta, 1981, 64, 2419.
- 773. De Bernardini, M.; Franza, G.; Scilingo, A.; Vidari, G.; Vita-Finzi, P. Tetrahedron, 1986, **42**, 4277.
- 774. White, J. D.; Bunton, L. P. J. J. Org. Chem., 1985, 50, 357.
- 775. Hayashi, Y.; Nishizawa, M.; Sakar, T. Tetrahedron, 1977, **33**, 2513.
- 776. Mehta, G.; Reddy, A. V. Tetrahedron Lett., 1979, 28, 2628.
- 777. Gonzalez, A. G.; Aguiar, J. M.; Darias, J.; Gonzalez, E.; Martin, J. D.; Martin, V. S.; Perez, C.; Fayos, J.; Martinez-Ripoli, M. Tetrahedron Lett., 1978, 3931.
- 778. Van Middlesworth, F. L. J. Org. Chem., 1986, 51, 5019.
- 779. Nakano, T.; Maillo, M. A.; Rojas, S. J. Chem Soc., Perkin Trans. 1, 1987, 2137.
- 780. Bertrand, M.; Monti, H.; Huong, K. C. Tetrahedron Lett., 1979, **1**, 15.
- 781. Piers, E.; Hall, T. W. Can. J. Chem., 1980, 58, 2613.
- 782. Money, T.; Kuo, D. C. J. Chem Soc., Chem. Commun., 1986, 1691.
- 783. Kuo, D. L.; Money, T. Can. J. Chem., 1988, 66, 1794.
- 784. Uyehara, T.; Yamada, J.; Furuta, T.; Kato, T.; Yamamoto, Y.

Tetrahedron, 1987, 43, 5605.

- 785. Durrani, A. A.; Sun, G. C.; Tyman, J. Lipids, 1982, 17, 561.
- 786. Sangaiah, R.; Rao, G. S. K. Indian, J. Chem., 1987, 26B, 357.
- 787. Bohlmann, F.; Kassner, H. Chem. Ber., 1981, 114, 2415.
- 788. Matsuo, A. Atsami, K.; Nakayama, M.; Hayoshi, S. J. Chem Soc., Perkin Trans. 1, 1981, 2819.
- 789. Armstrong, R. J.; Weiler L. Can. J. Chem., 1983, 61, 214.
- 790. Neukom, C.; Richardson, D. P.; Myerson, J. H.; Bartlett, P. A. J. Am. Chem. Soc., 1986, **108**, 5559.
- 791. Danishefsky, S.; Zamboni, R.; Kahn, M.; Etheredge, S. J. Am. Chem. Soc., 1981, **103**, 3460.
- 792. Burke, S. D.; Powner, T. H.; Kageyama, M. Tetrahedron Lett., 1983, **24**, 4529.
- 793. Hall, S. E.; Han, W. C.; Haslager, M. F.; Harris, D. H.; Ogletree, M. C. J. Med. Chem., 1986, 29, 2335.
- 794. Hijfte, L.; Vandewalle, M. Tetrahedron, 1984, 40, 4371.
- 795. Hamilton, R. J.; Mander, L. N.; Sethi, S. P. Tetrahedron, 1986, 42, 2881.
- 796. Thomas, A. F.; Ozainne, M. Helv. Chim. Acta, 1978, 61, 2874.
- 797. Julia, M.; Schmitz, C. Tetrahedron, 1986, 42, 2491.
- 798. Piers, E.; Geraghty, M. B.; Smillie, R. D.; Soncy, M. Can. J. Chem., 1975, **53**, 2849.
- 799. Ramana Rao, V. V.; Devaprabhakara, D. Tetrahedron, 1978, 34, 2223.
- 800. Welch, S. C.; Chou, C. Y.; Gruber, J. M.; Assercq, J. M. J. Org. Chem., 1985, **50**, 2668.
- 801. Mori, K.; Kato, M. Tetrahedron, 1986, 42, 5895.
- 802. Joshi, N. M.; Bhandari, R.; Mamdapur, V. R.; Chada, M. S. Indian J. Chem., 1984, 23, 698.
- 803. Miyashita, M.; Yoshikoshi, A. J. Am. Chem. Soc., 1974, 96, 1917.
- 804. Ireland, R. E.; Maienfisch, P. J. Org. Chem., 1988, 53, 640.
- 805. Lieb, F.; Niewoehner, U.; Wendisch, D. Liebigs Ann. Chem., 1987, 607.
- 806. Uyehara, T.; Kabasawa, Y.; Kato, T. Bull. Chem. Soc. Jpn., 1986, **59**, 2521.
- 807. Ziegler, F. E.; Cady, M. A.; Nelson, R. V.; Photis, J. M. Tetrahedron Lett., 1979, **30**, 2741.
- 808. Roll, D. M.; Biskupiak, J. E.; Mayne, C. L.; Ireland, C. M. J. Am. Chem. Soc., 1986, **108**, 6680.
- 809. Corey, E. J.; Smith, J. G. J. Am. Chem. Soc., 1979, 101, 1038.
- 810. Anderson N. H.; Golec, F. A. Tetrahedron Lett., 1977, 43, 3783.
- 811. Marshall, J. A.; Seletsky, B. M.; Coam, P. S. J. Org. Chem., 1994, 59,

- 812. Ohloff, G.; Vial, C.; Näf, F.; Pawlak, M. Helv. Chim. Acta, 1977, 60, 1161.
- 813. Marshall, J. A.; Ruden, R. A. J. Org. Chem., 1971, 36, 2569.
- 814. McMurry, J. E.; Bosch, G. K. J. Org. Chem., 1987, 52, 4885.
- 815. St. Enev, V.; Tsankova, E. T. Tetrahedron 1991, 47, 6399.
- 816. Amano, Y.; Heathcock, C. H. Can. J. Chem., 1972, 50, 340.
- 817. Corey, E. J.; Ishiguro, M. Tetrahedron Lett., 1979, 30, 2745.
- 818. Caldwell, C. G.; Derguini, F.; Bigge, C. F.; Chen, A.; Hu, S.; Wang, J.; Sastry, L.; Nakanishi, K. J. Org. Chem., 1993, **58**, 3533.
- 819. Corey, E. J.; Pan, B. C.; Hua, D. H.; Deardorff, D. R. J. Am. Chem. Soc., 1982, **104**, 6816.
- 820. Kulkarni, B. A.; Chattopadhyay, A.; Mamdapur, V. R. Synth. Commun., 1992, **22**, 2921.
- 821. Hernandez, J. E.; Cisneros, A.; Fernandez, S. Synth. Commun., 1983, 13, 191.
- 822. Fernandez, S.; Quintanilla, R.; Hernandez, J. E. Synth. Commun., 1983, 13, 621.
- 823. Marshall, J. A.; Audia, J. e.; Grote, J.; Shearer, B. G. Tetrahedron, 1986,
   42, 2893.
- 824. Kametani, T.; Suzuki, T.; Sato, E.; Nishimura, M.; Unno, K. J. Chem Soc., Chem. Commun., 1982, 1201.
- 825. Kametani, T.; Nagahara, T.; Ihara, M. Heterocycles, 1981, 16, 539.
- 826. Frater, G.; Muller, U.; Gunther, W. Tetrahedron, 1984, 40, 1269.
- 827. Ueno, Y.; Ohta, M.; Okawara, M. Tetrahedron Lett., 1982, 23, 2577.
- 828. Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. J. Am. Chem. Soc., 1993, **115**, 6548.
- 829. Becker, H. D.; Hansen, L.; Andersson, K. J. Org. Chem., 1986, 51, 2956.
- 830. Browne, E. J. Aust. J. Chem., 1986, 39, 783.
- 831. Manners, G. D.; Jurd, L. Phytochemistry, 1979, 18, 1037.
- Boyle, M. P.; Dow, R. L.; Bagheri, V.; Patrie, W. J. Tetrahedron Lett., 1980, 21, 2795.
- 833. Doyle, M. P.; Dow, R. L.; Bagheri, V.; Patrie, W. J. J. Org. Chem., 1983, 48, 476.
- 834. Paddon-Row, M. H.; Patney, H. K.; Pasupuleti, L. M. Aust. J. Chem., 1982, **35**, 307.
- 835. Cates, L. A.; Jones, G. S. Jr.; Good, D. J.; Tsai, H.; Li, V.; Caron, N.; Tu, S.; Kimball, A. P. J. Med. Chem., 1980, 23, 300.
- 836. Ruel, R.; Deslongchamps, P. Can. J. Chem., 1992, 70, 1939.

- 837. Pohmakotr, M.; Popuang, S.; Chancharunee, S. Tetrahedron Lett., 1989, **30**, 1715.
- 838. Martin, S. F.; Bonage, B.; Williamson, S. A.; Brown, S. P. Tetrahedron Lett., 1986, **42**, 2903.
- 839. Takahashi, T.; Manami, I.; Tsuji, J. Tetrahedron Lett., 1981, 22, 2651.
- 840. Barriere, J. C.; Chiaroni, A.; Cleophax, J.; Gero, S. D.; Riche, C.; Vuilhorgne, M. Helv. Chim. Acta, 1981, **64**, 1140.
- 841. Barriere, J. C.; Cleophax, J.; Gero, S. D.; Vuilhorgne, M. Helv. Chim. Acta, 1983, **66**, 1392.
- 842. Redlich, H.; Neumann, H. J. Chem. Ber., 1981, 114, 2029.
- 843. Liptak, A.; Kerekgyarto, J.; Popsavin, V.; Peredy, M.; Radics, L. J. Carbohydr. Chem., 1988, **7**, 337.
- 844. Majetich, G.; Defauw, J.; Ringold, C. J. Org. Chem., 1988, 53, 50.
- 845. Anderson, P. S.; Baldwin, J. J.; McClure, D. E.; Londell, G. F.; Jones, J. H. J. Org. Chem., 1982, 47, 2184.
- 846. Turecek, F. Coll. Czech. Chem. Commun., 1982, 47, 858.
- 847. Ireland, R. E.; Thompson, W. J.; Srouji, G. H.; Etter, R. J. Org. Chem., 1981, 46, 4863.
- 848. Anderson, R. C.; Fraser-Reid, B. J. Org. Chem., 1985, 50, 4786.
- 849. Gemot, A.; Florent, J. C.; Monneut, C. J. Org. Chem., 1987, 52, 1057.
- 850. Gibbons, E. G. J. Org. Chem., 1980, 45, 1540.
- 851. Lambardo, L.; Mander, L. M. J. Org. Chem., 1983, 48, 2300.
- Battersby, A. R.; McDonald, E.; Redfern, J. R.; Staunton, J.; Wightman, R. H. J. Chem Soc., Perkin Trans. 1, 1976, 266.
- 853. Rahman, M. A.; Kelly, D. R.; Ravi, P.; Underwood, R.; Fraser-Reid, B. Tetrahedron Lett., 1986, **41**, 2409.
- 854. Paquette, L. A.; Maynard, G. D.; Ra, C. S.; Hoppe, M. J. Org. Chem., 1989, 54, 1408.
- 855. Bakuzis, P.; Bakuzis, M. L. F. J. Org. Chem., 1977, 42, 2362.
- 856. Ando, M.; Sayama, S.; Takase, K. J. Org. Chem., 1985, 50, 251.
- 857. Corey, E. J.; Magriotis, P. A. J. Am. Chem. Soc., 1987, 109, 287.
- 858. Gulge, R.; Shaligram, A. M. Indian. J. Chem., 1985, 24B, 605.
- 859. Jackson, W. P.; Ley, S. V. J. Chem Soc., Perkin Trans. 1, 1981, 1516.
- 860. Piers, E.; Abeyeskara, B. F.; Herbert, D. J.; Suckling, I. D. Can. J. Chem., 1985, 63, 3418.
- 861. Bornack, W. K.; Bhaguat, S. S.; Ponton, J.; Helquist, P. J. Am. Chem. Soc., 1981, **103**, 4647.
- 862. Bailey, S. J.; Thomas, E. J.; Vather, S. M.; Wallis, J. J. Chem Soc., Perkin Trans. 1, 1983, 851.

- 863. Lo, V. M.; Shiao, M. J. Synth. Commun., 1986, 16, 1647.
- 864. Svirskaya, P. I.; Leznoff, C. C. Synth. Commun., 1980, 10, 391.
- 865. Sudwecks, W. B.; Broadbent, H. S. J. Org. Chem., 1975, 40, 1131.
- 866. Snider, B. B.; Kirk, T. C. J. Am. Chem. Soc., 1983, 2364.
- 867. Corey, E. J.; Kang, M.; Desai, M. C.; Ghosh, A. K.; Houpis, I. M. J. Am. Chem. Soc., 1988, **110**, 649.
- 868. Nelson, L.; Gomez, L.; Barreiro, E. J. J. Chem. Res., 1983, 5, 312.
- 869. Welch, S. C.; Walters, R. L. J. Org. Chem., 1974, 39, 2665.
- 870. Fernández, B.; Martínez-Pérez, J. A.; Granja, J. R.; Castedo, L.; Mouriño, A. J. Org. Chem., 1992, **57**, 3173.
- 871. Snowden, R. L.; Sonnay, P.; Ohloff, G. Helv. Chim. Acta, 1981, 64, 25.
- 872. Milgrom, L. R. J. Chem Soc., Perkin Trans. 1, 1984, 1483.
- 873. Trivedi, S. V.; Mamdapur, V. R. Indian J. Chem., 1986, 25B, 176.
- 874. Wilcox, C. F.; Blain, D. A.; Clardy, J.; Xu C. F. J. Org. Chem., 1987, **52**, 2635.
- 875. Zimmerman, H. E.; Little, R. D. J. Am. Chem. Soc., 1974, 96, 4624.
- 876. Oliver, M. J.; Patney, H. K.; Paddon-Row, M. H. Aust. J. Chem., 1980, 33, 795.
- 877. Hill, R. K.; Cullison, D. A. J. Am. Chem. Soc., 1973, 95, 1229.
- 878. Baxter, A. J. G.; Holmes, A. B. J. Chem Soc., Perkin Trans. 1, 1977, 2343.
- 879. Hunter, W. H.; Tupper, D. E. J. Chem Soc., Perkin Trans. 1, 1987, 207.
- 880. Mandal, S. B.; Pakrashi, S. C. Heterocycles, 1985, 23, 931.
- 881. Deslongchamps, D.; Cheriyan, U. O.; Lambert, Y.; Mercier, J. C.; Ruest, L.; Russo, R.; Soucy, P. Can. J. Chem., 1978, 56, 1687.
- 882. Eguchi, S.; Furukawa, Y.; Suzuki, T.; Kondo, K.; Sasaki, T.; Honda, M.; Katayama, C.; Tanaka, J. J. Org. Chem., 1985, **50**, 1895.
- 883. Heathcock, C. H.; White, C. T.; Morrison, J. J.; Derveer, P. V. J. Org. Chem., 1981, 46, 1296.
- 884. Ireland, R. E.; Grand, P. S.; Dickerson, R. E.; Bordner, J.; Rydjeski, D.
   R. J. Org. Chem., 1970, 35, 570.
- 885. Cambie, R. C.; Dalmer, B. D. Aust. J. Chem., 1982, 35, 601.
- 886. Yamamoto, H.; Nakamura, Y.; Kawamoto, H.; Inokawa, S.; Yamashita,M. Carbohydr. Res., 1982, **102**, 185.
- 887. Battersby, A. R.; Baker, M. G.; Broadbent, A. A.; Fooker, C. J. R.; Leeper, F. J. J. Chem Soc., Perkin Trans. 1, 1987, 2027.
- 888. Mori, K.; Takechi, S. Tetrahedron, 1985, 41, 3049.
- 889. Brimacombe, J. S.; Kabik, A. K.; Taylor, I. D. Carbohydr. Res., 1985, 140, C9.

- 890. Brimacombe, J. S.; Hanna, R.; Kabir, A.; Bennet, F.; Taylor, I. D. J. Chem Soc., Perkin Trans. 1, 1986, 815.
- 891. Brimacombe, J. S.; Hanna, R.; Kabir, A. K. S. J. Chem Soc., Perkin Trans. 1, 1986, 823.
- 892. Bell, R. A.; Gravestrock, M. B.; Taguchi, V. Y. Can. J. Chem., 1972, 50, 3749.
- 893. Somoza, C.; Darias, J.; Ruveda, E. A.; J. Org. Chem., 1989, 54, 1539.
- 894. Coxon, D. T.; Price, K. A.; Howard, B.; Curtis, R. F. J. Chem Soc., Perkin Trans. 1, 1977, 53.
- 895. Greenlee, M. L. J. Am. Chem. Soc., 1981, 103, 2425.
- 896. Maturana, H.; López, J.; Cortés, M. Synth. Commun., 1991, 21, 1533.
- 897. Klausener, A.; Runsink, J.; Scharf, H.-D. Liebigs. Ann. Chem., 1984, 783.
- 898. Liu, H. J.; Ramani, B. Tetrahedron Lett., 1988, 29, 6721.
- 899. Cambie, R. C.; Palmer, B. D. Aust. J. Chem., 1981, 34, 1265.
- 900. Meinwald, J.; Wheeler, T. N. J. Am. Chem. Soc., 1970, 92, 1009.
- 901. Mori, K.; Ueda, H. Tetrahedron Lett., 1981, 22, 461.
- 902. Knight, D. W.; Ojhara, B. Tetrahedron Lett., 1981, 22, 5101.
- 903. Mori, K.; Ueda, H. Tetrahedron, 1982, 38, 1227.
- 904. Knight, D. W.; Ojhara, B. J. Chem Soc., Perkin Trans. 1, 1983, 955.
- 905. Rossi, R.; Carpita, A. Tetrahedron, 1977, 33, 2447.
- 906. Mori, K.; Suguro, T.; Uchida, M. Tetrahedron, 1978, 34, 3119.
- 907. Rossi, R.; Salvadori, P. A.; Carpita, A.; Niccoli, A. Tetrahedron, 1979, 35, 2039.
- 908. Weichert, J. P.; Longino, M. A.; Schwender, S. W.; Counsel, R. E. J. Med. Chem., 1986, **29**, 1674.
- 909. Bartlett, D. A.; Johnson, W. S.; Elliot, J. D. J. Am. Chem. Soc., 1983, 105, 2088.
- 910. Mali, R. S.; Pohmakotv, M.; Weidman, B.; Seebach, D. Liebigs. Ann. Chem., 1981, 2272.
- 911. Sahali, Y.; Skipper, P. L.; Tannerbaum, S. R. J. Org. Chem., 1990, **55**, 2918.
- 912. Bremmer, M. L; Khatri, N. A.; Weinreb, S. M. J. Org. Chem., 1983, **48**, 3661.
- 913. Harwood, L. M.; Hodgkinson, L. C.; Sutherland, J. K. J. Chem Soc., Chem. Commun., 1978, 712.
- 914. Blatcher, P. Warren, S. J. Chem Soc., Perkin Trans. 1, 1979, 1074.
- 915. Schultz, A. G.; McMahon, W. G.; Kullnig, R. K. J. Org. Chem., 1987, **52**, 3905.

- 916. Narasimhan, N. S.; Bapat, C. P. J. Chem Soc., Perkin Trans. 1, 1984, 1435.
- 917. Kametani, T.; Honda, T.; Shiratori, Y.; Fukomoto, K. Tetrahedron Lett., 1980, **21**, 1665.
- 918. Zefinov, N. S.; Kozmin, A. S.; Kirin, V. M.; Sedov, B. B.; Ragu, V. G. Tetrahedron Lett., 1980, 1667.
- 919. Mondon, A.; Epi, M.; Wolff, C.; Claisen, T.; Vilhuber, H. G. Chem. Ber., 1979, **112**, 1126.
- 920. Lemoir, D.; Frank, R. M. Chem. Ber., 1981, 114, 3336.
- 921. Sinha, G.; Maji, S. K.; Ghatak, U. R.; Mukherjee, M.; Mukherjee, A. K.; Chakravarty, A. K. J. Chem Soc., Perkin Trans. 1, 1983, 2519.
- 922. Gravestock, M. B.; Johnson, W. S.; Myers, R. F.; Bryson, T. A.; Miles, D. H.; Ratcliffe, B. E. J. Am. Chem. Soc., 1978, **100**, 4268.
- 923. Yamashito, A.; Toy, A.; Scahill, T. A. J. Org. Chem., 1989, 54, 3625.
- 924. Marshall, J.; Crooks, S. L.; DeHoff, B. S. J. Org. Chem., 1988, 53, 1616.
- 925. Manners, G. D.; Wong, R. Y. J. Chem. Soc., Perkin Trans. 1, 1981, 1849.
- 926. Stojanac, N.; Stojanac, Z.; White, P. S.; Valenta, Z. Can. J. Chem., 1979, 57, 3346.
- 927. Burnell, R. H.; DuFour, J. M. Can. J. Chem., 1987, 65, 21.
- 928. Mabuni, C. T.; Garlaschelli, L.; Ellison, R. A.; Hutchinson, C. R. J. Am. Chem. Soc., 1979, **101**, 707.
- 929. Kraus, G. A.; Tashner, M. J. J. Org. Chem., 1980, 45, 1176.
- 930. Kaneko, T.; Schmitz, H.; Essery, J. M.; Rose, W.; Howell, H. G.;
  O'Herron, F. A.; Nachfolger, S.; Huftalen, J.; Bradner, W. T.; Partyka, R. A.; Doyle, T. W.; Davies, J.; Cundliffe, E. J. Med. Chem., 1982, 25, 579.
- 931. Patel, D. V.; Van Middlesworth, F.; Danaubauer, J.; Gannett, P.; Sih, C. J. J. Am. Chem. Soc., 1986, **108**, 4603.
- 932. Kienzle, F. Helv. Chim. Acta, 1980, 63, 563.
- 933. Bestmann, H. J.; Vostrowski, O.; Paulus, H.; Billmann, W.; Stransky, W. Tetrahedron Lett., 1977, **1**, 121.
- 934. Lansbury, P. T.; Serelis, A. K.; Hengeveld, J. E.; Hangauer, D. G. Tetrahedron, 1980, **36**, 2701.
- 935. Deutsch, E. A.; Snider, B. B. J. Org. Chem., 1982, 47, 2682.
- 936. Coates, R. M.; Robinson, W. H. J. Am. Chem. Soc., 1971, 93, 1785.
- 937. Wovkulich, P. M.; Bagglioni, E. G.; Hennessy, B. M.; Uskokovic, M. R.; Mayer, E.; Norman, A. W. J. Org. Chem., 1983, 48, 4436.
- 938. Larock, R. C.; Leach, D. R. J. Org. Chem., 1984, 49, 2144.
- 939. Hall, S. E.; Roush, W. R. J. Org. Chem., 1982, 47, 4611.

- 940. Colombo, M. I.; Zinczuk, J.; Bacigaluppo, J. A.; Somoza, C.; Ruveda, E. A. J. Org. Chem., 1990, **55**, 5631.
- 941. Coates, R. M.; Johnson, M. W. J. Org. Chem., 1980, 45, 2685.
- 942. Grieco, P. A.; Kanai, K.; Williams, E. Heterocycles, 1979, 12, 1623.
- 943. Hancock, W. S.; Mander, L. N.; Massey-Westrop, R. S. J. Org. Chem., 1973, **38**, 4091.
- 944. Peterson, P. E.; Breedlove-Leflew, R. L.; Jensen, B. L. J. Org. Chem., 1986, **51**, 1948.
- 945. Baggliolinni, E. G.; Iacobelli, J. A.; Hennessy, B. M.; Batcho, A. D.; Sereno, J. F.; Uskokovic, M. R. J. Org. Chem., 1986, **51**, 3098.
- 946. Sheu, J.; Yen, C.; Huang, H.; Hong, Y. V. J. Org. Chem., 1989, **54**, 5126.
- 947. Schreiber, S. L.; Hoveyda, A. H. J. Am. Chem. Soc., 1984, 106, 7200.
- 948. Finch, N.; Fitt, J. J.; Hsu, I. H. S. J. Org. Chem., 1975, 40, 206.
- 949. Brown, H. C.; Kulkarni, S. U.; Rao, C. G. Synthesis, 1980, 151.
- 950. Ballini, R.; Petrini, M.; Rosini, G. J. Org. Chem., 1990, 55, 5159.
- 951. Murai, A.; Abiko, A.; Masamune, T. Tetrahedron Lett., 1984, 25, 4955.
- 952. Newman, M. S.; Hussain, N. S. J. Org. Chem., 1982, 47, 2837.
- 953. Confalone, P. N.; Huie, E. M. J. Org. Chem., 1987, 52, 79.
- 954. Zimmerman, H. E.; Pasteur, R. J. J. Org. Chem., 1980, 45, 4876.
- 955. Van der Eycken, J.; De Clerq, P.; Vandewalle, M. Tetrahedron, 1986,
   42, 4285.
- 956. Khatri, N. A.; Schmitthenner, H. F.; Shringarpure, J.; Weinreb, S. M. J. Am. Chem. Soc., 1981, **103**, 6387.
- 957. Just, G.; Zamboni, R. Can. J. Chem., 1978, 56, 2720.
- 958. Keith, D. D.; Tortora, J. A.; Ineichen, K.; Leimgruber, W. Tetrahedron, 1975, **31**, 2633.
- 959. Lischewski, M.; Adam, G. Tetrahedron, 1980, 36, 1237.
- 960. Boger, D. L.; Patel, M.; Takusagawa, F. J. Org. Chem., 1985, 50, 1911.
- 961. Daniewski, A. R. J. Org. Chem., 1975, 40, 3124.
- 962. Daniewski, A. R. J. Org. Chem., 1975, 40, 3127.
- 963. Harrison, P. J. Tetrahedron Lett., 1989, 30, 7125.
- 964. Johnson, W. S.; Gravestock, M. B.; Parry, R. J.; Myers, R. F.; Bryson, T. A.; Miles, D. J. Am. Chem. Soc., 1971, **93**, 4330.
- 965. Torii, S.; Uneyama, K.; Kawahara, I. Bull. Chem. Soc. Jpn., 1978, **51**, 949.
- 966. Mastalerz, H.; Morand, P. J. Chem Soc., Perkin Trans. 1, 1982, 2611.
- 967. Daniewski, A. R.; Guzewska, M.; Kocor, M. J. Org. Chem., 1978, **43**, 349.

- 968. Danishefsky, S.; Barbachyn, M. J. Am. Chem. Soc., 1985, 107, 7761.
- 969. Halmos, T.; Komitos, D.; Antonakis, K. Carbohydr. Res., 1986, 156, 256.
- 970. Jones, J. B.; Gordon, K. D. Can. J. Chem., 1972, 50, 2712.
- 971. Cox, P. J.; Turner, A. B. Tetrahedron, 1984, 40, 3153.
- 972. Marshall, J. A.; Audia, J. E.; Shearer, B. G. J. Org. Chem., 1986, **51**, 1730.
- 973. Monti, M.; Corriol C.; Bertrand, M. Tetrahedron Lett., 1982, 23, 5539.
- 974. Lansbury, P. T.; Nickson, T. E. Tetrahedron Lett., 1982, 23, 2627.
- 975. Iseki, K.; Yamazaki, M.; Shibasaki, M.; Ikegami, S. Tetrahedron, 1981, **37**, 4411.
- 976. Niwa, H.; Hasegawa, T.; Ban, N.; Yamada, K. Tetrahedron Lett., 1984, **25**, 2797.
- 977. Niwa, H.; Hasegawa, T.; Bah, N.; Yamada, K. Tetrahedron, 1987, **43**, 825.
- 978. Carreno, M. C.; Farina, F.; Ruano, J. L. G.; Puebla, L. J. Chem. Res., 1984, **5**, 288.
- 979. Paquette, L. A.; Liao, C. C.; Barson, R. L.; Wingard, R. E.; Shih, C. N.; Fayos, J.; Clardy, J. J. Am. Chem. Soc., 1977, **99**, 6935.
- 980. Ashcroft, A. E.; Sutherland, J. K. J. Chem Soc., Chem. Commun., 1981, 1075.
- 981. Cho, B. P.; Harvey, R. G. J. Org. Chem., 1987, 52, 5668.
- 982. Neuman, M. S.; Sankaran, V.; Olson, D. R. J. Am. Chem. Soc., 1976, 98, 3237.
- 983. Chexal, K. K.; Holker, J. S. E.; Simpson, T. J.; Young, K. J. Chem Soc., Perkin Trans. 1, 1975, 543.
- 984. Mubarak, A. M.; Brown, D. M. J. Chem Soc., Perkin Trans. 1, 1982, 809.
- 985. Sala, T.; Sargent, M. V. J. Chem. Soc., Perkin Trans. 1, 1979, 2593.
- 986. Srikrishna, A.; Hemamalini, P.; Sharma, G. V. R.; J. Org. Chem., 1993, 58, 2509.
- 987. Bruckner, C.; Ressig, H. U. J. Org. Chem., 1988, 53, 2440.
- 988. Overman, L. E.; Jacobsen, E. J. J. Am. Chem. Soc., 1982, 104, 7225.
- 989. Paquette, L. A.; Balogh, D. W.; Ternasky, R. J.; Begley, W. J.; Banwell, M. G. J. Org. Chem., 1983, 48, 3282.
- 990. Singh, A. K. Synth. Commun., 1983, 13, 919.
- 991. Freeman, F.; Kim, D. S. H. L. J. Org. Chem., 1992, 57, 1722.
- 992. Eagle, G. A.; Rivett, D. E. A.; J. Chem Soc., Perkin Trans. 1, 1973, 1701.
- 993. McCrindle, R.; Nakamura, E.; Anderson, A. B. J. Chem. Soc., Perkin Trans. 1, 1976, 1590.
- 994. Sherwin, P. F.; Coates, R. M. J. Chem Soc., Chem. Commun., 1982,

- 995. Coates, R. M.; Bertram, E. F. J. Org. Chem., 1971, 36, 2625.
- 996. Coates, R. M.; Bertram, E. F. J. Org. Chem., 1971, 36, 3722.
- 997. Bevins, C. L.; Bantia, S.; Pollack, R. M.; Bounds, P. L.; Kayser, R. H. J. Am. Chem. Soc., 1984, **106**, 4957.
- 998. Corey, E. J.; Moinet, G. J. Am. Chem. Soc., 1973, 95, 7185.
- 999. Pinto, A. C.; de A. Epifanio, R.; Camargo, W. Tetrahedron 1993, **49**, 5039.
- 1000. Ireland, R. E.; Beslin, P.; Giger, R.; Hengantner, U.; Kirst, H. A.; Maag, H. J. Org. Chem., 1977, 42, 1267.
- 1001. Corey, E. J.; Wollenberg, R. H. Tetrahedron Lett., 1976, **51**, 4701.
- 1002. Tadano, K.; Isshiki, Y.; Minami, M.; Ogawa, S. J. Org. Chem., 1993, **58**, 6266.
- 1003. Nagata, W.; Wakabayashi, T.; Narisada, M.; Hayase, Y.; Kamata, S. J. Am. Chem. Soc., 1971, **938**, 5740.
- 1004. Nakano, T.; Martin, A.; Rojas, A. Tetrahedron, 1982, **38**, 1217.
- 1005. Joulain, D.; Rouessac, F.; Garnero, J. Tetrahedron Lett., 1977, **40**, 3585.
- 1006. Nakano, T.; Hernandez, M. I. J. Chem Soc., Perkin Trans. 1, 1983, 135.
- 1007. Marshall, J. A.; Gung, W. Y. Tetrahedron Lett., 1988, 27, 3899.
- 1008. Niwa, H.; Wakamatsu, K.; Hida, T.; Niiyama, K.; Kigoshi, H.; Yamada, M.; Nagase, H.; Suzuki, M.; Yamada, K. J. Am. Chem. Soc., 1984, **106**, 4547.
- 1009. Vlad, P. F.; Ungul, N. D.; Koltsa, M. N. Tetrahedron, 1983, 39, 3947.
- 1010. Burke, S. D.; Cobb, J. E.; Takeuchi, K. J. Org. Chem., 1990, **55**, 2138.
- 1011. Just, G.; Luther, C. Tetrahedron Lett., 1982, 23, 1331.
- 1012. Cardonna, M. L.; Fernandez, I.; Garcia, M. B.; Pedro, J. R. Tetrahedron, 1986, **42**, 2725.
- 1013. Ihara, M.; Takahashi, T.; Shimizu, N.; Ishida, Y.; Sudow, I.; Fukumoto, K.; Kametani, T. J. Chem Soc., Chem. Commun., 1987, 1467.
- 1014. Kern, W.; Lutz, A.; Spiteller, G.; Zeller, W. J. Angew. Chem. Int. Ed. Engl., 1992, **31**, 64.
- 1015. Poulter, C. D.; Aoki, T.; Daniels, L J. Am. Chem. Soc., 1988, **110**, 2620.
- 1016. Johnson, W. S.; Edington, C.; Elliot, J. D.; Silverman, I. R. J. Am. Chem. Soc., 1984, **106**, 7588.
- 1017. Anand, R. C.; Ranjan, H. Bull. Chem. Soc. Jpn., 1983, 56, 1889.
- 1018. Guella, G. Amade, P.; Pietra, F. Helv. Chim. Acta, 1986, 69, 726.
- 1019. Zimmerman, H. E.; Nuss, J. M. J. Org. Chem., 1986, 51, 4604.
- 1020. Verboom, W.; Visser, G. W.; Reinhoudt, D. N. Tetrahedron, 1982, 38,

- 1021. Krohn, K.; Radeloff, M. Chem. Ber., 1978, 111, 3823.
- 1022. Corey, E. J.; Albonico, S. M.; Koelliker, U.; Schaaf, T. K.; Varma, R. K. J. Am. Chem. Soc., 1971, **93**, 1491.
- 1023. Guzman, A.; Martinez, E.; Velarde, E.; Maddox, M. L; Muchowski, J. M. Can. J. Chem., 1987, **65**, 2164.
- 1024. Keck, G. E.; Boden, E.; Sonnewald, U. Tetrahedron Lett., 1981, **22**, 2615.
- 1025. Hua, D. H.; Saha, S.; Roche, D.; Maeng, J. C.; Iguchi, S.; Baldwin, C. J. Org. Chem., 1992, **57**, 399.
- 1026. Wuts, P. G. M.; Bigelow, S. S. J. Org. Chem., 1983, 48, 3489.
- 1027. Hanaoka, M.; Nagami, K.; Imanishi, T. Heterocycles, 1979, 12, 497.
- 1028. Ziegler, F. E.; Gilligan, P. J. J. Org. Chem., 1981, 46, 3874.
- 1029. Heissler, D.; Jung, F.; Vevert, J. P.; Riehl, J. J. Tetrahedron Lett., 1976, 4879.
- 1030. Knapp, S.; Hale, J. J.; Boston, M.; Gibson, F. S. Tetrahedron Lett., 1990, 31, 2109.
- 1031. Kozikowski, A. P.; Nieduzak, T. R.; Konoike, T.; Springer, J. P. J. Am. Chem. Soc., 1987, **109**, 5167.
- 1032. Ziegler, F. E.; Wang, T. F. Tetrahedron Lett., 1981, **22**, 1179.
- 1033. Schuda, P. F.; Heimann, M. R. Tetrahedron, 1984, 40, 2365.
- 1034. Lombardo, L.; Mander, L. N.; Turner, J. V. J. Am. Chem. Soc., 1980, **102**, 6626.
- 1035. Matsumoto, T.; Usui, S.; Kawashima, M.; Mitsuki, M. Bull. Chem. Soc. Jpn., 1981, **54**, 581.
- 1036. Papillaud, B.; Titon, F.; Taran, M.; Arreguy, B.; Delmond, B. Tetrahedron, 1985, **41**, 1845.
- 1037. Chakraborty, R.; Simpkins, N. S. Tetrahedron, 1991, **47**, 7689.
- 1038. Marshall, J. A.; DeHoff, B. S. Tetrahedron Lett., 1987, 43, 4849.
- 1039. Kerwin, S. M.; Paul, A. G.; Heathcock, C. H. J. Org. Chem., 1987, **52**, 1686.
- 1040. Campbell, M. M.; Craig, R. C.; Boyd, A. C.; Gilbert, I. M.; Redpath, J.; Roy, R. G.; Savage, D. S.; Sleigh, T. J. Chem Soc., Perkin Trans. 1, 1978, 2235.
- 1041. Hu, Y.; Zorumski, C. F.; Covey, D. F. J. Med. Chem., 1993, 36, 3956.
- 1042. Kulkarni, B. A.; Chattopadhyay, S.; Chattopadhyay, A.; Mamdapur, V. R. J. Org. Chem., 1993, 58, 5964.
- 1043. Tanis, S. P.; Chuang, Y. H.; Head, D. B. Tetrahedron Lett., 1985, **26**, 6147.

- 1044. Tanis, S. P.; Chuang, Y. H.; Head, D. B. J. Org. Chem., 1988, 53, 4929.
- 1045. Sardina, F. J.; Mourino, A.; Castedo, L. J. Org. Chem., 1986, 51, 1264.
- 1046. Burke, S. D.; Murtiashaw, C. W.; Oplinger, J. A. Tetrahedron Lett., 1983, 24, 2949.
- 1047. Ross, R. J.; Paquette, L. A. J. Org. Chem., 1987, **52**, 5498.
- 1048. Uyehara, T.; Furuta, T.; Kabawawa, Y.; Yamada, J.; Kato, T.; Yamamoto, Y. J. Org. Chem., 1988, **53**, 3669.
- 1049. Rice, J. E.; LaVoie, E. J.; McCaustland, D. J.; Fischer, D. L.; Wiley, J. C. Jr. J. Org. Chem., 1986, **51**, 2428.
- 1050. Amrein, W.; Schaffner, K. Helv. Chim. Acta, 1975, 58, 381.
- 1051. Hauser, F. M.; Hewawasam, P. J. Org. Chem., 1988, 53, 4515.
- 1052. Sala, T.; Sargent, M. V. J. Chem Soc., Perkin Trans. 1, 1981, 877.
- 1053. Pyne, S. G.; Hensel, M. J.; Fuchs, P. L. J. Am. Chem. Soc., 1982, **104**, 5719.
- 1054. Field, G. F.; Zally, W. J.; Sternbach, L. H.; Blount, J. F. J. Org. Chem., 1976, **41**, 3853.
- 1055. Philips, G. H.; Bailey, E. J.; Bain, B. M.; Borella, R. A.; Buckton, J. B.; Clark, J. C.; Doherty, A. E.; English, A. F.; Fazakerley, H.; Laing, S. B.; Lane-Allman, E.; Robinson, J. D.; Sandford, P. E.; Sanrrott, P. J.; Steeples, I. P.; Stonehouse, R. D.; Williamson, C. J. Med. Chem., 1994, **37**, 3717.
- 1056. Cava, M. P.; Laksmikantham, M. V.; Talapatra, S. K.; Yates, P.; Rae, I. D.; Rosenberger, M.; Szabo, A. G.; Douglas, B.; Weisback, J. A. Can. J. Chem., 1973, **51**, 3102.
- 1057. Hauser, F. M.; Caringal, Y. J. Org. Chem., 1990, 55, 555.
- 1058. Pitt, C. G.; Rector, D. H.; Cook, C. E.; Wani, M. C. J. Med. Chem., 1979, 22, 966.
- 1059. Tolf, B. R.; Crowe, D. F.; Johansson, J. G.; Peters, R. H.; Tanabe, M. Tetrahedron Lett., 1984, **25**, 4855.
- 1060. Lenz, G. R. Tetrahedron, 1979, 35, 2613.
- 1061. Wuts, P. G. M.; Ritter, A. R. J. Org. Chem., 1989, 54, 5180.
- 1062. Marshall, J. A.; Robinson, E. D.; Lebreton, J. J. Org. Chem., 1990, **55**, 227.
- 1063. Garcia-Granados, A.; Parra, A. Tetrahedron, 1991, 47, 9103.
- 1064. Piers, E.; Button, R. W.; Keziere, R. J.; Smillie, R. D. Can. J. Chem., 1971, **49**, 2620.
- 1065. Piers, E.; Britton, R. W.; Geraghty, M. B.; Keziere, R. J.; Kido, F. Can. J. Chem., 1975, **53**, 2838.
- 1066. Corey, E. J.; Behforouz, M.; Ishiguro, M. J. Am. Chem. Soc., 1979, **101**, 1608.

- 1067. Bhat, S. V.; Bajwa, B. S.; Dornauer, H.; Souza, N. J. J. Chem Soc., Perkin Trans. 1, 1982, 767.
- 1068. Trost, B. M.; Nishimura, Y.; Yamamoto, K.; McElvain, S. S. J. Am. Chem. Soc., 1979, **101**, 1330.
- 1069. Madden, B. A.; Prestwich, G. D. J. Org. Chem., 1994, 59, 5488.
- 1070. Kiong, L. S.; Tyman, J. H. P. J. Chem Soc., Perkin Trans. 1, 1981, 1942.
- 1071. Yankee, E. W.; Axen, U.; Bundy, G. L. J. Am. Chem. Soc., 1974, **96**, 5865.
- 1072. Gill, M.; Rickards, R. W. Aust. J. Chem., 1981, 34, 1063.
- 1073. Semmelhack, M. F.; Tomoda, S. J. Am. Chem. Soc., 1981, 103, 2427.
- 1074. Corey, E. J.; Shibasaki, M.; Nicolaou, K. C.; Malmsten, C. L.; Samuelsson, B. Tetrahedron Lett., 1976, **10**, 737.
- 1075. Deshpande, V. H.; Upadhye, B. K.; Wakharkar, R. D. Tetrahedron Lett., 1989, **30**, 1991.
- 1076. Schmidt, G.; Hofheinz, W. J. Am. Chem. Soc., 1983, **105**, 624.
- 1077. Cossio, F. D.; Aizpurua, J. M.; Palomo, C. Can. J. Chem., 1986, 64, 225.
- 1078. Chorvat, R. J.; Desai, B. M.; Radak, S. E.; McLaughlin, K. T.; Miller, J. E. J. Med. Chem., 1985, **28**, 194.
- 1079. Pyne, S. G.; Hensel, M. J.; Byrn, S. R.; McKenzie, A. T.; Fuchs, P. L. J. Am. Chem. Soc., 1980, **102**, 5962.
- 1080. Bosworth, N.; Magnus, P. D. J. Chem Soc., Perkin Trans. 1, 1973, 76.
- 1081. Yamamoto, H.; Hosoyamada, C.; Kawamoto, H.; Inokawa, S.; Yamashita, H. Carbohydr. Res., 1982, **102**, 159.
- 1082. McElroys, A. B.; Warren, S. Tetrahedron Lett., 1985, 26, 1677.
- 1083. Barrish, J. C.; Lee, H. L.; Mitt, T.; Pizzolato, G.; Baggiolini, E. G.; Uskokovic, M. R. J. Org. Chem., 1988, **53**, 4282.
- 1084. Gerlach, H.; Thalmann, A. Helv. Chim. Acta, 1977, 60, 2866.
- 1085. Conrad, P. C.; Fuchs, P. L. J. Am. Chem. Soc., 1978, 100, 346.
- 1086. Lenz, G. R.; Dorn, C. R. J. Org. Chem., 1983, 48, 2696.
- 1087. Marinier, A.; Deslongchamps, P. Tetrahedron Lett., 1988, 29, 6215.
- 1088. Cooley, G.; Kirk, D. M. J. Chem Soc., Perkin Trans. 1, 1984, 1205.
- 1089. Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pilli, R.; Baderschen, U. J. Org. Chem., 1985, **50**, 2095.
- 1090. Vanderah, D. J.; Djerassi, C. J. Org. Chem., 1978, 43, 1442.
- 1091. Fraser-Reid, B.; Magdzinski, L.; Molino, B. F.; Mootoo, D. R. J. Org. Chem., 1987, **52**, 4495.
- 1092. Kitahara, T.; Mori, K. Tetrahedron, 1984, 40, 2935.
- 1093. Kitahara, T.; Mori, K. Tetrahedron Lett., 1979, **32**, 3021.
- 1094. De Lera, A.; Saá, J. M.; Suau, R.; Castedo, L. J. Heterocycl. Chem.,

1987, **24**, 613.

- 1095. Nitta, M.; Sugiyama, H. Bull. Chem. Soc. Jpn., 1982, 55, 1127.
- 1096. Fish, R. H.; Broline, B. M. J. Organomet. Chem., 1977, 136, C-41.
- 1097. Katano, K.; Chang, P.; Millar, A.; Pozsgay, V.; Minster, D.; Ohgi, T.; Hecht, S. M. J. Org. Chem., 1985, **50**, 5807.
- 1098. Jensen, N. P.; Brown, R. D.; Schmitt, S. M.; Windholz, T.; Patchett, A. A. J. Org. Chem., 1972, **37**, 1639.
- 1099. Whitesell, J. K.; Buchanan, C. M. J. Org. Chem., 1986, **51**, 5443.
- 1100. Swaminathan, S.; Bakshi, R. K.; Dev, S. Tetrahedron, 1987, 43, 3827.
- 1101. Evidente, A.; Randazzo, G.; Ballo, A. Tetrahedron, 1982, 38, 3169.
- 1102. Colombo, L.; Gennari, C.; Potenza, D.; Scholastico, C.; Aragozzini, F. J. Chem Soc., Chem. Commun., 1979, 1021.
- 1103. Nagaoka, H.; Shibuya, Y.; Yamada, Y. Tetrahedron 1994, 50, 661.
- 1104. Bégué, J.; Lefort, D.; Thac, T. D. J. Chem Soc., Chem. Commun., 1981, 1086.
- 1105. Henderson, M. A.; Heathcock C. H. J. Org. Chem., 1988, 53, 4736.
- 1106. Boger, D. L.; Jacobson, I. C. J. Org. Chem., 1990, 55, 1919.
- 1107. Wilt, J. W.; Curtis, V. A.; Yang, C. O. J. Org. Chem., 1982, 47, 3721.
- 1108. Yoshii, E.; Oribe, T.; Tumura, K.; Koizumi, T. J. Org. Chem., 1978, **43**, 3946.
- 1109. Tadano, K.; Hishino, M.; Ogawa, S.; Suami, T. J. Org. Chem., 1988, **53**, 1427.
- 1110. Hamilton, R. G.; McLean, S. Can. J. Chem., 1981, 59, 215.
- 1111. Mazur, P.; Nakanishi, K. J. Org. Chem., 1992, 57, 1047.
- 1112. Tietze, L. F.; Henke, S.; Bartels, C. Tetrahedron, 1988, 44, 7145.
- 1113. DaSilva, E. D.; Scheuer, P. J. Tetrahedron Lett., 1981, 22, 3147.
- 1114. Gibbons, E. G. J. Am. Chem. Soc., 1982, 104, 1767.
- 1115. Ohuchida, S.; Hamanaka, N.; Hayashi, M. Tetrahedron, 1983, 39, 4263.
- 1116. Yankee, E. W.; Bundy, G. L. J. Am. Chem. Soc., 1972, 94, 3652.
- 1117. Baret, P.; Barreiro, E.; Greene, A. E.; Luche, J. L.; Texeira, M. A.; Crabbé, P. Tetrahedron, 1979, **35**, 2931.

# The Retro–Diels–Alder Reaction Part II. Dienophiles with One or More Heteroatom

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# 1. Introduction

This review (Part II) is topically organized around the dienophile that is generated in a retro [4 + 2] reaction, and to the extent possible follows the principles adopted for Part I, which covers reactions in which both dienophile bonding centers are carbon atoms. (1) The present chapter encompasses retro–Diels–Alder (rDA) reactions in which one or both of the dienophile reaction centers are heteroatoms, as illustrated.



Any of the other atoms in the starting material (cycloadduct) may be carbon or heteroatom. Substituents on all positions are encompassed, and any bond order available to any oxidation state of an element is included, as is bonding to non-nearest neighbor atoms (e.g., bicyclics).

The reader is directed to Part I for general discussion of the rDA reaction, the features that affect rates and outcome, and the use of acids, bases, other catalysts, and scavengers. Certain subclassifications (e.g., processes proposed under MS conditions, polymer applications) of rDA reactions have been omitted from both sections; these topics are listed in the Introduction to Part I. Citations to over 100 reviews on various aspects of the rDA reaction are collected at the beginning of the References to Part I. Those that are especially pertinent to Part II will be repeated here, in the context of the particular dienophile under discussion.

# 1.1.1. Literature Coverage

The decision to split the review of the rDA reaction into two parts was based on the volume of literature encountered, as outlined in the Introduction to Part I. Active literature searching was concluded for both Parts in April 1995, although occasional more recent references have been included.

# 2. Mechanism

The expelled dienophiles described in this chapter include some very stable species such as  $CO_2$  and  $N_2$ , for which there are no known examples of reversibility, i.e., no DA reactions have been described for these species. There is relatively little mechanistic information on the rDA reactions of these simple dienophiles, but the studies that have been carried out are discussed in the context of the particular dienophile. To the extent that generalization is possible, heteroatom-containing dienophiles are expelled more rapidly than their all-carbon analogs in rDA reactions.

The polarity of functional groups such as nitrile and carbonyl is such that one might expect a significant effect on mechanism when these groups are formed as dienophiles. However, there is no evidence to suggest that the commonly accepted rDA reaction mechanism, a concerted but usually nonsynchronous bond reordering, is altered by the inclusion of a heteroatom in the expelled dienophile. The more extensive discussion of Mechanism in Part I also pertains to the topics of this section.

# 3. Scope and Limitations

The discussion in this section follows the order chosen for the Tables, with subsections on each major dienophile or general reactant type, beginning with the several classes of rDA reactions that generate nitriles (Table I). To assist the reader in locating the tabulated information on a particular kind of rDA reaction, comments about organizational principles are included in the introductory comments of some sections, in addition to the general discussion in the Organization of Tables section. The general order is: dienophiles with one C-atom are treated first, with heteroatom N (starting with nitriles) before O, then other heteroatoms in order of increasing atomic number, and finally those reactions in which both dienophile centers are heteroatoms.

## 3.1.1. Nitriles as Expelled Dienophiles

The cyano functional group rarely serves as a dienophile in DA reactions, and then generally only under forcing conditions. In contrast, rDA expulsion of HCN and RCN from cycloadducts (usually prepared by non-DA or alternative DA routes) is quite common, and of considerable synthetic value. The large number of such reactions suggested that further subdivision of the tabulated data would be useful. This has been done in four parts, as shown in the Table of Contents and by the headings below.

## 3.1.1.1. Nitriles from Miscellaneous Reactions (Table I-A)

Although only a few examples of (formal) cyclopentadiene (CP) adducts of nitriles have been described, the parent HCN analog has been prepared and shown to decompose readily at 25°. (2)

$$\frac{1}{t_{1/2} = ca. 0.5 \text{ h}} \text{HCN} + \text{CP}$$

The alkyl(aryl)sulfonyl cyanide analog has recently been described, and is reported to give *reversible* DA-rDA reaction with CP. (3)

Low temperature irradiation of pyridine leads, presumably via the bicyclic

intermediate depicted, to HCN and cyclobutadiene. (4) As usual, the distinction between an r[2 + 2] and r[4 + 2] reaction is lost when cyclobutadiene is formed.



High temperature pyrolysis or irradiation of maleic anhydride derivatives may lead to loss of CO and  $CO_2$ , with concomitant formation of new unsaturation. When applied to a highly arylated pyridine, the presumed aryne intermediate gives a formal rDA reaction, a conclusion supported by the product specificity. (5)



Most of the remaining examples of "miscellaneous" rDA reactions that generate nitriles involve pyridines that contain additional ring heteroatoms. A few reactions of aza-azulenes with acetylenic dienophiles complete the relatively short Table I-A.

#### 3.1.1.2. Nitriles from Oxazoles and Related Ring Systems (Table I-B)

The general process described in this section utilizes a DA reaction between a five-membered ring aromatic heterocycle and an acetylenic dienophile to give a (reactive) intermediate that expels a nitrile or HCN to form a new heterocyclic product. The process is shown in simplest form for dienes in which X = NR (no NH examples are known), O, or S.



Reactions of this kind are unknown for the parent heterocycles imidazole, oxazole, and thiazole with any acetylenic dienophile. Very few examples have been reported for imidazoles (found at the beginning of Table I-B), and similarly very few examples, mostly intramolecular reactions, involve thiazoles (end of Table I-B). In contrast, numerous substituted oxazole reactions have been described. This very useful sequence is limited primarily by the occasionally difficult preparation of the starting oxazole. (6)

The relative stability of the bicyclic intermediate remains of interest. Many (most) of these sequences require heating to effect the DA step, and the temperatures used are such that the second rDA step occurs too rapidly to allow isolation or observation of the intermediate. Both steps are affected by substituents, although relatively little information on the rDA step is available. To illustrate, in an early example, 5-ethoxyoxazole was found to react with dimethyl acetylenedicarboxylate (DMAD) in "cold ether", to give the final products with no indication of detection of an intermediate. (7)



Clearly in this instance the 5-ethoxy substituent enhances the rate of the DA reaction, but only a lower limit on the temperature needed for rDA reaction is provided by this experiment. Most of the entries in Table I-B are similar in this regard.

A few claims of isolation of bicyclic compounds analogous to the intermediates proposed for these reactions are found in the literature. In some instances the product structures have not been rigorously proven, and others may be suspect on different grounds. For example, an intramolecular DA reaction of a nitrile to a furan reportedly gives an isolable cycloadduct, but the products have been characterized only by IR and combustion analysis. (8)



Reactions of rare 2-aminooxazoles with DMAD have similarly been reported to give isolable cycloadducts, along with smaller amounts of the bis-dienophile adduct expected from further rDA-DA reaction. (9) The isolation of the 1:1 cycloadduct in this instance is unexpected, based on comparison with reactions of other electron-donor substituted oxazoles and the inherently reactive nature of the functionality present in this structure, which one might expect to ring open to form an aniline derivative.



No such reservations attend the structures of the cycloadducts obtained from certain reactions of oxazoles with benzyne. When this very reactive dienophile is generated at sufficiently low temperatures, the 1:1 cycloadducts of a number of oxazoles can be isolated, and some have been fully characterized. (10)



These cycloadducts are undoubtedly more stable thermally than analogous furan derivatives because of the disruption of benzene aromaticity that accompanies the formation of isobenzofuran in the rDA step. A study of three related aryl adducts (Ar = p-O₂NC₆H₄,p-MeOC₆H₄, or Ph) showed modest substituent rate effects, as well as the relatively low activation entropies that characterize most rDA reactions. (11)



Examination of the complete list in Table I-B reveals that almost all reactions of imidazoles, oxazoles, and thiazoles require (or have utilized) temperatures ³100°, with no evidence of cycloadduct detection. A few lower temperature reactions involve electron-donor substituted oxazoles; again, these occur without detection of the intermediate when common acetylenic dienophiles are used. In general, very electrophilic (EWG-substituted) alkynes react at lower temperatures than alkyl- or arylacetylenes. No direct comparisons have been made, but it appears that thiazoles require much higher temperatures than imidazoles, which in turn may be less reactive than oxazoles.

The reaction of oxazoles with benzyne generated in situ at 101° leads to the formation of bis-benzyne adducts, showing that the cycloadduct undergoes rapid rDA reaction at this temperature. The good yields of 9,10-epoxyanthracene derivatives obtained from these sequences reflect the high reactivity of isobenzofuran as a diene in DA reactions. (10-12)

$$\begin{array}{c} R^{3} & O \\ R^{2} & R^{n} \\ R^{2} & R^{n} = H, alkyl, or aryl \end{array} \xrightarrow{101^{\circ}} R^{2}CN + \left( \begin{array}{c} & R^{1} \\ O \\ R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{2}CN + \left( \begin{array}{c} & R^{2} \\ R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{2}CN + \left( \begin{array}{c} & R^{2} \\ R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{2}CN + \left( \begin{array}{c} & R^{2} \\ R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right) \xrightarrow{R^{1}} R^{3}CN + \left( \begin{array}{c} & R^{3} \end{array} \right)$$

Bis-dienophile adducts are also potential products from reactions of oxazoles with simpler acetylenes, but have been reported in only a few instances. The unexpected formation of symmetrical tetraphenylphenol, albeit in low yield, in a high temperature reaction is believed to occur via the bis-dienophile adduct. A reduction is formally required to give this product instead of the anticipated hydroquinone analog. (13)



An interesting bridgehead methoxy ketal bis-adduct was isolated, along with the expected 1:1 adduct, in a reaction with DMAD that occurs at much lower temperature. (14)



Little is known about the relative reactivity of oxazoles vs. furans as DA dienes. The formation of these bis-adducts shows that in general the use of excess dienophile in reactions with oxazoles should be avoided when the simpler furan product is desired.

Substituents clearly play a role in determining the rate of the rDA step of initially formed cycloadducts. The very facile expulsion of LiCN came to light during attempts to generate benzyne at moderate temperature under strongly basic conditions, in which the 4-position of the oxazole is completely lithiated. The major product, triphenyloxazole, is thought to arise from nucleophilic addition to benzyne, but partial DA-rDA reaction of the lithiated oxazole also occurs, leading ultimately to the bis-benzyne adduct. A rational alternative mechanism involving DA reaction of triphenyloxazole followed by expulsion of PhCN was ruled out by demonstrating that this independently prepared cycloadduct is moderately stable under these reaction conditions. (15)



Several furanoid natural product analogs have been synthesized by intramolecular oxazole-acetylene reaction sequences, often in excellent yield. One example, from among many listed in Table I-B, is illustrated. (16)



A review of this general synthetic approach has appeared. (17)

#### 3.1.1.3. Nitriles from Pyrimidines and Pyrazines (Table I-C)

The reactions of pyrimidines with acetylenic dienophiles usually occur by DA reaction across the 2,5-positions followed by expulsion of a nitrile to form substituted pyridines. The process is quite versatile. Pyrimidines bearing EWG groups react readily with electron-rich acetylenes, as illustrated. (18)



Many of the reactions listed in Table I-C appear to involve inverse electron demand DA steps. These include reactions with electron-rich olefinic dienophiles, in which the substituent serves the dual purposes of activating the olefin, and as a leaving group (masked alkyne), leading to the aromatic product. (19)



In general, 5-nitropyrimidine is well-behaved in such reactions, although the very similar reaction with 1-(diethylamino)propyne is anomalous. (20)

Electron-rich pyrimidines give analogous DA-rDA sequences with EWG-bearing dienophiles, as exemplified by DMAD. (21)



Pyrimidines bearing a tethered alkyne, usually at the 2- or 4-position, have frequently been used in intramolecular variants. Several interesting bi- and tricyclic heterocycles have been prepared in this manner. (22)



The intramolecular sequence applied to 4,6-dihyroxypyrimidines leads to pyrimidone products. The expelled dienophile is formally HNCO (see also Isocyanates, Table II-B), but examples are included in Table I-C to stress the relationship with other pyrimidine reactions. (23)



*N*-Alkylated pyrimidines appear to give relatively facile DA reactions. Subsequent formation of HCN is favored over expulsion of the alkylated (isonitrile) species. (24)



This observation suggests that pyrimidine DA reactions may be susceptible to acid catalysis. Although some reactions have been carried out in acidic media, and in some instances protonation leads to alternative reactions, this topic remains relatively unexplored. (24)

Pyrazines enter into similar DA-rDA sequences to form nitriles and pyridines; the cyclization takes place at the 2,5-positions. Only one study of the intermolecular reaction has been reported; mixtures are formed, with both overall yield and product ratio highly dependent on substituents. (25)

In contrast, numerous intramolecular pyrazine reactions have been reported. All involve alkynes tethered at C-2 of the ring (*i.e.*, no *N*-tethered examples have been reported). These inherently unsymmetrical systems typically give rise to mixtures of products in ratios that depend on the nature of the tether as well as the presence of other ring substituents. A relatively simple example is shown. (26)



Reaction conditions can strongly influence both the rate and outcome of these reactions, as a comparison of thermal and acidic conditions illustrates. (27)



The trifluoroacetic acid solvent is almost certainly providing acid catalysis for the DA step of this sequence. The rate and product selectivity effects may be due to preferential protonation of the N atom distal to the 2-tether. Control of regiochemistry has also been achieved by N-alkylation. (27)



Other pyrazine reactions similarly affected by TFA solvent are included in Table I-C. The regiochemical control is often striking, and the use of acid avoids the need to remove the N-alkyl group if the free base is desired.

The products of reactions of alkynes with both pyrimidines and pyrazines are pyridines, which can undergo further reaction with dienophiles. Typically these require appreciably higher temperatures than the diaza analogs. An intramolecular example involving a nitropyridine is shown for comparison purposes in Table I-C. In related fashion, the use of a doubly tethered substrate gives a DA-rDA-DA-rDA sequence at high temperature; this reaction is effectively halted after the first DA-rDA sequence when carried out at lower temperature (120°). (26)



Interception or isolation of the presumed bicyclic intermediate has not been reported in any reaction of either pyrimidines or pyrazines with acetylenic dienophiles. Thus the temperature needed for overall reaction reflects the activation energy for the DA step, and no information is available on the rates of rDA loss of nitriles from the presumed bicyclic intermediates.

#### 3.1.1.4. Nitriles from 1,2,4- and 1,3,5-Triazines (Table I-D)

Unsymmetrical 1,2,4-triazines can in principle react in several ways as DA dienes with an acetylenic dienophile. An early report suggested that pyridazines are formed, (28) but this was rapidly corrected to show that in fact pyrimidines are generated. (29, 30) Pyrimidines result from cycloaddition across N-2 and C-5, followed by loss of N-1 in the nitrile that is generated in the rDA step. Only a handful of examples are found in Table I-D, reflecting the small number of reactions in which this is the major pathway. Far more

common are the sequences that begin with cycloaddition across C-3 and C-6, followed by loss of  $N_2$  to give pyridine products. These useful reactions are addressed in a later section and listed in Table VI-D. The two processes compete, and many examples of formation of both pyrimidines and pyridines from 1,2,4-triazines are known. Substituents play a major role in determining the preferred pathway, as noted in some early work. (29)



The reactions of 1,2,4-triazines to give pyrimidines as major products occur especially readily with electron-rich dienophiles, and usually exhibit useful regiocontrol.

An unusual reaction of a 1,2,4-triazine with *N*-cyanoamines as dienophiles yields mixtures of symmetrical and unsymmetrical triazine products. (31)



The reactions of 1,3,5-triazines commonly also involve electron-rich dienophiles; these invariably lead to the formation of a pyrimidine product after expulsion of a nitrile. The DA step necessarily involves cycloaddition across an N,C-1,4-diene. Dienophiles employed to initiate the sequence include aminoalkynes, enamines, ketene acetal analogs, and amidines, which usually

react via the tautomeric enamine double bond. These reactions often lead to good yields of single isomers. Consequently, *sym*-triazines have found use in a number of synthetic applications. To avoid mixtures of products, most reactions have been carried out with either 1,3,5-triazine itself or symmetrically trisubstituted derivatives.

Most of the reactions of 1,3,5-triazines listed in Table I-D occur at or below 100°, and further reaction of the pyrimidine product is not commonly encountered.

Enamines have been extensively employed as dienophiles. One example is shown to illustrate the general reaction. (32)



As noted above, amidines typically react via the enamine tautomeric form. (33)



When tautomerism is precluded, the imine double bond itself can serve as the dienophile (a masked nitrile). (34)



In contrast to all of the other six-membered nitrogen heterocyclic "dienes" described above, some *sym*-triazine reactions allow isolation of the bicyclic intermediate. For example, reaction of the triester derivative can be carried out directly at 101° to give the pyrimidine, or at room temperature to generate the bicyclic compound. (35)



The cycloadduct of tri(thiomethyl)-*sym*-triazine and an aminoalkyne proved to be exceptionally stable. It required heating ³150° to effect rDA expulsion of MeSCN. (36)



In the presence of strong acid (p-TsOH), this rDA reaction occurs under somewhat milder conditions (100°). Interestingly, peracid oxidation to the trisulfone analog affords a much more reactive species, which expels MeSO₂CN at or slightly above room temperature. (36)

Reviews that describe the use of triazines and other heterodienes in multistep syntheses of natural products have appeared. (37-41)

## 3.1.2. Heterodienophiles Expelled (C = X), Other than $CO_2$ and COS

This section is devoted to rDA reactions that expel a double-bonded dienophile in which one reaction site is carbon and the other a heteroatom. The order of tabulation is N, O, S, and finally miscellaneous heteroatoms in order of increasing atomic number. Discussion of reactions that generate  $CO_2$  or COS are deferred to later sections.

### 3.1.2.1. Imines (Table II-A)

The simplest heterocyclic rDA reaction gives methyleneimine (formimine) and butadiene. (42) The activation energy is lower for this reaction (51.4 kcal/mol) than that of the all-carbon analog (*ca.* 66 kcal/mol; see discussion in Part I of this review). (1)



Imine adducts of other common dienes have been examined under typical rDA conditions (heat, FVP, UV). Although quantitative rate data are generally lacking, it is safe to conclude that these materials constitute a well-behaved class of substrates for rDA treatment. Reactive diene coproducts can be generated, as shown by the formation of *o*-xylylene. (43)



No direct comparison has been made between imine and nitrile formation in rDA reactions, but an inference can be drawn from the conditions used to crack the formimine-CP adduct, (44) when compared with the room temperature expulsion of HCN from the CP adduct discussed previously.

$$\underbrace{ \begin{array}{c} & \\ & \\ & \\ \end{array}}^{\text{NH}} \xrightarrow{\text{FVP, 450-600}^{\circ}} \text{CH}_2 = \text{NH} + \text{CP} \end{array}$$

A different situation exists in a reaction in which the choice to form

imine + aromatic is strongly favored over the prospective formation of nitrile + diene. (45)



The discovery that the rates of rDA reactions to generate imines are greatly enhanced by acids has opened a new chapter in the utility of these reactions. Attention has been focused mainly on CP adducts. Protonated *N*-alkyl adducts react readily in aqueous solution near ambient temperature, to give (note hydrolysis of the imine) an alkylamine, formaldehyde, and CP. In order to prevent back reaction with the very reactive iminium cation dienophile, a scavenger for CP (*N*-methylmaleimide, NMM) was employed. (46)

$$NR \cdot HCl + NMM \xrightarrow{aq. solution} RNH_2 + CH_2O + CP-NMM$$

When very similar substrates are treated in a mixed TFA solvent containing  $Et_3SiH$ , the iminium salt is reduced to the corresponding *N*-methylamine. This procedure has been applied to a series of amino acid derivatives, giving products in good yield without racemization. (47) Other related examples, including one study on the efficacy of Lewis acids, are shown in Table II-A.

#### 3.1.2.2. Isocyanates (Table II-B)

Perhaps surprisingly, rDA reactions that generate isocyanates are the most numerous of the mono-heteroatom double bonded dienophile types. This frequency is mainly due to two general reactions, DA reactions of acetylenic dienophiles with 2-pyridones or with various mesionics, respectively.

Although far less commonly encountered than the CO₂-producing reactions with 2-pyrones (see Table III), 2-pyridones behave similarly in many applications. A recent review covering synthetic applications has appeared. (48) The isocyanates that are formed from the initially produced cycloadducts are usually not the products of interest. An exception is used to illustrate the general reaction type. (49)



Some 2-pyridones exist primarily in the enol form, but these give analogous reactions, as shown by several entries in Table II-B. Bicyclic intermediates are usually inferred, but some have been isolated and examined for rDA reactivity, as shown by a few examples in this Table.

Mesionics, mainly five-membered ring heterocyclics, behave in an analogous manner. Again, reactions that generate  $CO_2$  (Table IV) are far more numerous, but mesionics that give isocyanates are well represented, with many subtle differences in substrate type and outcome shown in Table II-B. A moderately complex example is presented to illustrate the process. (50)



#### 3.1.2.3. Carbonyl Compounds (Table II-C)

Formaldehyde and acetone are the most commonly expelled carbonyl group dienophiles, but other aldehydes and ketones are represented, in both intraand intermolecular variants. The "parent" reaction leads to formaldehyde and butadiene. This process was reported in early work to occur at high temperature, (51) but the activation parameters for this process have apparently not been determined, unlike the previously discussed rDA reaction of the nitrogen analog.



Alder-Rickert-like DA-rDA sequences are also encountered in this section. The oxadiene ring system may exist in equilibrium with the open-chain dienone isomer, but still gives reactions ascribed to the cyclic form. The reaction of methyl propiolate exhibits useful regioselectivity. (52)



Substrates containing a second heteroatom in the ring are commonly employed in carbonyl-forming rDA applications. These reactions in general occur at easily attainable temperatures, although uncharged substrates require heating. The 1,3-dioxene ring system is relatively reactive, presumably because of the formation of two new carbonyl groups. The position of the double bond relative to the substituent determines whether the "diene" fragment is an unsaturated aldehyde or ketone. (53, 54)



An  $\alpha$  -pyrone analog has been widely employed to generate an acylketene intermediate. The ketene functionality reacts with a range of in situ nucleophiles to form acetoacetyl derivatives in a useful synthetic procedure. The activation parameters for the rDA step have been determined. (55)



Carbenoid organometallic analogs react with electron-rich dienophiles in an apparent DA-rDA sequence to form a new substituted cyclohexadiene, with the metal carbonyl as the expelled dienophile. (56)



Cycloadducts of the reactive diene CP with simple aldehydes and ketones are unknown, perhaps because of facile rDA reaction and equilibria favoring educts. However, the very electrophilic hexafluoroacetone forms a cycloadduct with CP at room temperature. The adduct undergoes rDA reaction on attempted distillation. (57)



3.1.2.4. Thiocarbonyl Compounds and Oxidized Analogs (Table II-D) The carbonyl dienophile fragment is usually not of primary interest in the reactions described in the preceding section. The opposite is true for rDA reactions that generate highly reactive thiocarbonyl compounds as expelled dienophiles. Evidence for the formation of these species usually takes the form of interconversion of stereoisomers, or trapping by an added diene. A review indicates that the rDA reaction is one of a very few general methods to generate thioaldehydes. (58)

Few simple alkyl thioaldehydes have been formed by rDA reactions, although thioformaldehyde is presumably generated in the FVP (650°) reaction of the anthracene adduct, (59) and thioacetaldehyde is formed on modest heating (130°) of the corresponding 9,10-dimethylanthracene cycloadduct. (60, 61) Thiobenzaldehyde is generated readily by heating the anthracene adduct, as shown by trapping with 2,3-dimethylbutadiene. (60, 61)



Thioaldehydes bonded to electron-withdrawing groups (CN, ester, amide, ketone, aryl and other unsaturation), as well as diaryl thioketones, are common dienophile fragments of rDA reactions. Substrates are often CP or anthracene adducts, although more complex dienes are represented. An example is thebaine; one regioisomer is formed in a low temperature DA reaction, but interconverts, presumably via rDA reaction, as the temperature is increased. (62, 63)



 $\alpha$ ,  $\beta$ -Unsaturated thiocarbonyl compounds tend to undergo DA dimerization, which may be reversed by heating. The C = S double bond may participate either as dienophile or part of the diene, or both. Interconversion of a dithiane to a thiocarbonyl isomer may result. (64)


Sulfoxide derivatives may also give rDA reactions, and for one isomeric pair the reaction has been shown to be stereospecific. (65)



Related sulfones are less susceptible to rDA reaction, tending instead to give rearrangement with loss of SO₂. (66) However, the generation of  $CH_2SO_2$  from a benzenoid cycloadduct has been improved by phenyl substitution. (67, 68) The sulfene must be scavenged by an in situ reagent, or it rapidly decomposes to SO₂ and undefined polymeric material.



As expected, anthracene adducts are less reactive than substrates that generate benzenes. The formal anthracene adduct of  $CH_2SO_2$  gives no rDA reaction, instead expelling  $SO_2$  and forming 9-methylanthracene in unspecified yield. (69)



# 3.1.2.5. Miscellaneous C = X Dienophiles (Table II-E)

Expelled dienophiles that contain one carbon atom double-bonded to Si, P, Se, Sb, or Bi are encompassed in this section, and discussed in order of increasing atomic number.

Evidence for double-bonded silicon was long an elusive target, recognized as a very reactive functionality, susceptible to rearrangement (70) and cyclodimerization. (71) Trapping at liquid helium temperature, however, allows isolation of the parent  $CH_2SiH_2$  and some simple derivatives. (72) Successful rDA reactions almost universally involve formal (substituted)benzene cycloadducts under FVP conditions with temperatures ³350°.



More highly substituted derivatives give rDA reactions under milder conditions, which allows use of anthracene cycloadducts. The reaction is stereo-specific, as demonstrated by use of both stereoisomers. (73)



To the extent that this effect can be isolated from other structural factors, an increase in atomic number of the dienophile heteroatom results in greater rDA reactivity. For example, the relatively simple bicyclic phosphine decomposes near room temperature. (74)



Phosphacyclopentadiene dimers exhibit reversible rDA reactions. The presence of substituents clouds interpretation, but the DA dimer structures imply preference for inclusion of P at the terminus of the diene, and dienophile reactivity of the P-terminus double bond, leading to the head-to-head cycloadduct. (75)



endolexo interconverted

Selenabenzaldehyde is generated at a somewhat lower temperature than the sulfur analog described in the preceding section. Unfortunately no direct comparison of rDA rates has been made. (76)



Only a few examples of higher atomic number heterodienophiles are found in the literature. The antimony- and bismuth-containing "benzenes" are very reactive, and exist in facile equilibrium with their head-to-head DA dimers. Thermodynamic parameters have been determined for a few related cases. A bismuth example illustrates the general conclusion; the rDA reaction is highly endothermic, but dissociation is favored by the typically large  $\triangle$  S°. (77)



# 3.1.3. Carbon Dioxide from α -Pyrones

The large number of applications of  $\alpha$  -pyrones in cycloaddition chemistry dictated subdivision of the Table dealing with this topic. The categories, as listed in the Table of Contents, were made according to the substitution pattern on the pyrone. They range from reactions involving the unsubstituted parent through alkylated, arylated, electron-withdrawing group (EWG)-substituted, heteroatom-substituted, to aza- and oxa-(ring substituted)  $\alpha$  -pyrones. These subdivisions are more or less arbitrary, made to help locate specific reactions; they do not reflect fundamental differences in reactivity, or the kinds of reactions encountered.

Several common themes are found in the reactions of  $\alpha$  -pyrones that include rDA expulsion of CO₂:

- a. direct thermal reaction of monocyclic dihydro derivatives;
- b. reactions with alkynes to give aromatics;
- c. reactions with alkenes bearing an easily eliminated substituent, leading to aromatics;
- d. reactions with quinones under oxidizing conditions, also leading to aromatics;
- e. reactions with olefins under conditions that may lead to both loss of CO₂ and possible addition of a second equivalent of the olefin.

An attempt has been made to follow this order in each of the Tables dealing with  $\alpha$  -pyrones. In the discussion to follow, representative examples are illustrated without a focus on substituent.

Two early reviews dealing with the preparation and reactions of  $\alpha$  -pyrones are useful sources for older and relatively inaccessible Russian work. (78, 79) A thorough recent review on "Diels-Alder Cycloaddition of 2-Pyrones and 2-Pyridones" provides extensive discussion of chemistry beyond the scope of this review. (48)

 $\alpha$  -Pyrones can in principle serve as either diene or dienophile in DA applications, but the vast majority of reactions utilize the diene role. Although the rDA reactions of the products have apparently not been examined, the parent molecule itself undergoes triplet-photosensitized [4 + 2] cycloaddition to give at least two formal DA dimers. (80)



Direct UV irradiation of  $\alpha$  -pyrone leads to the formation of CO₂ and cyclobutadiene. The reaction occurs via a bicyclic intermediate, which can be isolated by careful irradiation of  $\alpha$  -pyrone at low temperature. (4) Further UV absorption converts the intermediate into the final products. Mechanistic insights were obtained by carrying out the reaction with specifically deuterated  $\alpha$  -pyrones, (81) these reactions are listed among "unsubstituted"  $\alpha$  -pyrone reactions in Table III-A.



The (formal rDA) conversion of the bicyclic intermediate to CO₂ and cyclobutadiene has also been accomplished thermally by FVP at high temperature ( $^{3}400 - 850^{\circ}$ ). At lower temperature, reversion to  $\alpha$  -pyrone is favored. (82)

Scores of DA reactions of  $\alpha$  -pyrones with acetylenic dienophiles have been described. In no instance has the presumed intermediate bicyclo[2.2.2]octane been isolated, attesting to the facile expulsion of CO₂ in this variant of the Alder-Rickert reaction. The temperature needed for the rate-determining DA step is usually modest. An alternative approach used in an attempt to isolate the bicyclic intermediate shows that it loses CO₂ below 0°, but does not disclose the temperature below which it might be isolable. (83)



In addition to mono- and disubstituted acyclic alkynes, many cycloalkynes, including reactive species such as benzyne that must be generated and trapped in situ, have been employed in DA reactions with  $\alpha$  -pyrones. Polyacetylenes react in similar fashion to form the corresponding aromatics; the formation of a novel silacycle illustrates the point. (84)



The only reported failure of an alkyne to react with  $\alpha$  -pyrone involves di-*t*-butylacetylene. (85) Instead of alkyne incorporation, cinnamic acid is formed in unspecified yield, presumably from an intermediate DA dimer of  $\alpha$  -pyrone. (85)



In contrast to the alkyne reactions, the DA cycloadducts of  $\alpha$  -pyrones and

alkenes are often isolable, although the temperature needed for rDA loss of  $CO_2$  may be only slightly higher than that needed for cycloaddition. The adduct of ethylene has been prepared and shown to lose  $CO_2$  with formation of cyclohexadiene at 115°. (86)



Many structures of theoretical or synthetic interest are accessible from reactions of alkenes with  $\alpha$  -pyrones. Cyclopropenes, which are generally quite reactive in cycloadditions, may give stereoisomeric adducts that differ sharply in the ease of loss of CO₂. One such reaction, carried out at 25° under high pressure, yields a mixture of the *exo* DA adduct and the cycloheptatriene formed by homo-rDA loss of CO₂, presumably from the *endo* isomer. (87) The isolated *exo* cycloadduct required heating to 140° to give the same rDA products. Similar reactions with ester-substituted  $\alpha$  -pyrones appear to give the corresponding cycloheptatriene products even more readily. (87)



Benzocyclopropene reacts with  $\alpha$  -pyrone (88) and with some EWG-substituted derivatives at moderate temperatures to give novel 1,6-methano[10]annulene derivatives. (89)



## Dienes can be used to generate interesting structures by sequential

DA-rDA-DA reactions, and many such processes have been examined. It is difficult to generalize about the selectivity of these reactions; they vary from high to quite modest levels of regio- or stereoselectivity. Various tether lengths and types, all-carbon or heteroatom-included, have been employed. Even simple dienes such as butadiene give, usually in low yield, quadricyclic products derived from intramolecular second DA reactions. The second dienophile site may also be introduced after initial cyclization. Several examples are found in the Tables, and only a few are discussed here. A reaction that exhibits little selectivity is used to illustrate the range of structures that can be accessed. (90)



Other diene/  $\alpha$  -pyrone reactions give high yields of single products, or generate structures that may be difficult to access by other means. For example, the reaction of  $\alpha$  -pyrone with 1,5-cyclooctadiene affords the symmetrical quadricyclic product in a one-pot reaction. (91)



DA reactions of maleic anhydride with  $\alpha$  -pyrones are the most numerous of the many cycloadditions that this diene class undergoes. As with other olefinic dienophiles, if the reaction can be carried out at a sufficiently low temperature, the initial cycloadduct can often be isolated. Further heating then causes evolution of CO₂ to give either the cyclohexadiene, or if carried out in the presence of a second dienophile, the mixed bis adduct. Alternatively, initial use of higher temperatures, often with ³ two equivalents of maleic anhydride, results in the symmetrical bis-adduct. The latter reactions are especially common in early studies of  $\alpha$  -pyrones, and cover a wide range of  $\alpha$  -pyrone substitution patterns, as reflected in the Tables.

The stereochemical course of both DA steps is of interest, although this feature was usually not addressed in any but recent studies. Although stereochemistry is commonly inferred by analogy even in recent work, there are only a few instances in which this feature has been experimentally demonstrated.  $\alpha$  -Pyrone itself reacts with maleic anhydride to give, at least predominantly, the *endo* isomer (*endo* and *exo* are defined as distal and proximal to the heteroatom-containing bridge, respectively). The kinetics of expulsion of CO₂ from this isomer have been studied, and activation parameters have been determined. (92, 93)



Mechanistic details of this reaction were explored by examining the isotopic composition of products after partial decomposition, making use of natural abundance ¹³C and ¹⁸O material. It was concluded that the C-C bond cleavage precedes or is more advanced than C-O cleavage in the transition state. (94)

Maleimides often give DA reactions that parallel those of maleic anhydride, as one would expect based on the similarity of structures. The bis (*N*-phenyl-maleimide) cycloadducts formed in good yields by DA-rDA-DA sequences have been shown to have the *endo*,*endo* configuration for several substituted  $\alpha$ -pyrones as well as the parent. (95)



Intriguing peroxide cycloadducts result from  ${}^{1}O_{2}$  addition to  $\alpha$  -pyrones. These adducts undergo rDA loss of CO₂ just above ambient temperature with concomitant scission of the peroxide O-O bond. The unsubstituted parent

gives the predicted (*Z*)-2-butenedial, (96, 97) and some phenyl, carboxy, and ester-substituted  $\alpha$  -pyrones afford analogous dicarbonyl products. (97)



A metastable tautomer of toluene is isolated when the cycloadduct of  $\alpha$ -pyrone with allene is heated. The rate constant for the reaction was determined at 100°, the lower limit for useful rDA loss of CO₂ from this material. (98)



The dihydro benzolog of  $\alpha$  -pyrone, 3,6-dihydro-4,5-benzo-2-pyrone, is an excellent source of *o*-xylylene, as shown by the yield of the ring-closed isomer dihydrobenzocyclobutene. (99) Several aryl-ring substituted analogs are found in Table III-C.



The parent unsaturated benzopyran itself is too reactive to be used as an isolated starting material, but it can be generated from an acyclic precursor, and trapped by in situ dienophiles such as DMAD. (100) As expected, the 3,6-diphenyl analog is less reactive and can be isolated. It has been used in similar DA-rDA sequences. (101)



Homophthalic anhydrides provide rich and synthetically useful chemistry. The thermal reaction is analogous to that of dihydrobenzopyrone, yielding benzocyclobutanone and the interesting decarbonylation/rearrangement product fulvenallene. The allene is favored by higher temperature FVP. (99)



Reaction of homophthalic anhydride in the presence of a reactive dienophile gives a product that can be rationalized by DA cycloaddition to the ketene intermediate generated by loss of  $CO_2$ , followed by enolization to the phenol. However, the steps may be reversed, with enolization preceding DA-rDA reaction. This alternative mechanism seems likely given the moderate temperature used for these reactions, typically 150–200°. The naphthol derivative is formed in moderate yield when DMAD is used as the dienophile, while with ethyl propiolate the reaction appears to be regioselective, but the yield is low. (102)



#### The utility of homophthalic anhydrides was enhanced by the finding that a

base-induced DA pathway is easily accessed. Conversion to the sodium enolate is usually accomplished by treatment with NaH. Reactions with traditional EWG-substituted dienophiles and the enolate occur readily at  $0 - 25^{\circ}$ , and the yields are often significantly higher than those of the neutral thermal reaction. For example, the ethyl propiolate adduct just described is formed in 50% yield via the sodium enolate. (103) Many complex products have been formed using this methodology, including several tetracene quinones of medicinal interest. One example, (104) from among many in Table III-E, is illustrated.



Heteroatom-substituted derivatives, including homophthalic and related anhydrides, comprise the largest subcategory of  $\alpha$  -pyrone DA-rDA substrates (Table III-E). Many nitrogen-linked substituents are represented, ranging from simple amines to heterocycles, with indolo-  $\alpha$  -pyrones especially numerous. The typically non-selective dienophile 3-pyridyne is used to illustrate the reaction of an indole system. (105, 106)



In general, heteroatom-linked substituents lower the temperature needed to initiate the DA-rDA sequence with EWG-bearing dienophiles. Similar or even greater reactivity is exhibited by  $\alpha$  -pyrones with one or two additional heteroatoms in the pyrone ring. These are mainly oxazines (azapyrones), with 3-aza- (carbamates), 4-aza, 5-aza-, and 3,6-diaza-2-pyrones all represented; along with a few related systems these are collected in Table III-F. The reactions are similar in all respects to those of simpler  $\alpha$  -pyrones, but the products are usually pyridines or analogs.

The 4- and 5-aza-2-pyrone reactions presumably occur via the usual bicyclic intermediate, which in principle could expel either  $CO_2$  or a nitrile. Only the former pathway has been described. These reactions occur very readily, even when sterically demanding substituents are present. (107)



Brief mention is made here of 4,5-diaza-2-pyrones, which are treated in greater detail in a later section. In reactions of these compounds, the rDA competition in the bicyclic intermediate is between loss of  $CO_2$  or  $N_2$ , and the latter is invariably expelled. Loss of  $N_2$  generates a new  $\alpha$  -pyrone, which may react further in the usual fashion. An example of such a sequence is illustrated for a reaction with benzyne. (108)



Although few examples exist to demonstrate the point, conversion of the diazene to the analogous amine oxide could in principle result in expulsion of  $N_2O$  (a topic treated in greater detail in a later section), but instead results in the "normal" loss of CO₂. It is clear that  $N_2O$  is a much poorer rDA dienophile

than  $N_2$ , but to the extent that this generalization is appropriate,  $N_2O$  is also a poorer rDA dienophile than  $CO_2$ . (109)



A few novel cyclic carbonates that may be viewed as dihydro-  $\alpha$  -pyrones have been prepared. These heterocycles rapidly undergo loss of CO₂ at room temperature, and this reactivity makes them difficult to isolate. (110)



In the reactions of mesionics to be discussed next,  $CO_2$  is the most commonly expelled dienophile. However, there are enough substrates that eject COS to warrant a separate table. The situation is quite different for  $\alpha$  -pyrones; sulfur analogs are far less frequently encountered, and only one example of rDA loss of COS has been located. (111)



## 3.1.4. Carbon Dioxide from Mesionics

The term "mesionic" is used to describe a class of heterocycles, mostly five-membered rings, for which aromatic zwitterionic 1,3-dipolar resonance forms can be written. Mesionics undergo dipolar [3 + 2] cycloaddition reactions with dipolarophiles, presumably to form bicyclic intermediates that decompose

typically without isolation. The expelled minor (dienophile) fragment is most commonly  $CO_2$ , COS, or an isocyanate. These sequences can be divided into two major categories based on the nature of the dipolarophile employed. With acetylenic dipolarophiles, the last step is formally an rDA reaction, and thus these sequences are appropriate for inclusion in this review. The reaction of acetylene itself with *N*-phenylsydnone is shown. (112)



Formation and reactions of mesionics was an especially active field of research in the period 1960–1980, and some reviews covering this period have appeared. (113-115)

The reactions of mesionics with alkynes that lead to isocyanates (and a few carbodiimides) are included in Table II-B. Those that generate  $CO_2$  are included in Table IV. And finally, reactions of mesionics that expel COS are listed in Table V. The generalizations made here will for the most part apply to all such reactions.

With olefins, the final step is a retro[3 + 2] reaction, as illustrated for the reaction of styrene, again with *N*-phenylsydnone. (116) Since no rDA step is involved, the reactions of mesionics with olefinic dipolarophiles are not compiled in the Tables.



Readers who wish to pursue the extensive literature on reactions of mesionics with olefins are directed to some especially informative papers (117-124) and the reviews mentioned previously. (113-115) Both reaction types (alkene and alkyne) have been thoroughly studied from a mechanistic standpoint, and numerous kinetic data are available. (125, 126) Since the DA step is typically rate-controlling with acetylenic dienophiles, these data do not provide

information on the rDA stage of the sequence.

The numerous reactions of mesionics with acetylenic dipolarophiles that expel  $CO_2$  lead primarily to pyrroles (in mono-, bi-, and polycyclic structures: Table IV-A) and pyrazoles (Table IV-B), but several different ring systems including imidazoles, furans, thiophenes, and pyridines have been generated (Table IV-C). The mesionics used in these reactions may be prepared in advance or formed in the presence of the dipolarophile. A particularly simple approach to substituted pyrroles utilizes an  $\alpha$ -amino acid heated with an anhydride and dipolarophile. The *N*-acylamino acid is formed initially, and can also serve as the starting material in analogous reactions. (127)

In rare instances the cycloadduct is isolated, usually in conjunction with the decarboxylated final product. Further heating causes loss of  $CO_2$  to complete the reaction. (128)



Pyrazole-forming reactions are typified by the reaction of acetylene with *N*-phenylsydnone described previously. EWG-substituted dipolarophiles are most commonly employed; regioselectivity with unsymmetrical reagents tends to be modest, as shown by several examples in Table IV-B. Arynes and bis-acetylenic substrates have been successfully employed. An example of the latter is illustrated. (129)



Nitriles can serve as dipolarophiles with some mesionics. The usual products are imidazoles. (130)



Sydnones and a few related mesionics react with cyclopropenes and cyclopropenone analogs to give dihydropyridines by a route involving a homo-rDA step. Some highly substituted products have been formed in this manner. (131)



A similar reaction with EWG-substituted cyclobutenes has been reported. An interesting example of the process that illustrates preferential reaction at the EWG-substituted site (in modest yield) is found for a Dewar benzene derivative. (131)



## 3.1.5. COS from Mesionics

The reactions of mesionics with dipolarophiles that, after initial cycloaddition, generate COS are listed in Table V. These processes parallel those of mesionics to form CO₂. The heterocyclic products that result likewise depend upon the heteroatom(s) present in the mesionic. Typically pyrroles, furans, and thiophenes are formed. Most reactions utilize aryl- or EWG-substituted substrates. A reaction that illustrates several of these features leads to a thia analog of isobenzofuran. (132)



## 3.1.6. Dinitrogen as Expelled Dienophile

Reactions that evolve  $N_2$  in rDA processes are numerous and varied. The large number of such reactions dictated further subdivision, which has been done by treating first aliphatic diazenes, followed by the various aromatic diazines, triazines, and tetrazines that enter into reactions that result in formation of  $N_2$ . The extreme stability of  $N_2$  is indicated by its failure to enter into DA reactions. Conversely, rDA reactions that expel  $N_2$  tend to be more rapid than for other dienophiles. Diazenes that can form simple conjugated dienes upon loss of  $N_2$  have not been isolated. They are generated as reactive intermediates.

## 3.1.6.1. From Aliphatic Diazenes

Diazene intermediates that lead to simple dienes are most commonly generated by oxidation of the corresponding hydrazine. The parent dihydropyridazine has apparently not been examined experimentally. Alkylated derivatives exhibit stereospecificity that is in keeping with "normal" rDA processes that form carbon-carbon and carbon-heteroatom dienophiles. (133)



Efforts to isolate diazenes that can yield simple conjugated dienes by rDA reaction established that decomposition occurs rapidly even at  $-78^{\circ}$ . (134)



Homo-rDA reactions are also stereospecific, as shown by the formation of the less stable Z,Z non-conjugated diene from the all-cis substrate. (133)



Although related homo-rDA processes occur at modest temperatures, these reactions are clearly slower than similar reactions that form conjugated dienes. For example, the tricyclic substrate that yields 1,4-cycloheptadiene upon expulsion of  $N_2$  requires modest heating to react at a reasonable rate. (135, 136)



In spite of the higher activation energies for homo-rDA compared to related rDA reactions, the *exo* cyclopropane ring strongly activates the system relative to the unsubstituted derivative. It has been estimated that the homo-rDA reaction occurs  $10^{17}$  times faster than loss of N₂ from the saturated diazene analog to give a 1,4-diradical. (135)

o-Xylylene formation occurs at low temperature, (137) although the diazene has been formed and isolated at  $-90^{\circ}$ , and activation parameters for loss of N₂ have been obtained. (138)



prepared at -90°

Substrate stereochemistry is critical to the outcome of some reactions, as expected from orbital symmetry considerations for concerted processes. A useful illustration is provided by the trans- and cis-epoxide substrates for a prospective homo-rDA reaction. The trans isomer gives the expected dihydrooxepin in a facile reaction at 0°. The cis isomer is much more thermally stable, eventually losing N₂ at 180° to form cyclohexenone, presumably by a stepwise process. (139)



An alternative route to diazenes utilizes  $Si_2Cl_6$  to deoxygenate the diazene N-oxide. The success of this method relies on the N-oxide being more thermally stable than the diazene. While clearly the case, N₂O can also serve as the expelled dienophile in rDA processes, as described in a later section. The deoxygenation method is illustrated by a reaction that leads to semibullvalene. (140)



A novel group transfer of  $H_2$  precedes rDA loss of  $N_2$  in systems of appropriate geometry. (141)



## 3.1.6.2. From Pyridazines and Analogs

Pyridazines can serve as dienes in DA reactions to give intermediate bicyclic diazenes, which in turn lose  $N_2$ . Most commonly the pyridazines bear EWG groups, and electron-rich dienophiles such as aminoacetylenes are employed. The reactions occur at the 3,6-positions of the pyridazine. The regioselectivity

of intermolecular reactions is strongly dependent on substituents and on temperature (see Table VI-B). (142)



Numerous intramolecular pyridazine DA-rDA reactions are known, and several heterocyclic systems have been generated in this manner. These reactions often require fairly high temperatures, but they are reasonably tolerant of substituents and give respectable yields in many instances. (143)



The reaction of luminol with  $O_2$  under basic conditions may involve an rDA step to form the photoactive species. (144)



The furan analogs of pyridazines are 1,3,4-oxadiazoles. Although relatively little explored, some EWG-substituted derivatives have been shown to react

with electron-rich or strained acetylenic dienophiles to give DA-rDA sequences with evolution of  $N_2$ . (145)



The 4,5-diaza-2-pyrone ring system invariably behaves like a pyridazine in DA-rDA processes, i.e.,  $N_2$  rather than  $CO_2$  is expelled from the presumed intermediate to form a new carbocyclic pyrone. The reactions tend to occur under mild conditions that allow isolation of the pyrone. (108)



With the more reactive dienophile benzyne, the loss of  $N_2$  is followed by a second DA-rDA sequence with expulsion of CO₂. Some complex polycyclic aromatic compounds have been prepared in this manner. (146)



Diazapyrones also react with strained olefins, and the intermediate bicyclic compounds lose  $N_2$  with surprising ease. A zwitterionic process has been suggested to account for the facile loss of  $N_2$ , (146) which may thus be regarded as an rDA reaction. IR evidence for a ketene intermediate has also been reported, (147) in further support of this mechanism. The isolated products are usually proton-shifted dihydropyrones (see Table VI-B).



#### 3.1.6.3. From 1,2,3-Triazines

Although few examples are available, 1,2,3-triazines can react with electron-rich dienophiles, typically enamines, to give pyridine products that may arise by cycloaddition followed by rDA loss of N₂. (148) Yields are usually modest (see Table VI-C).



At higher temperatures, isomeric products are also formed that cannot arise from a straightforward DA-rDA sequence. These have been rationalized by direct thermal loss of N₂ from the triazine, followed by azacyclobutadiene formation, [2 + 2] cycloaddition, and rearrangement. (149) There is direct evidence to support this mechanistic suggestion from studies of related reactions. (150, 151)

#### 3.1.6.4. From 1,2,4-Triazines

As noted previously, 1,2,4-triazines are known to undergo two fundamentally different DA-rDA sequences. A relatively small percentage follow, as a major pathway,  $N^2$ -C⁵ cycloaddition, with subsequent loss of a nitrile and formation of a pyrimidine. These reactions are collected in Table I-D. The far more common mode of cycloaddition takes place across C³-C⁶, followed by loss of N₂ to form

a pyridine (Table VI-D). The two modes of reaction compete, and mixtures of pyridines and pyrimidines sometimes result, as shown by entries in both Tables.

The 1,2,4-triazine system has been extensively studied and utilized in synthesis, and several reviews describe various aspects of its chemistry. A lengthy and comprehensive review published in 1978 contains relatively little on DA-rDA applications, (152) reflecting minor use prior to that time. Subsequently, numerous syntheses have made use of this methodology, and it is a major focus of several more recent reviews. (37-41, 153)

Unsubstituted triazine has been used with enamine dienophiles, and in an especially direct pyrrolidine-catalyzed reaction of enolizable ketones to form substituted pyridines. (154) The regioselectivity observed in this reaction is common for process involving substituted triazines with electron-rich dienophiles, although the direction of addition depends to a significant degree on the nature and location of the substituent(s), as will be evident from many examples in Table VI-D.



Regioselectivity can also be determined by the solvent, although this feature has not been widely explored. In a reaction with 1,1-di(dimethylamino)ethene, the ratio of 3- to 4-dimethylaminopyridine changes from 100:0 to 37:63, depending upon whether methanol or acetonitrile solvent is employed. (155)



Many substitution patterns on triazines have been successfully employed in

cycloadditions. Aryl groups and esters predominate, but alkyl, halo, and several other substituents are represented. In general, EWGs increase triazine reactivity, although counterbalancing steric effects may lead to only modest changes in rate. (156) With electron-rich dienophiles, temperatures between ambient temperature and 100° are usually sufficient for reaction. Simpler dienophiles such as phenylacetylene require somewhat higher temperatures (150°), and many intramolecular reactions have been successfully carried out above 200°. The 1,2,4-triazine ring exhibits considerable thermal stability. Complex polycyclic products have been formed by both inter- and intramolecular DA-rDA sequences. (157)



Simpler substrates also provide interesting and useful reactions. Although acetylene itself has apparently not been used as a dienophile in reaction with a triazine, its surrogate norbornadiene has found several applications. (158)



Of course enamines also serve as acetylenic equivalents in reactions with triazines; the amine activates the double bond for the DA step, and then functions as a leaving group to convert diene to arene. A novel reaction utilizing diethylamine is thought to occur via air oxidation to the enamine. (159)

$$MeN \xrightarrow{N_{N}} N_{N} + Et_{2}NH \xrightarrow{55^{\circ}} N_{2} + MeN \xrightarrow{N_{N}} N_{2} + M$$

Cyclopropenes react readily with triazines to give azepines, which are in facile equilibrium with the bicyclic diene tautomer. (160)



At elevated temperatures (*ca*.150° higher than needed for the analogous acetylene) the nitrile functional group can act as the dienophile in intramolecular applications. The products of these reactions are pyrazines. (161)



The numerous entries in Table VI-D attest to the generality and utility of these reactions.

# 3.1.6.5. From 1,2,4,5-Tetrazines

A comprehesive review of preparative methods and reactions of 1,2,4,5-tetrazines, including many DA applications, appeared in 1978. (162) A review devoted to the "Carboni-Lindsey Reaction", as the DA-rDA sequence is sometimes labeled after its discoverers, was published in 1981, (163) and several examples are found in reviews devoted more generally to the use of heterodienes in synthesis. (37-41)

The 1,2,4,5-tetrazine ring system has proven remarkably versatile in cycloaddition reactions, as reflected in the longest Table (VI-E) of this review. Essentially all work involves either mono- or disubstituted tetrazines, and the vast majority of substituents that have been employed are electron-withdrawing, either by inductive or resonance effects. Alkyl and dialkyltetrazines have however also been used, as have alkoxy, thioether, and amine-substituted derivatives, although few examples of DA applications of the latter have been reported. The most commonly encountered tetrazines are symmetrically disubstituted, with di-phenyl, -2-pyridyl, and -esters (methoxy- or ethoxycarbonyl) being especially numerous. The di(2-pyridyl)tetrazine owes its popularity at least in part to fairly easy access. (164)

The original DA application work was done with fluorinated alkyl substituents, and these tetrazines are still occasionally used. (165, 166) The reaction with unsubstituted allene reflects the double bond rearrangements that occur quite readily in the dihydropyridazine products when olefinic dienophiles are employed.



The bis-ester is significantly more reactive than the bis-aryltetrazine; with some simple dienophiles, the reactions require temperatures of 30° and 120°, respectively, according to an early relative rate study. (167) Additional details on relative dienophile reactivities are given in Table VI-E, but some generalities emerge: olefins are more reactive than similar acetylenes, and one EWG on the dienophile slows, but does not prevent, the reaction. (167) Terminal olefins appear to be more reactive than disubstituted alkenes, (167) but steric effects do not prevent facile reaction of tetramethylethylene with di(trifluoromethyl)tetrazine. (168)



Tetrazines are good oxidants ( $H_2$  acceptors), and a common side reaction when olefinic dienophiles are used is redox disproportionation, transfer of  $H_2$ from the dihydropyridazine cycloadduct to form the dihydrotetrazine, which is illustrated generically.



Since the disproportionation consumes an equivalent of tetrazine, it must be taken into account in carrying out experiments; unfortunately, relative rates and disproportionation equilibrium values are in general not known. Although the phenomenon is widely recognized, dihydrotetrazines have been isolated and yields reported in only a few studies. An effort has been made to include this information in the Table.

With acetylenic dienophiles, the DA-rDA process forms pyridazines directly. These aromatics are usually isolated without concern for further reaction with dienophile. Although pyridazines can serve as dienes in DA reactions (section VI-B), they require significantly higher temperatures than tetrazines. When olefinic dienophiles are employed, the initially formed product is a relatively DA-reactive 1,3-diene. If it is not stabilized by double bond rearrangement to the 1,4-diene or consumed by disproportionation, a second mole of dienophile could in principle add. In practice, this second DA step is rarely observed under the conditions needed for the reaction with tetrazine, again reflecting a large difference in activation energies. Unusually reactive dienophiles are exceptions. Examples are certain cyclopropenes (169) and cyclobutadiene. (170, 171)

The intramolecular nature of the second DA reaction presumably favors the formation of substituted semibullvalenes. (172)



As previously noted, similar reactions take place with pyrones and 1,2,4-triazines as the diene component in DA reactions with bis-cyclopropenes, but higher temperatures are needed for these less reactive systems.

Quantitative rate data have been obtained for some tetrazine reactions. The presumed bicyclic tetra-aza intermediate has never been isolated, and it is clear that the rate-determining step is the DA reaction. A nearly  $10^3$  range in rates was found for the reaction of di(methoxycarbonyl)tetrazine and a series of 1- and 1,1-substituted ethylenes. (173)

Interesting solvent-dependent remote substituent effects were uncovered in a kinetic study of di(2-pyridyl)tetrazine with a tetracyclic olefin ( $R^1$ , $R^2$  = H, OH, OMe, carbonyl); (174, 175) the data are displayed in Table VI-E. These reactions have high negative activation entropies, as commonly encountered in traditional DA reactions.



Tetrazine DA reactions are clearly inverse electron demand processes, and electron-rich dienophiles typically react quite rapidly, even at –78° for the di(alkoxycarbonyl)tetrazines. The breadth of reactivity is nonetheless impressive, since even mono-EWG substituted dienophiles react. However, the literature is nearly devoid of reactions with dienophiles bearing two or more EWGs. A curious exception involves maleimide and dimethyltetrazine. (176) Surprisingly, the analogous reaction with maleic anhydride does not occur, (176) although these two dienophiles rarely differ by more than a factor of two in relative rate with other dienes. (177)



Formation of the aromatic pyridazine product in the maleimide reaction requires an oxidation. The oxidant was not identified, but may have been the tetrazine, via the disproportionation mentioned previously. The methyl groups may alter the reactivity of the tetrazine, but it is unlikely that they change the intrinsic inverse electron demand nature of the reagent; for instance, the reaction of this tetrazine with 1-(diethylamino)propyne at 0° is exothermic. (176)

Although data are sparse on this point, reactions of tetrazines are likely to have thermal limitations. The diphenyl derivative decomposes to  $N_2$  and benzonitrile at 225°, (165) and analogous decomposition occurs with UV irradiation of bis(trifluoromethyl)tetrazine. (168)

$$\begin{array}{c} Ph \\ N \\ N \\ N \\ N \\ Ph \end{array} \xrightarrow{N} N_2 + 2 PhCN \\ Ph \end{array}$$

Norbornadiene can serve in its commonly encountered role as an acetylene

surrogate in reactions with tetrazines. Both di(trifluoromethyl)tetrazine, (168) and di(2-pyridyl)tetrazine exhibit this behavior. For the latter system, the intermediate has been shown to form rapidly and survive at  $-20^{\circ}$ , but it loses CP above  $-10^{\circ}$  to form the pyridazine. (178)



In one instance the second olefinic site of norbornadiene reacts with a second mole of tetrazine before CP is expelled. (165) Insufficient detail is available to determine if this altered reaction course is due to an experimental variable or inherent reactivity differences.



Tetrazines, along with pyrones and cyclopentadienones, have proven very useful reagents to effect the formal rDA expulsion of acetylene from bicyclic dienes, and this property has been used to prepare some reactive and unusual dienes. A synthesis of isobenzofuran illustrates the overall sequence, which consists of a DA reaction followed by two rDA steps, generating N₂ and the aromatic pyridazine, respectively. The second rDA step generates a C-C bond in the pyridazine, and has been discussed briefly in Part I of this review. In many applications all three steps occur without isolation of intermediate, but in DMSO, in spite of an exotherm at room temperature, precipitation of the dihydropyridazine as a solid stabilizes it sufficiently for isolation. It undergoes the second rDA step near room temperature in solution. (179)



Analogous sequences have been applied to the preparation of several polycyclic aromatic analogs of isobenzofuran, (180) isoindoles, (181) and arsenic-containing aromatic rings; (182) several additional examples of unusual dienes are listed in Table VI-E.



The simple aromatic heterocycles (furans, pyrroles, thiophenes) generated in some reactions with tetrazines are normally regarded as stable end products. However, the high reactivity of tetrazines can induce these aromatic heterocycles to enter into DA reactions, surprisingly as the dienophile component. Thus *N*-methylpyrrole reacts with di(methoxycarbonyl)tetrazine at moderate temperature to form a bipyridazine. All four carbon atoms of the pyrrole ring are incorporated in a sequence that presumably involves two DA-rDA steps and two distinct elimination steps leading to the formation of methylamine and the bipyridazine. (183, 184)



Some electron-rich nitriles react with tetrazines, even in intermolecular fashion, to form 1,2,4-triazines, (185) but these reactions do not appear to be general.



Enamines are among the most frequently employed dienophile partners of tetrazines. These reactions are unexceptional, leading either to the dihydropyridazine or the pyridazine formed by elimination of the amine. Imines and their analogs that cannot tautomerize react directly with tetrazines to generate 1,2,4-triazine derivatives; those that can tautomerize to the related enamine almost invariably react through the latter form. This generalization holds for simple imines and derivatives such as *N*,*N*-dimethylhydrazones and oximes. For example, acetone oxime yields the methypyridazine, presumably by reaction through the enamine tautomer followed by elimination of hydroxylamine. (186)



The unusual reaction of diethylamine with 1,2,4-triazines (previous section) has also been observed with a tetrazine. (159) An analogous reaction leading to the methylpyridazine (no yield given) has also been reported. (187) The detailed mechanism of these reactions remains unclear, but presumably involves oxidation of the amine to the imine = enamine, which then undergoes the expected cycloaddition-elimination. The oxidant that initiates this process may be the tetrazine.



This view is reinforced by the observation that lithium diethylamide and lithium diisopropylamide (LDA) give analogous reactions at  $-70^{\circ}$  (188) These bases are known to serve as reducing agents, and facile redox reaction with the oxidant tetrazine seems likely. The use of LDA for other purposes will clearly be problematic in the presence of a tetrazine ring because of this reaction.

Enolates are good dienophiles in combination with tetrazines, and both in situ generated potassium enolates (189) and preformed lithium enolates have been successfully employed. (190)



An unusual reaction of tetrazines occurs with benzyl isonitrile to form pyrazole products. The process works equally well with di(trifluoromethyl)-, diphenyl-, and di(methoxycarbonyl)tetrazine. A mechanism involving [4 + 1] cycloaddition has been proposed. (191)



Pyrazoles may also be formed when tetrazines interact with thiocarbonyl derivatives, although thionoformate esters allow isolation of the DA cycloadduct. (192) Similar adducts are thought to be intermediates that undergo desulfurization with ring contraction to pyrazoles in related processes.



Interestingly, when thiobenzaldehyde is generated by thermal rDA reaction of its cycloadduct with anthracene in the presence of a tetrazine, the expected pyrazine is formed along with the oxidized adduct from anthracene and the tetrazine in an uncommon involvement of this aromatic hydrocarbon as a dienophile. (192)


Although both species may be regarded as highly electrophilic, tetrazines react readily with benzyne to form the expected benzopyridazines. (173) A related but more exotic use of diphenyltetrazine is to trap dehydrocyclopentadienyl anion. (193)



# **3.1.7. Expelled Bis-Heterodienophiles (X = X, X = X', Other than N₂)** 3.1.7.1. Diimide and Derivatives

Early attempts to hydrolyze/decarboxylate the cycloadduct of CP and diethyl azodicarboxylate provided indirect evidence for the formation of diimide ( $N_2H_2$ ); either starting material or organic coproduct was reduced, presumably by this active species. (194, 195) Only recently has the intermediate hydrazine been isolated, and the rate of rDA expulsion of diimide determined. (196) In order to prevent reduction of the starting material in this kinetic study, norbornadiene was added as a scavenger for the diimide.

$$\begin{bmatrix} NH \\ I \\ NH \end{bmatrix} = \frac{k (45^{\circ}) = 1.02 \times 10^{-4} \text{s}^{-1}}{M} \begin{bmatrix} N_2 H_2 \end{bmatrix} + CP$$

The analogous anthracene cycloadduct was introduced as a synthetically useful precursor of diimide, since neither the starting material nor the anthracene coproduct reacts readily with  $N_2H_2$ . (197) Under the same conditions used for the CP adduct, the anthracene adduct was found to give rDA expulsion of diimide about three times faster. (196)



*N*,*N*¢-Dimethylhydrazine analogs were examined to see if stereochemical information for the rDA process could be obtained. (198) The trans diazene was favored relative to cis (93:7) from the butadiene adduct, which required the highest temperature of the systems examined, and it was the exclusive product from the anthracene adduct, which expelled product at the lowest temperature. Conversely, cis diazene was slightly favored (40:60) from the CP analog, examined at intermediate temperatures. These data indicate that there is a relationship between the precursor and product configurations, even though the precursor is stereochemically labile because of N-inversion.



When the N-alkyl groups form a ring, constraining the system to cis geometry, rDA reactions occur much more readily. For example, whereas the  $N,N\phi$ -dimethyl analog requires heating to above 200°, (198) the cyclic analog that also forms CP undergoes rDA reaction at room temperature. (199, 200)



Interesting pH dependence of the DA/rDA equilibrium position was

demonstrated for the CP and some related systems, one of which is illustrated. The educts are favored under neutral or basic conditions, while the cycloadducts are formed rapidly and favored under acidic conditions. This thermodynamic effect is attributed to the considerably higher basicity of the hydrazine than the diazene. (199)



The effect of acid on the rates of the DA and rDA reactions has not been established, although catalysis appears probable.

In this context, it is noted that the related N-oxide undergoes rDA reaction very rapidly; (201) the equilibrium constant has not been established for this reaction, but it is clear that the educts are favored under the conditions used to determine the rate.



The 2,3-diaza analog of cyclopentadienone has never been isolated, and one might expect, based on analogy, that it would decompose readily to  $N_2$ , CO, and acetylene. For example, attempts to generate the benzolog have instead resulted in benzyne formation, as shown by the formation of [2 + 2] dimer. (202)



The relatively high temperature used in this pyrolysis sheds little light on the stability of intermediates. However, the sulfone analog in solution is reported to lose CP reversibly at 75°, a temperature also sufficient for decomposition to  $SO_2$ ,  $N_2$ , and benzyne. Generated in solution, the benzyne undergoes rapid DA reaction with the CP formed in the first step. (203)



The 2,3-diaza analogs of benzo- and naphthoquinone are known, highly reactive dienophiles that have been prepared by low temperature oxidation of the corresponding hydroquinones. These and related quinone systems have also been generated by rDA reactions involving fairly high temperature vacuum pyrolyses. Under these conditions, N₂ is also lost, and the presumed *o*-xylylenyl diketenes then undergo [2 + 2] cycloaddition to give benzocyclobutandiones. (202)



Insufficient information prevents generalization regarding the effects of substituents on rDA reactions that generate diazenes. The classical dienophile diethyl azodicarboxylate is one of the few acyclic substrates for which evidence is available; early work set some (presumably upper) limits on temperatures needed to carry out the DA and rDA steps with anthracene. (204)



It is not clear that temperatures above 200° are in fact needed to carry out this rDA reaction. The related *N*-cyano-*N*¢-ethoxycarbonyl adduct decomposes to educts  $^{3}150^{\circ}$ , (205) the same temperature needed for rDA reaction of the *N*,*N*¢-dimethyldiazene-anthracene adduct mentioned previously. (198)

*N*-Phenyltriazolinedione (PTAD) and its *N*-methyl analog (MTAD) are well known very reactive dienophiles, and PTAD especially has been extensively used as a diene protecting group for steroids related to ergosterol. Attempts to remove the PTAD have led to several recipes; many of these use hydrolytic conditions that may result also in decarboxylation with formation of the hydrazine followed by loss of diimide. In general, mechanistic details and even the fate of the PTAD fragments are unknown. One example is illustrated, (206, 207) from among many included in Table VII-A.



Direct thermal rDA expulsion of PTAD may occur under mild conditions if the diene that is generated is stabilized, e.g., as an aromatic. Thus,

[7]paracyclophane forms an adduct with PTAD by DA cycloaddition at a temperature a few degrees lower than that needed for rDA regeneration. (208)



An even lower temperature is sufficient to release PTAD along with an unstrained aromatic ring. This point is nicely illustrated in a sequence in which MTAD adds at very low temperature to an open diene to generate the precursor bicyclic diene for an aromatic ring, which in turn expels PTAD at  $-10^{\circ}$ . (209) This net migration of dienophile can be carried out by addition of catalytic dienophile at higher temperature. (209)



A novel application of the rDA reaction utilizes optically active *N*-(2-bornyl)triazolinedione to prepare diastereomers of 1,2,3-trimethylcyclooctatetraene, which differ only in the ring-fusion binding site of the allylic methyl group. Careful hydrolysis affords enantiomeric hydrazines, which upon oxidation lose N₂. The resultant cyclooctatetraenes are enantiomeric, a result that requires that the COT ring be nonplanar. (210)



# 3.1.7.2. N₂O

The rDA reactions that expel N₂O comprise a small but distinct class of reactions, warranting separate tabulation (Table VII-B). Most of the azoxy substrates have been prepared by oxidative hydrolysis of MTAD cycloadducts. Although the azoxy compound is orders of magnitude more thermally stable than the corresponding diazene, loss of N₂O can still occur readily if the substrate is strained or the coproduct diene is stabilized. The reaction of the MTAD-CP cycloadduct illustrates this point. (140)

$$\underbrace{ \left( \begin{array}{c} N \\ N \\ N \\ O \end{array} \right)^{O} }_{O} \underbrace{ aq. \ KOH, \ H_2O_2, \ 30^{\circ} }_{O} \left[ \begin{array}{c} \left( \begin{array}{c} N \\ I \\ N \end{array} \right)^{O} \\ O \end{array} \right] \xrightarrow{O} N_2O + CP$$

The relative stability of the azoxy function is apparent from the temperature needed to effect the expulsion of N₂O with formation of 1,3-cyclohexadiene. (140) The corresponding diazine (Table VI-A) loses N₂ rapidly at  $-78^{\circ}$ . (134) As already noted, the azoxy function can also serve as a protecting group; the oxygen can be removed by treatment with Si₂Cl₆ to give the much more reactive diazene.



### The azoxy derivative of a 3,4-diazacyclopentadienone reacts rapidly with an

electron-rich acetylenic dienophile in what appears to be a simple DA-rDA sequence. (211)



The related bis-oxides that have been examined do not behave in a similar manner, but instead give rearranged products, some of which have lost the elements of  $N_2O_2$ . (212)



In a related vein, the azoxy derivative of a 4,5-diazapyrone in reaction with an EWG-bearing acetylene might have shed further light on the interesting question of preference for rDA loss of  $CO_2$  vs.  $N_2O$ , but instead rearranged products thought to arise by r[3 + 2] reactions were obtained. (213)



# 3.1.7.3. NO and NS

Nitroso compounds are typically reactive free radicals, that either dimerize, enter into other reactions, or if the NO is bound to carbon bearing a hydrogen, tautomerize to oximes. In spite of this high reactivity, nitroso compounds are generated relatively easily in rDA reactions. Only the 9,10-dimethyl derivative, among anthracenes, has been used in rDA processes to generate nitroso compounds. The nitrogen is, with very few exceptions, substituted by aryl, acyl, or similar EWG. *N*-Formylation slows the rDA reaction, but apparently not by a large factor. (214)



The nitrosobenzene cycloadduct of CP has been prepared at 0°, but decomposes to educts at room temperature. (215, 216) The cyclohexadiene analog requires moderate heating. (215) Nitrosobenzene is thus expelled more readily than  $N_2O$ ; based on comparison of the CP adducts, PhNO is also formed more rapidly than diimide. Nitrosobenzene is also ejected relatively easily in non-rDA reactions that generate diradicals. (217)



The N-O single bond appears to be fairly robust, as judged by early work in which the DA reaction of PhNO with 1,3-diphenylisobenzofuran is reported to be reversible at 270°. (218)



However, the similar adduct of AcNO with 1,3-diphenylisobenzofuran, which is presumably formed when the nitroso compound is generated in the presence of this reactive diene, gives products at milder temperature that suggest

homolytic cleavage. (219) The similarity of furan cycloadducts to ozonides is evident.



The nitroso functionality enters into ene reactions readily, perhaps reflecting its radical character. Hydroxamic acids and related esters may be formed in high yields (Table VII-C), given appropriate substrates. (220, 221) Some interesting heterocyclic systems have been prepared using this methodology. (220)



Simple sulfur analogs (N = S) of nitroso compounds have apparently not been generated by rDA reactions, although sulfoxide analogs have been generated in this manner. These reactions appear to follow the stereochemical features of common rDA processes. In one instance, facile low temperature reversible DA-rDA reaction was observed, along with higher temperature regioisomer conversion. (222, 223) The relative stereochemistry (Ph, O: cis or trans) was not examined in this instance.



## 3.1.7.4. Oxygen

The endoperoxide of rubrene was shown in 1926 to evolve  $O_2$  upon heating, in a luminescent rDA reaction. (224-226)



A review of cycloaddition reactions published in 1967 contains an extensive list (over 150 entries) of polycyclic aromatic endoperoxides. (227) Many bear a notation that  $O_2$  is evolved upon heating. Since little additional information is available, these are not repeated in Table VII-D, which instead focuses on more recent applications and detailed studies.

Simple diene endoperoxides give rearrangement products rather than rDA reactions. Cyclohexadiene endoperoxide, for example, rearranges thermally to the isomeric cis-diepoxide. Alternative methods are therefore required to effect a formal rDA loss of  $O_2$  from such substrates, and low-valent Ti has proven useful for this purpose. (228)



Orbital symmetry rules require that the initially formed  $O_2$  from a concerted thermal reaction be in the singlet state,  1O_2 . A stepwise process that allows intersystem crossing to the more stable triplet state ( 3O_2 ) is also feasible. The formation of singlet oxygen, sometimes in high yield, has been demonstrated in several endoperoxide rDA reactions. A substituted 1,4-anthracene

endoperoxide, for example, generates  ${}^{1}O_{2}$  in over 90% yield; this reaction has  $\triangle S^{\ddagger} = \pm 3$  eu, a value much like many other concerted rDA processes. The yield of singlet oxygen is not affected by a strong magnetic field in this instance. (229)



The 9,10-diphenyl-9,10-endoperoxide affords significantly less  ${}^{1}O_{2}$  (32%) in the simple thermal reaction, and in this instance the yield is diminished (23%) when the reaction is carried out in a strong magnetic field. (229) The magnetic field effect has been ascribed to interaction with magnetically active  ${}^{17}O$ , increasing intersystem crossing at a stepwise intermediate peroxy radical stage. (230)



Some oxazoles react with singlet oxygen to give high yields of products that appear to arise from DA cycloaddition to form an ozonide, followed by homolytic O-O bond cleavage coupled with expulsion of a nitrile. Although not formally an rDA reaction, the analogy is clear. (231)



# 3.1.7.5. Silylene and SiO Analogs

Materials with Si double-bonded to C are discussed in an earlier section, and listed in Table II-E. Silylenes (Si = Si derivatives) and their Si = O analogs that have been generated by rDA processes are found in Table VII-E. Silvlene itself, Si₂H₄, has not been formed in this manner, but some tetraalkyl (mainly tetramethyl) analogs have been generated as reactive intermediates in rDA reactions. These materials have not been isolated directly, but formation of either [2 + 2] cyclodimer or [4 + 2] cycloadduct with an added diene provides strong evidence for these intermediates. The cycloadduct precursors are formally derived from aromatics, and the formation of these aromatic coproducts is an important driving force for the rDA step, which nonetheless requires moderately high temperatures. Data in Table VII-E allow the expected conclusion that the order of thermodynamic stability of the adducts is: benzene < naphthalene < anthracene. Thus if the benzene cycloadduct is heated in the presence of naphthalene, the naphthalene cycloadduct is formed along with benzene. (232) There is too little information to allow firm conclusions about the relative kinetic rDA reactivity of these cycloadducts.



Attempts to carry out rDA reactions by UV irradiation are only partly successful, because of side reactions including competing rearrangement. (233)



It appears that the Si = O linkage can be generated more easily than Si = Si by rDA reaction, although no direct comparisons have been made. The cycloadduct formed from a silyl ether analog of cyclohexadiene and hexafluoro-2-butyne undergoes apparent rDA generation of  $Me_2Si = O$  under mild conditions; the reactive species is trapped in this instance by another silyl ether. (234, 235)

$$\begin{array}{c|c} & Me & CF_3 \\ & & Si & Me \\ & & O \\ & & O \\ & & CF_3 \end{array} \xrightarrow{Me_2Si(OMe)_2} Me_2Si(OMe)OSi(OMe)Me_2 + (72\%) \\ & & (72\%) \\ & & (72\%) \end{array}$$

At higher temperature, the same dienophile is expelled along with a diene coproduct, from a substrate that cannot directly form an aromatic. In the absence of a trapping agent, the reactive intermediate forms the cyclotrimer. (234)



# 3.1.7.6. Phosphorus = X

Reactions that generate P = C educts are found in Table II-E. Bis-heteroatom dienophiles that contain phosphorus consist mainly of  $RR \notin P = O$  examples, in addition to two reactions that generate P = P dienophiles. These are listed in Table VII-F.

There is some variation in the oxidation state of phosphorus in these reactions, but the expelled P = O species is always a reactive intermediate, and evidence its for formation typically involves isolation of a new cycloadduct or a solvent-trapped product. Studies utilizing optically active substrate or solvent allow the conclusion that the reactive intermediate is planar, attacked with equal probability from either face. (236, 237)



A phosphono analog of  $\alpha$  -pyrone behaves in the same manner, yielding dimethyl phthalate when heated with DMAD, and the characteristic bis-adduct when heated with maleic anhydride. (238)



The cis-trans isomerization exhibited by an unusual diphosphacyclohexene is attributed to reversible DA-rDA reaction, with interconversion occurring at the intermediate P = P species. (239)



## 3.1.7.7. Sulfur and its Oxides

Table VII-G lists the rDA reactions that emit SO₂, SO₃, S₂, or S₂O. The cycloadducts that emit SO₂ are in some instances proposed intermediates that rapidly undergo rDA reaction, and in others isolated and characterized starting materials. An interesting example of the latter demonstrates that the kinetically controlled reaction of SO₂ and an *o*-xylylene affords the DA cycloadduct. Upon heating, reversible rDA reaction occurs, followed by [4 + 1] cheletropic addition of the educts to form the more stable sulfone. (240)



kinetic control

thermodynamic control

The expulsion of  $SO_3$  in rDA reactions has been documented in only a few cases, involving initial DA reaction of an electron-rich dienophile to a heterocyclic diene. (241)



The formation of  $S_2$  as a reactive intermediate has been proposed in a number of rDA reactions in which the co-educts are CP, (242) cyclohexadiene, (243) and anthracene. (244) Evidence for the formation of  $S_2$  has been obtained by trapping with an in situ diene. (242)



Absent an added trapping reagent, the  $S_2$  is converted to stable  $S_8$ , which has been isolated in some instances. (243) Interestingly, in the presence of norbornadiene, a novel trithia cycloadduct is formed in good yield by an unknown mechanism. (242)



Very few examples of proposed  $S_2O$  formation in rDA reactions exist. One of these involves the coproduct 2,3-diarylbutadiene. The reaction occurs under mild thermal conditions, and appears to be susceptible to acid catalysis. (245)



3.1.7.8. Miscellaneous Expelled Bis-Heteroatom Dienophiles This final section is relatively brief, since Table VII-H contains very few examples. An unusual reaction that generates o-xylylene and a Co = Co species has been studied in detail. (137, 246)



Tetramethylgermylene, ( $Me_2Ge = GeMe_2$ ), has been generated from several substituted naphthalene cycloadducts, as shown by trapping with added anthracene. (247, 248)



A (Zr = O) bond is presumably formed in the Alder-Rickert-like reaction of an oxazirconadiene. The expelled dienophile is stabilized by formation of cyclotrimer. (249)



# 4. Experimental Conditions

As pointed out in Part I of this review, (1) rDA reactions are first-order processes whose rates are influenced primarily or only by internal energy. The energy is most often introduced by heating, or occasionally by UV or other irradiation. For the vast majority of related rDA reactions, structure of both adduct and educts is the most important feature in determining the ease of reaction. Very often temperature is the only variable cited for a reaction, and there are no experimental procedures that can be regarded as typical (hence the usual *Organic Reactions* section by this name has been omitted).

In comparison with the carbon-carbon dienophiles covered in Part I, a greater percentage of highly volatile "dienophile" educts (HCN,  $CO_2$ , COS,  $N_2$ ) are encountered in Part II. Many of these reactions are functionally irreversible in any event, but may be further facilitated by removal of the volatile product.

# 5. Organization of Tables

The Tables, and the like-numbered subsections of the Scope and Limitations section, are arranged to the extent possible in the manner adopted for Part I. Each Table deals with a single or related class of expelled dienophiles. Those containing carbon at a dienophile reaction site are listed first; the order of presentation of heteroatom(s) follows atomic number. The decision to list nitriles (Table I) before imines (Table II) illustrates the general organizing principle to list triple- before double-bonded dienophiles. In general, acyclic are presented before cyclic dienophiles within a Table, and intermolecular reactions are treated before intramolecular analogs.

For a given dienophile, the order of listing is generally in terms of increasing complexity (substituents— atomic number, oxidation state, etc.). Many of the Tables are subdivided by dienophile type within a class, or diene fragment formed; this method was chosen to help the reader locate material of interest. Many of the Tables and sub-Tables are relatively short, which will also assist in locating materials. The longest Table (VI-E) deals with expulsion of N₂ from reactions of tetrazines; the order used here, by tetrazine substituent is: unsubstituted, monosubstituted (H, alkyl, aryl, ester, heteroatom linked), disubstituted (same order). Reactions of diphenyltetrazine are listed before those of di-(2-pyridyl)tetrazines in the diaryl grouping, and methyl esters are listed prior to ethyl analogs. For a given tetrazine, the order is determined by the "diene" educt, using the factors listed previously. To the extent that they pertain, these same principles were used in other Tables.

# 6. Tabular Survey

Abbreviations used in Tables.

- Bn benzyl
- Bz benzoyl
- Cp cyclopentadienyl
- CP cyclopentadiene
- CPBA *m*-chloroperoxybenzoic acid
- DBN 1,5-diazabicyclo[4.3.0]non-5-ene
- DBU 1,8-diazabicyclo[5.4.0]undec-7-ene
- DCC dicyclohexylcarbodiimide
- DMAD dimethyl acetylenedicarboxylate
- DMF dimethyl formamide
- DMPS dimethylphenylsilyl
- DMSO dimethylsulfoxide
- GLC gas-liquid chromatography
- MA maleic anhydride
- MOM methoxymethyl
- NCS N-chlorosuccinimide
- NMM N-methyl maleimide
- NPM N-phenyl maleimide
- (OC) Oxidative Conditions. This notation is used in some entries after the conditions to indicate that a balanced reaction would require oxidation. In most cases, the oxidizing agent was not specified in the reference, and may have been air. In other examples, dehydrogenation may have occurred without a specific oxidant.
- PTAD 4-phenyl-1,2,4-triazoline-3,5-dione
- RTAD 4-R-1,2,4-triazoline-3,5-dione
- TBDM *t*-butyldimethylsilyl
- TCNE tetracyanoethylene
- TFA trifluoroacetic acid
- THP tetrahydropyranyl
- TMS trimethylsilyl
- Ts *p*-toluenesufonyl
- FVP flash vacuum pyrolysis

**Table I-A. Nitriles from Miscellaneous Reactions** 

View PDF

Table I-B. Nitriles from Oxazoles and Related Rings

**View PDF** 

Table I-C. Nitriles from Pyrimidines and Pyrazines

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Table I-D. Nitriles from 1,2,4- and 1,3,5-Triazines

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Table II-A. Imines

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Table II-B. Isocyanates

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Table II-C. Carbonyl Compounds

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Table II-D. Thiones

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Table II-E. Other C = X Dienophiles

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Table III-A. CO₂ from Unsubstituted Pyrones

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Table III-B. CO₂ from Alkyl-Substituted Pyrones

Table III-C. CO₂ from Benzo- and Aryl-Substituted Pyrones

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Table III-D. CO₂ from EWG-Substituted Pyrones

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 Table III-E.
 CO₂ from Heteroatom-Substituted Pyrones

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Table III-F. CO₂ from Oxazines (Azapyrones) & Analogs

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Table IV-A. CO₂ from Mesionics to Form Pyrroles

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Table IV-B. CO₂ from Mesionics to Form Pyrazoles

Table IV-C. CO₂ from Mesionics to Form Other Heterocycles

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Table V. COS from Mesionics

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Table VI-A. N₂ from Aliphatic Diaza Compounds

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Table VI-B.  $N_2$  from Pyridazines and Analogs

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Table VI-C. N₂ from 1,2,3-Triazines

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Table VI-D. N₂ from 1,2,4-Triazines

Table VI-E. N₂ from 1,2,4,5-Tetrazines

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Table VII-A. Diimide and Derivatives

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Table VII-B. N₂O

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Table VII-C. NO and NS Derivatives

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Table VII-D. Dioxygen

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Table VII-E. Silylenes and SiO Analogs

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Table VII-F. Phosphorous-Containing Dienophiles

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Table VII-G. Sulfur and its Oxides

View PDF

Table VII-H. Miscellaneous Bis-Heteroatom Dienophiles



TABLE I-A. NITRILES FROM MISCELLANEOUS REACTIONS	TABLE I-A.	NITRILES FROM MISCELLANEOUS REACTIONS	
--------------------------------------------------	------------	---------------------------------------	--

Starting MaterialConditionsProduct(s) and Yield(s) (%)Refs. $\swarrow$  $\swarrow$  $250^{\circ}$ PhCN + $\checkmark$ (60)255 $\square_N$ - $\left[\square_N\right] - \left[\square_N\right] - HCN + \left(\square$ (-)256

TABLE I-A. NITRILES FROM MISCELLANEOUS REACTIONS (Continued)

" The diene product was not isolated.



TABLE I-B. NITRILES FROM OXAZOLES AND RELATED RINGS

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$Ph \xrightarrow{O}_{N} Ph + \left[ \square \right]$	101°	HCN + (55) 11	
$\begin{array}{c} Bn \longrightarrow O \\ R \end{array} + \begin{array}{c} CO_2H \\ R \\ R = H, Ph, or CO_2Me \end{array}$	130°	$RCN + O Bn + O Bn (12-15) 261$ $HO_2C major minor CO_2H$	1
$BuO \xrightarrow{O}_{N} + \parallel$	80-115°, 5-10 h	HCN + $O$ OBu () 262 CO ₂ Et	2
$EtO \rightarrow O + DMAD$ R = H  or  Me	Et ₂ O	$RCN + (51-53) 7$ $MeO_2C CO_2Me$	
$R^2 \xrightarrow{0} N$ + DMAD $R^1$	Heat	$R^{1}CN + \begin{pmatrix} R^{2} & 0 \\ MeO_{2}C & CO_{2}Me \end{pmatrix} = \begin{pmatrix} R^{1} & R^{2} & (\%) \\ Me & OEt & 85 \\ " & OPr & 90 \\ " & OBu & 76 \\ H & " & 77 \\ Me & Me & 44 \\ rBu & H & 71 \\ H & T1 \end{pmatrix}$	3
<i>t</i> -BuO	80°	HCN + (21) $HCN + (21) $ $HCN + (21)$	4
$\int_{N}^{O} + \ $	190°	MeCN + $(67)$ (67) 265	15
Сн ₂ он +    Сн ₂ он	Hydroquinone, 170°, 24 h	MeCN + $(67)$ (67) 266	6
$\begin{array}{c} CH_2OAc \\ + \\ CH_2OAc \end{array}$	170°, 24 h	$MeCN + \underbrace{\int_{AcOCH_2}^{O} (80)}_{CH_2OAc} $	7
$R^{1}$ $M^{0}$ $R^{2}$ $+$ $H^{0}$ $R^{3}$	80-115°, 5-10 h	$MeCN + \begin{array}{c} R^{1} & R^{2} & R^{3} & (\%) \\ \hline OPr & H & H & 50 \\ Me & " & " & 35 \\ H & Ph & " & 30 \\ CO_{2}Et & H & " & 45 \\ COMe & " & " & 58 \\ OPr & " & Me & 65 \\ OBu & " & " & 70 \\ H & Ph & " & 35 \\ OPr & H & Et & 50 \\ OBu & " & " & 55 \\ H & Ph & " & 62 \\ \end{array} $	2
$ \begin{array}{c} NC \\ \searrow \\ N \\ N$	200°	$MeCN + \bigvee_{C_{5}H_{11}}^{NC} R + \bigvee_{R}^{O} \bigvee_{C_{5}H_{11}}^{O} R + \sum_{R}^{O} \bigvee_{C_{5}H_{11}}^{O} \frac{\frac{R}{H} (\%)}{C_{5}H_{11}} \frac{I:II}{CH(OEt)_{2} 29} \frac{268}{4.5:1}$	8
$\int_{N}^{0} \int_{1}^{1} \int_{1$	170-220°	MeCN + $AcOCH_2$ (88) 269	9

TABLE I-B. NITRILES FROM OXAZOLES AND RELATED RINGS (Continued)



#### TABLE I-B. NITRILES FROM OXAZOLES AND RELATED RINGS (Continued)

Starti	ing Material	Conditions	Product(s) and Yield(s) (%)	Refs.
n-PrO N	+ HO	100°	MeCN + $(EtO)_2OP$ $OH$ (73)	273
$EtO \xrightarrow{O}_{N} Ph$	+ DMAD	100°, 10 min	RCN + $EtO$ $O$ $Ph$ $R$ $(%)$ MeO ₂ C $CO_2Me$ $Ph$ 71 Ph 77	274
r-Bu N +		80-115°, 5-10 h	t-BuCN + $(-)CO2Et$	262
	+ DMAD	rt, exotherm	$RCN + \underbrace{MeO_2C}_{MeO_2C} + \underbrace{NH_2}_{ReO_1C} + \underbrace{MeO_2C}_{I} + \underbrace{MeO_2C}_{I} + \underbrace{MeO_2C}_{I} + \underbrace{MeO_2C}_{II} + \underbrace{MeO_2C}_{I$	1₂Me 9
			<i>t-</i> Bu 50 14 Ph 37 19	
$Ph \xrightarrow{O}_N + Bn + Bn$		130°	BnCN + $(17)$ CO ₂ Me	261
Ph +	CH ₂ OMe	170-220°	PhCN + $MeOCH_2$ CH ₂ OMe (89)	269
Ph +	CH ₂ OAc	205°	PhCN + $AcOCH_2$ CH ₂ OAc (70)	275
×°> +	Ph	255°	PbCN +  (38)	13
Ph N	Ph		Ph Ph	
Ph +	$ \begin{array}{c} \mathbf{R}^{1} \\ \  \\ \mathbf{R}^{2} \end{array} $	Heat	PhCN + $R^{1}$ $R^{2}$	$\frac{2}{1}$ (%) $\frac{83}{50}$ 276 $\frac{90}{1}$ 50 $\frac{90}{5}$
	TMS		(CH ₂ )OAc H 220° 48 H	ı 70
+	 TMS	250°	PhCN + $TMS$ (80)	277
+	R    	115°	PhCN + $(\%)$ R Ac 32	278
+	CHO	200°, 3.5 h	PhCN + $OHC$ R (73) R = MeO ₂ C(CH ₂ ) ₆ -	279
Ph +	DMAD	80°	PhCN + $MeO_2C$ $CO_2Me$ (60)	264
Ph +	DMAD	112°	PhCN + $MeO_2C$ $CO_2Me$ (69)	7
Bn O + Ph +	DMAD	130°	PhCN + $Bn \rightarrow O$ (13) MeO ₂ C CO ₂ Me	261

TABLE I-B. NITRILES FROM OXAZOLES AND RELATED RINGS (Continued)



TABLE I-B. NITRILES FROM OXAZOLES AND RELATED RINGS (Continued)



Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
R $R = H, Ts$	240°, 20 h	RCN + $S \longrightarrow (\leq 5)$	292
	164°, 72 h	MeCN + $HeO \longrightarrow O$ (48)	292, 293
North Contraction of the second secon	325°, 21 h	HCN + $H$ (81)	292
R = H, Ts	350°, 21 h	$RCN + \bigcup_{O} S = \frac{R  (\%)}{H  74}$	294
$\begin{array}{c} Ph \underbrace{S} \\ N \underbrace{S} \\ OH \end{array} + DMAD$	115°	(HNCO) + $Ph$ $S$ $Ar$ $Ar$ $Time$ (%) Ph $48 h$ $28P-ClC_6H_4 120 h 10$	295

TABLE I-B. NITRILES FROM OXAZOLES AND RELATED RINGS (Continued)

" Hückel calculations to predict regiochemistry are in "good agreement" with experimental results.

Product(s) and Yield(s) (%) Starting Material Conditions Refs. NEt₂ NEt₂ NEt₂ R⁴CN + 296 rt or heat R² `R¹  $\mathbb{R}^2$ R II I  $\mathbb{R}^3$  $\mathbb{R}^2$  $\mathbb{R}^4$ RI Temp I (%) II (%) н CO₂Me H Н 101° 10 -" н ... 81° CO₂Me 90 ----" " CO₂Me .... rt 80 _ .. CO₂Me ... Н 101° ____ 81 н " ., CO₂Me 25 rt 64  $\frac{R^1}{H}$ NEt₂  $\mathbb{R}^2$ (%) Me 97 Et₂N  $\|$  $\mathbf{R}^2$ rt-65° HCN + 18 " Ph 20 `N CN Me NC Me 36  $R^{2}$ HCN + R Heat 297 N  $\frac{R^1}{CO_2Et} \frac{R^2}{Me}$  $\mathbb{R}^3$ Temp Time (%) Et 80° 1 h 64 SO₂Me . 35° 3 h 66 " 101° 24 h 29 " " 43 Ph Me " --(CH₂)₄--- "

TABLE I-C. NITRILES FROM PYRIMIDINES AND PYRAZINES


TABLE I-C. NITRILES FROM PYRIMIDINES AND PYRAZINES (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs
$NO_2$ $N \sim N$ $H$ $R$ $H$	π-78°	HCN + $N$ $HCN$ + $N$ $HCN$ + $N$ $HCN$ + $N$ $R$ $HCN$ + $HCN$ $HCN$ + $HCN$	300
NO ₂ Bn NH	20°, 50 h	$ \frac{R  I(\%)  II(\%)}{NH_2  86 } $ $ NMe_2  17  36 $ $ NEt_2   trace $ $ OEt•HC1  63  $ MeSCN + I (43)	300
SMe R		NO ₂	
$NO_{2} + R + NH$ $NII_{2} + ISN (ca. 8\%)$	rt-78°	HCN + $(-)$ ca. 5% ¹⁵ N N $(-)$ ca. 5% ¹⁵ N R = Me, <i>t</i> -Bu, or Ph	301
+ (EWG)CH ₂ CN	0-70°	HCN + $O_2N$ EWG = CN, PhSO ₂ . $HCN$ + $(13 - 75)$ 4- $O_2NC_6H_4$ , 3-CF ₃ C ₆ H ₄ , $NH_2$ CO ₂ Et, etc.	302
	130°	HCN + $R^{1}$ NC CN $R^{1}$ $R^{2}$ (%) HCN + $R^{1}$ NC CN $R^{1}$ $R^{2}$ (%) H H 92 H 96 H CN 94	254
$R^1$ $N$ $R^2$ $R^2$	175°	HCN + $R^{1}$ $R^{2}$	303
Ar N NC CN	180°, 1 h	HCN + $\begin{array}{c} Ar \\ N \\ NC \\ NC \\ CN \\ X = Mc, Br, OMc, Cl, NO_2 \\ \end{array}$	304
	180-210°, 12-24 h	HCN + $\begin{array}{c} R \\ N \\ N \\ N \\ \end{array}$ $\begin{array}{c} X \\ W \\ X \\ \end{array}$ $\begin{array}{c} X \\ W \\$	305
$R^2$ $R^3$ $R^4$ $R^4$	180-210°, 12-96 h	$R^{1}(R^{3})CN + R^{2} + R^{4} + R^{2} + R^{3} + R^{4} + R^{$	306, 305
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
		н 09 " Н Рћ " " 75 SO ₂ " Н " " 63	

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
	180°, 24 h	HCN +		22
Ph N N N	170°, 4 h	HCN +	$\stackrel{\text{Ph}}{\overbrace{N}} (30)$	22
$\mathbb{R}^{2} \xrightarrow{\mathbb{R}^{1}} \mathbb{R}^{2}$	200°, 4 h	R ² CN +	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	22
	210°	HCN +	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	307
$ \begin{array}{c}                                     $	Heat	HCN +	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	(%)         92           96         307           94         100
R ¹ N NC CN	Heat	HCN +	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\frac{(\%)}{82}$ 72 307 75
$ \begin{array}{c} R^{1} \\ R^{2} \\ N \\ NC \\ CN \end{array} $	210°	HCN +	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	307
$\mathbb{N}$ \mathbb{N} $\mathbb{N}$ $\mathbb{N}$ $\mathbb{N}$ $\mathbb{N}$ $\mathbb$	PhNEt ₂ , reflux, 1 h	HCN +		308
	160°	HCN +	$\begin{array}{c} X & t_{1/2}(h) \\ \hline O & 0.47 \\ \hline NAc & 0.30 \\ \hline S & 1.74 \\ \hline CH_2 & 0.82 \\ \hline CO & <0.05 \end{array}$	309
$R^2$ $N$ $R^3$ $R^3$ $R^3$	140°	R ¹ CN +	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	310
$\mathbb{E}_{t} \stackrel{+}{}_{X} \mathbb{N} \mathbb{N}$	180°, 15 min	HCN +	$\begin{array}{c} Ph \\ \downarrow \\ + \\ N \\ + \\ I \\ Et \\ I \\ $	(%) ly 24 5

TABLE I-C. NITRILES FROM PYRIMIDINES AND PYRAZINES (Continued)

Starting Material	Conditions	Product(s) and Vield(s) (%)	Pefs
$\begin{array}{c} R^{2} \\ R^{2} \\$	TFA, reflux, 24 h	$R^{2}CN + \begin{array}{c} R^{1} \\ R^{2}CN \end{array} + \begin{array}{c} R^{1} \\ R^{2} \\ R^{2} \\ R^{2} \\ N \\ R^{2} \\ N \\ R^{2} \\ R^{2$	24
	110°, 2 h	HCN + $Et \xrightarrow{N}_{R}$ $R$ $(\%)$ R Ph high	24
	180°, 12-34 h	HCN + $R$ N $N$ $R$ $N$ $R$ $N$ $R$ $N$ $R$ $N$ $R$ $N$ $R$ $N$ $R$ $N$ $R$ $N$ $R$ $N$ $N$ $N$ $R$ $N$ $N$ $R$ $N$ $N$ $N$ $R$ $N$	306, 305
HO, OH N N R	200°	(HNCO) + $NH$ $NH$ $R$ $(\%)$ R $NH$ $R$ $(\%)$ R $Me$ 46 Ph 40	23
HO OH	200°	(HNCO) + (87) NH	23
$ \begin{array}{c} R^2 \\ R^1 \\ R^3 \\ N \\ N \\ R^4 \end{array} $	140°	$HCN + \begin{array}{c} R^{3} \\ R^{4} \\ R$	310
$R^2$ $R^3$ + $CO_2Me$ $R^1$ $R^4$	250°	$R^{1}CN$ + $R^{2}$ $R^{1}CN$ + $R^{3}$ (40 - 60) $R^{1} = H \text{ or } Me; R^{2} = CO_{2}Me \text{ or } CN$ $MeO_{2}C$ $R^{4}$ $R^{3}, R^{4} = CO_{2}Et \text{ or } CN$	311
$R^{1}$ $R^{3}$ + DMAD $R^{1}$ $R^{4}$	DMF, 100°	$R^{1}CN + MeO_{2}C$ $MeO_{2}C$ $MeO_{2}C$ $R^{4}$ $R^{3}$ (80)	311

TABLE I-C. NITRILES FROM PYRIMIDINES AND PYRAZINES (Continued)

 $R^1$  = H or Me;  $R^2$  = CO₂Me or CN  $R^3$ ,  $R^4$  = CO₂Et or CN



TABLE I-C. NITRILES FROM PYRIMIDINES AND PYRAZINES (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	195°	HCN + $R^2$	315
$N \sim 0$ $R^2$		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
	Heat, 4 h	HCN + $($ $X$ + $($ $X$ $X$ 2	26
		X         Temp         I (%)         II (%)           NAc         165°         17         83           O         210°         12         44           S         180°         24         68           SO         120°         57 $$ SO2         150°         88 $$	
NC CN N NC CN	120°, 2 h	HCN + $NC$ CN	26
	210°, 25 h	HCN + $NC + CN$ (60) 2	26
	130°, 2.5 h	HCN + $I$	27
-	TFA, 72°, 20 min	HCN + II (88) 2	27
	100°, D ₂ O	HCN + $+$ $N$ (88) 2	27
	n	HCN + $(\%)$ Et N X X $(\%)$ S 15 min 71 SO <<1 min 65	27
	TFA, 72°	HCN + $(N \times X) \times X$ $(N \times Y) $	27
	TFA, 72°, 45 h	HCN + $(85)$ (85)	27
	D ₂ O, 100°, 8 min	HCN + $+$ $N$ $O$ (75) 2	27

TABLE I-C.	NITRILES FROM PYRIMIDINES AND PYRAZINES (	Continued
		commuca

"The reaction of the chloride is abnormal, with a ring-opening route leading to this product.

^b MNDO calculations and X-ray data suggest that the rate effect of CN is due to conformation and inductive effects.

 c  The reaction was carried out with  $BF_{3}$  at 81°.

^d Yields are those of products after amide hydrolysis.



N = N + Heat + HCN + N = N + OEt + Heat + HCN + N + N + OEt + N + OEt + N + OEt +

TABLE I-D. NITRILES FROM 1,2,4- AND 1,3,5-TRIAZINES

TABLE I-D	. NITRILES FR	OM 1,2,4- AND	1,3,5-TRIAZINES	(Continued)
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	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
		······································		
	+ NAr	MgSO _{4.} rt	HCN + $\left( \begin{array}{c} N \\ N \end{array} \right) \xrightarrow{N} \left( \begin{array}{c} N \\ N \end{array} \right) \xrightarrow{N} \left( \begin{array}{c} 3 \end{array} \right)$	322
	Ar = 4-t-butoxycarbonylphenyl			
			$\mathbf{R}^2$ pl $\mathbf{P}^2$ (%)	
	+ N	90°	HCN + R ¹ $\frac{\kappa}{Et}$ $\frac{\kappa}{R}$ $\frac{\kappa}{R}$ $\frac{\kappa}{R}$	32
	$R^{2}$		$N \longrightarrow N = -(CH_2)_3 - 72$ $-(CH_2)_4 - 47$	
			(CH ₂ ) ₅ 76	
			<i>c</i> -C ₆ H ₁₁ H 66	
			Ph 80	
	+	"	HCN + $N$ (251)	32
	$\sim$ $N$		N CO ₂ Me	
	+ MeO ₂ C ^{-N}	Ψ	HCN + $N$ ( $\geq$ 50)	32
	HCI+HN NH2		Ph	
	+	120°	HCN + $NH_2$ (64)	323
	Ph			
			$\bigcirc$	
	+	125°	HCN + (64)	323
	V `NH•HCI			
			$\frown$	
	+ ( <u>N</u>	120°	HCN + NH (36)	323
	∽ `SMe			
			~	
N N	N DMAD	DME 100°		311.
	+ DMAD	DMF, 100	MeCo-C (20)	324
	N		MeO ₂ C CN	
			N N N N	
		MeCN, 81°	HCN + $(15)$	311, 324
			$MeO_2C$ $\uparrow$ $\downarrow$ $CO_2Me$ $MeO_2C$ $CO_2Me$	<i>324</i>
Ar			Ph	
	NH II	112° 00 b	ATCN + N (63)	34
	Ph NH ₂	112,901		
Ph N	`Ph Ar = 2-pyridyl		Ph N Ph	
	м – 2-рунаут			
(	H ₂ N NH•HCl		EtO ₂ C NH ₂	22
N	N +	DMF, 100°	$EtO_2CCN +      (80)$	33
EtO ₂ C	N ^{CO} 2Et		CO ₂ Et	
			R R (%)	
	H ₂ N, NH•HCl		EtO ₂ C NH ₂ H 85	
	+	DMF, 80-120°	$EtO_2CCN + 1 Me 85$	323,
	R		$CO_{\rm e}Et$ Db $22$	325, 326
				35
			$(CH_2)_{n-2}$ n (%)	
	NH•HCl //		$EtO_2C$ NH $\overline{3  32}$	
	+ $(CH_2)_n^{+}$ NH	100°	$EtO_2CCN +          4 75$ $N \swarrow N 5 28$	323
	$\smile$		r CO ₂ Et	

Starting Matarial	Conditions	Product(s) and Yield(s) (%)	Refs
CO ₂ Et N + MeS NH•HCl	100°	$EtO_2CCN + \frac{EtO_2C}{N} N $ (73)	323
+	п	$EtO_2CCN + EtO_2C + NH $ $N = N $ $CO_2Et$ $(11)$	323
+	101°	$EtO_{2}CCN + N + N + OO_{2}Et +$	36, 35
+	rt	$\begin{array}{c} CO_2Et \\ Bn_2N \\ N \\ CO_2Et \\ \end{array} \\ \begin{array}{c} CO_2Et \\ N \\ CO_2Et \end{array} \\ \begin{array}{c} Io1 \\ O \\ $	327, 35
+ H ₂ N NH-HCl	DMF. 100°	$EtO_{2}CCN + N CO_{2}Et ()$ $CO_{2}Et$	327
+ $R^2$ $R^1$	CH ₂ Cl ₂ , HOAc, 100°	$EtO_{2}CCN + \begin{matrix} R^{2} \\ I \\ N \\ CO_{2}Et \end{matrix} \xrightarrow{R^{1}} CO_{2}Et \end{matrix} \xrightarrow{R^{1}} \begin{matrix} R^{2} \\ -(CH_{2})_{3}- \\ -(CH_{2})_{4}- \\ R^{1} \\ -(CH_{2})_{3}- \\ CH_{2} \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ R^{2} \\ R^{2} \\ -(CH_{2})_{3}- \\ R^{2} \\ $	36
+		EtO ₂ CCN + $\begin{array}{c} R^1 \\ N \\ CO_2Et \end{array}$ $\begin{array}{c} R^1 \\ -(CH_2)_3 \\ -(CH_2)_4 \\ -(CH_2)_4 \\ -(CH_2)_4 \\ -(CH_2)_4 \\ -(CH_2)_5 \\ -(C$	36
MeS N SMe N MeS NFt ₂	150-230°	$MeSCN + Net_2 $ $MeSCN + N $ $MeS $ $MeS $ $MeS $ $MeS $ $MeS $	36
	<i>p</i> -TsOH, 100°	MeSCN + " (76)	36
MeS N SMe N MeS NBn ₂	<i>m</i> -CPBA, rt	$MeSO_2CN + MeSO_2 + NBn_2 $ $MeSO_2CN + NCN $ $MeSO_2 + NCN $	36

TABLE I-D. NITRILES FROM 1,2,4- AND 1,3,5-TRIAZINES (Continued)

Starting Material	Conditions	$\mathbf{D}_{roduct(a)}$ and $\mathbf{V}_{rodd(a)}(0)$	D.6.
~	Conditions	Product(s) and Tield(s) (%)	Keis
	377-1177°; E _a = 51.4	$H_2C=NH$ + ()	42
$\checkmark$	UV 185 nm	" + " (_)	328
			520
	0	$H_2C = NMe^{-} + (-)$	328
		b	
	FVP, 450-600°	$H_2C=NH$ + $CP$ (—)	44
()			
NH	"	$H_2C=NH$ + ()	44
1	111/ 105		
NMe	U v, 185 nm	$H_2C=NMe$ + (-)	328
∕~v			
X = 0, NH, or S	500-750°	$H_2C = X + (-)$	43
Mener	Aqueous solution	$RNH_2$ + $CH_2O$ + $CP-NMM$	46
-	Hunni seavenger (1.5 eq)	R Time Temp RNH ₂ (%)	
		H 5 h 50° —	
		<i>п</i> -ви 81 СН-СО.Ма 5 h "	
		$CH_2CO_2Me$ $3 H$ $$	
		$3.4-(MeQ)_2Bn$ " 50° 61	
		Bn 2 h " 81	
		CH(Bu)CONHCH(Bu- $i$ )CO ₂ Me 4 h 23° 97	
Me N	50°, 4 h		
A)	UV, 185 nm	/////NMe (52)	328
	UV, 185 nm BF ₃ •Et ₂ O, toluene, 100°, 2 h	NMe (52) V = 0 V = 0	328 329
R $R$ $Ph$ $R = Me, Ph$	UV, 185 nm BF3•Et2O, toluene, 100°, 2 h PPA	$ \underbrace{ \begin{pmatrix} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & $	328 329 330
$ \begin{array}{c}                                     $	UV, 185 nm BF3•Et2O, toluene, 100°, 2 h PPA	(52) $(52)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1)$ $(1$	328 329 330 45
$ \begin{array}{c}  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\ $	UV, 185 nm BF3•Et2O, toluene, 100°, 2 h PPA 80°	(52) $(52)$ $(52)$ $(52)$ $(52)$ $(51) + CP$ $(61) + CP$ $(61)$	328 329 330 45

TABLE II-A. IMINES

TABLE II-A. IMINES (Continued)				
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.	
Ar O Ar	112°	$Ar = Ph, 4-Cl, 4-Me, 4-MeO, 4-O_2NC_6H_4, 2-furyl, 2- or 3-pyridyl$	332	
R N	TFA:CHCl3 (1:1), Et3SiH, rt	MeNHR + CP R (no racemization) (%) Leu-OMe (TFA) 91 Phe-OMe 92 Val-OMe (TFA) 78 Tyr-OMe 75 phenylGly-OMe 88 Lys(Prot.)-OMe 76 Ser-OMe (TFA) 83 Leu-Phe-OMe 78 Ala-Ala-Ala-OMe 67	47	
	Sulfonic acid ion exchange resin	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	333	
	CuSO4 (0.05 eq) aqueous EtOH, 70°	$MeO$ $MeO$ $NH_2$ $(82) + CP$	333	
NR	FVP, 450°	$CH_2 = NR$ (22-77) + CP R = CHO; COMe; COPr- <i>i</i> ; CO ₂ Et; MeSO ₂	334	
	u.	(-) + CP	334	
CO ₂ Me	BF ₃	$CH_2 = N_{CO_2Et} + CO_2Me_{CO_2Me}$ ()	335	
$R^{2}$ $N$ $R^{1}$ $R^{1}$ $R^{1}$	MeCN, reflux	$CH_2 = N \stackrel{R^1}{\longrightarrow} R^2 \stackrel{+}{\longrightarrow} CO_2Me \qquad (low)$ $R^1 = CN, CONH_2, \text{ or } CO_2Me$ $R^2 = Me, Bn, \text{ or } Ph$	336	
	Pyridine-d ₅ , 75°, 4 h	$Cl_3C \xrightarrow{Ts} + CP (-)$	337	
CN N, CO ₂ Et OTs	80°	$TsO_N \neq CN \leftarrow CP (-)$	338	
$\begin{array}{c} c^{-C_{0}H_{11}},  P^{\bullet} O \\ \downarrow \\ CHCIR^{1} \end{array} \qquad $	l. AgBF4 in SO2 2. Basic Al2O3	$c-C_{6}H_{11}NHCHO + \begin{cases} R^{2} & (\%) \\ R^{2} & R^{2} \\ R^{1} & R^{2} \\ R^{2} \\$	339	

TABLE II-A. IMINES (Continued)			
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$c - C_6 H_{11}$ $N \to 0$ $C_5 H_{11} - n$ $C_5 H_{11} - n$ $C_5 H_{11} - n$	1. AgBF4 in SO2 2. Basic Al ₂ O ₃	$c - C_6 H_{11}$ - NHCHO + $n - C_5 H_{11}$ (80) Et	339
<i>n</i> -C ₅ H ₁₁ O _N C ₆ H ₁₁ - <i>c</i>	40°; t _{1/2} = 0.5 h	$N = C_5 H_{11} + O $ $V = C_1 + C_2 H_{11} + C_2 + C$	339
O O Ph OMe	GLC, 225°	$\begin{array}{c} N \\ H \\ Ph \\ OMe \end{array} OMe + \left[ \begin{array}{c} 0 \\ 0 \\ 0 \end{array} \right]$	340

^a The imine reacts further to form a cyclotrimer.

^b The imine decomposes at  $\geq -80^{\circ}$ .

^c The Lewis acid efficacy in this reaction is as follows:  $TiCl_4 > AlCl_3 > ZrCl_4 > Et_2AlCl > BF_3 \cdot Et_2O$ .





TABLE II-B. ISOCYANATES (Continued)			
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
O NH HN O	198°, 72 h	HNCO + $(40)$	347
HO N N Ph	198°, 48 h	HNCO + $HN$ (54) + $HN$ (-)	347
$(CH_2)_n \longrightarrow (CH_2)_n \longrightarrow (NH)$	180-200° (OC)	HNCO + $(CH_2)n$	350
	198°, 20 h (OC)	HNCO + $\begin{array}{c} R \\ R \\ R \\ R \end{array} \qquad \begin{array}{c} R \\ R $	347
HO CN N NH	u	HNCO + $N \rightarrow NH$ ()	347, 350
	180°	HNCO + (60)	350
	180°	HNCO + $(-)$	350
$MeO_{2}C$ $O$ $Ph$ $N$ $Ph$ $Ph$	210°	PhNCO + $MeO_2C$ $N_Ph$ $MeO_2C$ $N_Ph$ (90)	351
$\begin{array}{c} H_2N \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & $	Heat	$R^{1}NCO + H_{2N} + R^{2} + $	352
$\sim 0$ + N NPh + DMAD $R^1$ $R^2$	54°	$PhNCO + MeO_2C + MeO_2C + R^2 (\%)$ $R^2 + MeO_2C + R^2 Me Ph - Me Ph$	351
Bn OH HON + DMAD	rı	$\begin{array}{c} & & & & & \\ & & & & \\ HN & & & \\ HN & & & \\ O & & & \\ O & & & \\ CO_2Me & & & \\ & & & \\ & & & \\ CO_2Me & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$	348, 353
Bn N OH HO N Bn	150°	HNCO + $\begin{array}{c} Bn \\ MeO_2C \\ MeO_2C \\ MeO_2C \\ Bn \end{array} $ (95)	353





Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} \text{Ar} \swarrow 0 \\ N \swarrow 1 \\ N \swarrow 1 \\ \text{R}' + \\ \text{Ar} = 4 \cdot O_2 N C_6 H_4 \end{array} + DMAD$	101°	$CF_{3}CONCO + \underbrace{\begin{pmatrix} R & (\%) \\ N & Ar & Me & 78 \\ MeO_{2}C & CO_{2}Me & Ph & 75 \\ \end{pmatrix}$	367
$HN \qquad O \qquad R^{1}$ $HN \qquad Ph \qquad + \qquad H$ $BF_{4}^{-} \qquad R^{2}$	п	HNCO + $\binom{R^2}{N} \frac{R^1}{Ph} = \frac{R^1}{CO_2Me} \frac{R^2}{CO_2Me} \frac{(\%)}{90}$ CO ₂ Et Ph -	368
$\begin{array}{c c} HN & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ $	ЕЮН, CH ₂ Cl _{2.} 41°	HNCO + $Ar^2$ $R$ $Ar^1$ () $Ar^1 = Ph, 4 \cdot MeOC_6H_4, \text{ or } 3 \cdot ClC_6H_4$ $Ar^2 = Ph, 4 \cdot MeOC_6H_4, \text{ or } 4 \cdot O_2NC_6H_4$ $R = CO_2M_2 \text{ or } CO_2F_4$	369
$ \begin{array}{cccc} HN & O & Ph \\ & & & Ph & + \\ & & & & BF_4^- & Ph \end{array} $	DMF, 153°	HNCO + $Ph$ (28)	370
$R^{1}$ $R^{1}$ Ph NH $R^{2} = CO_{2}Me \text{ or } CO_{2}Et$ $R^{2} = Me, CO_{2}Me, \text{ or } Ph$	230°	HNCO + $N p_h$ (65-80)	371
O Ph CN + DMAD	HCl, DMF, heat	HNCO + $Ph$ $CO_2Me$ (10)	371
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	_	HNCO + $R^{3}$ $R^{2}$ $R^{1}$ $R^{1}$ $R^{2}$ $R^{3}$ $(%)$ Ph H Ph 57 " Ph " 28 Me CO ₂ Me CO ₂ Me 64 <i>i</i> -Pr " " 26 c-C ₄ Hs " " 47	372
$H_{2}N \qquad O \qquad CO_{2}Et$ $N + Ph \qquad + \qquad H$ $BF_{4} - Ph \qquad Ph$	150°	HNCO + $\begin{pmatrix} Ph \\ N \\ $	50
+ DMAD	100°, DMF	HNCO + $N$ Ph (82)	50
$Me^{N^{-}_{N}} + DMAD$ $Me^{+}_{Me^{-}}$	80°	MeMeNCO + $MeO_2C$ $CO_2Me$ (60)	373
$Me^{Ar} + DMAD$ $Me^{Ar} + Ar = 4-CH_3C_6H_4$	u.	ArNCO + $Me$ MeO ₂ C $CO_2Me$	374
$N_{H} = \frac{1}{2} \frac{1}{2} \frac{1}{NBz} + DMAD$	138°	$BzNCO + MeO_2C + CO_2Me$	375
$\begin{array}{ccc} Ph & & \\ & & \\ & & \\ & & \\ Me' & + & \\ & & \\ Me' & & \\ \end{array} \qquad \qquad$	0-110°	MeNCO + $Ph \rightarrow O \qquad Ar \qquad R^1 = H, Me, Ph, or CO_2Me$ $(27-91) \qquad R^2 = Ph, CO_2Me, Bz, or n-Bu \qquad 3$ $R^1 \qquad R^2 \qquad Ar = 4-O_2NC_6H_4$	376

TABLE II-B. ISOCYANATES (Continued)

Starting Material	Conditions	Product(s) and Yield(s	(%) Re
$^{Ph} \checkmark ^{S} \checkmark ^{Ph}$		$Ph \swarrow S \swarrow Ph = \frac{R}{R}$	<u>(b)</u>
<u>N</u> +	80°	PhNCO + Bz 4	2 377
Ph' + `O-		$\mathbf{R}'\mathbf{R}$ CF ₃ 9	0
ĸ		CN 9	5
Bz		Db S. Ph	
+ 11	"	PhNCO + $(42)$	378
1			
Bz			
MeS. S. Ph		March S. Ph	
	"	$\frac{\text{MeS}}{\text{PhNCO}} + \frac{(100)}{(100)}$	370
			517
CO ₂ H		$HO_2C$ $CO_2H$	
$R^1 \leq S \leq R^2$		$R^1 \sim S \sim R^2 = R^1$	$R^2$ (%)
T + DMAD	"	PhNCO + SMe	Ph 67 379
$Ph$ + $O^-$		MeCoC COoMe SEt	" 63
		SPr	" 46
		NMe ₂	" 69
		"	CO ₂ Me 16
Ph > S > Ph		$P_h \sim S_{S_h} P_h$	-
+ DMAD	u	PhNCO + (90)	380
Ph' + 0-		MeQ.C CO Ma	330,
		MeO ₂ C CO ₂ Me	
$r^{Ar} \sim P^{Ph}$		$^{Ph} \checkmark ^{S} \checkmark ^{Ar}$	
$\stackrel{\text{``}}{} + \text{DMAD}$		MeNCO + (80)	381
Me O		$MeO_2C$ $CO_2Me$ $Ar = 4-N$	leOC ₆ H ₄
Ar S 0		DL S Ar	
	1400	$Ph \bigvee AI $ $(28)$	291
h'' + Ph + DWAD	140	Ar = 4 - W	IeOC₄H₄
0-		MeO ₂ C CO ₂ Me	
$Ph \xrightarrow{S} Ph$ N  + DMAD	80°	(S) + $MeO_2C$ $N$ (70)	377
Ph O ⁻		MeO ₂ C III	Ar
R ^I S Ar		R ¹ Ar MeO ₂ C	
N = + DMAD	135°	R ² NCO + +	382
$R^{2^{+}}$ $O^{-}$ $Ar = 4 - XC_{6}H_{4}$		MeO ₂ C CO ₂ Me MeO ₂ C	^N Ph
		_	, ^k '
		I	11
		$\mathbf{X} \mathbf{R}^{1} \mathbf{R}^{2} \mathbf{I}$	(%) <b>II</b> (%)
		OMe Ph Ph	80 —
		Н " "	99 —
		Cl " "	80 —
		NO ₂ " "	97 —
		" SPh "	94 —
		" CN "	98 —
		H " "	92 —
		NO ₂ Me "	59 32
		" NMe ₂ "	98 —
		Ph Bn	- 80
			80
		$NO_2$ N(Me)CH=CH— Cl " "	00 52
		e. Ar	
		1	
Me ₂ N		MeO ₂ C 0	
$Me_2N \bigvee_{N} Se Ar + DMAD$	135°, 0.5 h	MeO ₂ C	382
$Me_2N \bigvee_{N=1}^{Se} Ar + DMAD$ $Ph'^+ O^- Ar = 4 - O_2NC_6H_4$	135°, 0.5 h	$MeO_2C \xrightarrow{N} Ph (-)$	382
$Me_2N \xrightarrow{N} Ar + DMAD$ $Ph + O^- Ar = 4 - O_2NC_6H_4$	135°, 0.5 h	$MeO_2C \xrightarrow{N} Ph $ $MeO_2C \xrightarrow{N} Ph$ $NMe_2$ $(-)$	382
$Me_2N \xrightarrow{Se} Ar + DMAD$ $Ph \xrightarrow{Ph} O^- Ar = 4 \cdot O_2NC_6H_4$	135°, 0.5 h	$MeO_2C \xrightarrow{N} Ph $ $MeO_2C \xrightarrow{N} Ph$ $NMe_2$ $(-)$	382 N.
$Me_2N \xrightarrow{Se} Ar + DMAD$ $Ph \xrightarrow{Ph} O^{-} Ar = 4 \cdot O_2NC_6H_4$ $O \xrightarrow{Ph} CO_2Me$ $PhN \xrightarrow{S} N \xrightarrow{H} I_1 T_S$	135°, 0.5 h 112°	$MeO_2C \xrightarrow{N} Ph$ $MeO_2C \xrightarrow{N} Ph$ $NMe_2$ $PhNCO + Ph \sqrt{S} Ph (88) + (68)$	382 Ts N (82) 383

Starting M	aterial	Conditions			Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} Ph \\ O \\ Ph \\ Ph \\ Ph \\ Ph \\ Ph \\ Ph \\ $		Heat	PhNCO	+	- furan + $Ph$ $S$ $Ph$ (84) $S$ $MeO_2C$ $CO_2Me$ $S$	384, 385
S Ph O Ph Ph		138°	PhNCO	+	+ S (67)	32
$\begin{array}{c} O^{-} \\ Ph \\ N \\ Ph \\ N \\ Ph \\ Ph \\ Ph \end{array} + I$	DMAD	132°	PhNCO	+	$+ \underbrace{MeO_2C}_{Ph} \underbrace{R}_{N} \underbrace{R}_{O} \underbrace{R}_{H} \underbrace{R}_{H} \underbrace{(\%)}_{H} \underbrace{R}_{83} \underbrace{R}_{Ph} \underbrace{(\%)}_{Ph} \underbrace{R}_{H} \underbrace{R}_{83} \underbrace{R}_{H} \underbrace{(\%)}_{H} \underbrace{R}_{H} \underbrace{R}_{H} \underbrace{R}_{H} \underbrace{(\%)}_{H} \underbrace{R}_{H} \underbrace{R} \underbrace{R}_{H} \underbrace{R} \underbrace{R}_{H} \underbrace{R}_{H} \underbrace{R}_{H$	386
$S \xrightarrow{0}{N} S \xrightarrow{1}{Et} O$	DMAD	61°	EtNCO	+	$CO_2Me$ (65)	387
N $N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$	$ \begin{array}{c c} R^{1} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	135°	MeNCO	+	+ $R^{1}$ $R^{2}$ $R^{1}$ $R^{2}$ $(\%)$ $CO_{2}Me$ $CO_{2}Me$ $64$ CN $CN$ $33CO_{2}Me H 47$	388
$\begin{array}{c} & \overset{Me}{}_{} \overset{O^-}{}_{} \\ & \overset{N}{}_{} \overset{\overset{Me}{}}{} \overset{O^-}{} \\ & \overset{N}{} \overset{}{} \overset{}{} \overset{O^-}{} \end{array} + \\ \end{array}$	R      R	140°	MeNCO	+	+ $N$ $R$ $R$ $(\%)$ N $Bz$ 47 O $CN$ $-$	389
Formation of Carbodiimides $ \begin{array}{c} Me \\ Ph \\ N \\ Ph' \\ Ph' + \\ N \\ N \\ Ac \end{array} $	+ DMAD	80°	N A II II Ph	с	+ $Me$ MeO ₂ C $N$ Ph (45) 3 MeO ₂ C $CO_2Me$	390
$\stackrel{Me}{\underset{Ph' + \underbrace{N}}{\overset{N}{\underset{P}{\overset{N}}}}, Bz}}$	+ DMAD	v	N B U C II N Ph	z	+ $Me = 1$ MeO ₂ C $Ph$ (38) $MeO_2C = CO_2Me$	390, 375
$\overset{Ph}{\overset{N}{\leftarrow}} \overset{S}{\underset{Ph'}{\overset{N}{\leftarrow}}} \overset{S}{\underset{N}{\overset{N}{\leftarrow}}} \overset{Bz}{\underset{N}{\overset{Bz}{\overset{N}{\leftarrow}}}}$	+ DMAD	138°	N B C II N Ph	z	+ $MeO_2C$ $CO_2Me$ ()	375

TABLE II-B. ISOCYANATES (Continued)

" Note change in mechanism to non-rDA.

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\bigcirc$	600°	CH ₂ O (66) + (38)	51
Č Č	FVP, 685°	CH ₂ O + ()	391
	NaH, rt	$\begin{bmatrix} 0 \\ N \end{bmatrix} \longrightarrow CH_2O + N (ca. 60)$	392
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Me ₃ N	$\begin{bmatrix} R^{1} \\ R^{2} \\ 0^{-N} \\ Et \end{bmatrix} \longrightarrow CH_{2}O + R^{1} \\ R^{2} \\ R^{2}$ (280)	393
R = alkyl, alkenyl, Bn, hydroxyalkyl	112°	$CH_2O + R^{CHO} (45-83)$	53
OTBDMS	a. 150°, 72 h <i>or</i> b. Et ₂ AICl, 40°, 1 h	CH ₂ O + $(50)$ OTBDMS $(50)$	53
0_0	112°	$CH_2O + C_8H_{17}$ (80)	54
0_0		$CH_2O$ + $C_8H_{17}$ (69)	54
$C_{13}H_{27}$	u	$CH_2O + C_{13}H_{27}$ (100)	394
	112°	$CH_2O + R - O = R - CH_2O + R - CH_2O + R - CH_2O + R - CH_2O - H - CH_2O + R - CH_2O + $	395
	FVP, 610°	$\begin{bmatrix} 0 \\ \vdots \\ \vdots \\ -0 \end{bmatrix} \xrightarrow{C:} \\ 0 \end{bmatrix} \xrightarrow{CH_2O (60)} + \xrightarrow{C:} \\ (30)$	396
ОСНО	Heat	МеСНО + (—)	397
$O + O CO_2Me$ R R	104°	MeCHO + $O_{R}$ $CO_{2}Me$ $\frac{R}{H}$ $\frac{(\%)}{70}$ Me 60	52
$Ac \xrightarrow{0} Ac \xrightarrow{0} CO_2Me$	n	MeCHO + $Ac$ $CO_2Me$ (65)	52
+ DMAD	110°	MeCHO + $Ac$ $CO_2Me$ (69)	52

TABLE II-C. CARBONYL COMPOUNDS

	TABLE II-C. CAR	RBONYL COMPOUNDS (Continued)	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \underset{O \searrow N}{R^2} \underset{N}{\overset{S}{\bigvee}} \underset{N}{\overset{R^1}{\bigvee}} $	120-140°	$R^{2}CHO + \begin{bmatrix} S \\ R^{1} \end{bmatrix}_{2} \frac{R^{1}}{Ph} \frac{R^{2}}{H} \frac{I(\%)}{60}$ $I \qquad I \qquad$	398
<u>^</u>		$4-CH_3C_6H_4 \qquad Me \qquad 48$ $4-CIC_6H_4 \qquad " \qquad 81$ $2,6-Cl_2C_6H_3 \qquad " \qquad 16$	
[ <u>}</u> 0	FVP, 400°	(258)	399
	290-600°	" (—)	400
$\stackrel{Ph}{\underset{H}{\overset{O}}} \stackrel{+}{\underset{N}{\overset{N}{\underset{H}{\overset{D}}}}} BF_4^-$	Aqueous K ₂ CO ₃	PhCHO + $CH_2O$ + $(N H_2)$ ()	401
$ \begin{array}{c}                                     $	DBU	$R^{1}$ $R^{1} = H \text{ or } Me$ $R^{2} = H \text{ or } CH_{2}OTBDMS$	401
$\left\langle \bigcup_{O'}^{\mathbb{N}} \right\rangle^{\mathbb{R}} \rightleftharpoons \left\langle \bigcup_{O'}^{\mathbb{N}} \right\rangle^{\mathbb{R}}$	Heat	$\left[\overbrace{\bigcirc 0}^{R} \\ NH \\ NH \\ R \\ $	402, 403
O-N Ph	1. 200° 2. H ₂ O	(32)	402, 403
$ \begin{array}{c}                                     $	1. 0 [°] , K ₂ CO ₃ 2. π-80°	$ \begin{array}{c}  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & & & \\  & &$	404
Ph CHO	Melt, <i>ca</i> .100°	Ph CHO ()	405
O + $O$	104°	$ \begin{array}{c} 0 \\ + \end{array} \begin{array}{c} \\ CO_2 Me \end{array} $ (73)	52
Ph Ph Ph	Air oxidation	$\begin{bmatrix} Ph \\ 0 \\ Ph \\ Ph \end{bmatrix} \longrightarrow \begin{pmatrix} 0 \\ Ph \\ Ph \\ Ph \end{pmatrix} + \begin{pmatrix} Ph \\ 0 \\ Ph \\ Ph \end{pmatrix}$	406
0 + DMAD	rt	$ \begin{array}{c} O \\ \downarrow \\$	235
of mero	180°		235
$R$ + $CO_2Me$	240°	$\begin{array}{c} O \\ O \\ P \\$	407



TABLE II-C. CARBONYL COMPOUNDS (Continued)



Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
S	FVP, 650°	$\begin{bmatrix} S \\ II \\ CH_2 \end{bmatrix}  ()  +  C_{14}H_{10}  (100)$	59
	130°, 24 h	S (49) + (69)	60, 61
S + $S$	400°	<i>S</i> (−)	426, 427
s + 1	99°, 1 h	$(92) + C_{14}H_{10}$	60, 61, 192
Ph S S Ph Ph Ph Ph	rt	$\begin{bmatrix} Ph & S \\ & & \\ & & \\ & & \\ & Ph \end{bmatrix} \longrightarrow \begin{array}{c} Ph & S & Ph \\ & & & \\ & & \\ & & Ph & S \end{array} $ ()	64
Ph S S Ph SPh SPh	80°	$\begin{bmatrix} Ph & S \\ SPh \end{bmatrix} \qquad (-)$	428
S ^{-S} SPh ⁻ SPh	80°	$\begin{bmatrix} S \\ SPh \end{bmatrix} (-)$	428
s S	п	$\begin{bmatrix} S \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	429
S S S	20-50°	" + C ₁₄ H ₁₀ ()	429
	rt	$\frac{Cl}{Cl} + \frac{Cl}{Cl} + \frac{Cl}{Cl} $	429
R = H  or  Me	112°	$\begin{bmatrix} R_2 H C_{1} N_{1} S \end{bmatrix}$ + $(-)$	430
S	FVP, 500°	$\begin{bmatrix} \mathbf{R} \\ \mathbf{S} \\ \mathbf{N} \\ \mathbf{H} \end{bmatrix} \xrightarrow{-60^{\circ}} \mathbf{S} \\ \mathbf{S} \\ \mathbf{N} \\ \mathbf$	430
s	100°, DMF	$\begin{bmatrix} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & $	431

TABLE II-D. THIONES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
S NMe S Ph	90°	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	432
R +	120°	S (79-84) + CP (—) R R = CO ₂ Et. CONHPh. Bz. CN. or 4-O ₂ NC ₆ H ₄	433
S S S S S S S S S S S S S S S S S S S	FVP, 515°	$\begin{bmatrix} S \\ H \\ CN \end{bmatrix} + CP (-)$	434
NC Ph S Ph	Melt, ca. 120°	$ \begin{bmatrix} S \\ S \\ CN \\ CN \\ Ph \end{bmatrix} + C_{10}H_{14}  () $	435
EIO ₂ C	$\frac{112^{\circ}}{K_{exo/endo}} = 2.3 \text{ at } 112^{\circ}$	$\begin{bmatrix} S \\ H \\ CO_2Et \end{bmatrix} + CP \implies S \\ CO_2Et$	436
EtO ₂ C S	t _{1/2} (100°) = 109 min	$\begin{bmatrix} S \\ H \\ CO_2Et \end{bmatrix} + C_{10}H_{14}  ()$	437, 62, 63
CO2Et s + thebaine	110°, 5 h	$MeO$ $KO_2Et$ $KO_2$	62, 63
MeO NMeO H CO ₂ Et	110°, 8 h	$MeO \longrightarrow NMe (-)$ $MeO \longrightarrow H \longrightarrow CO_2Et$	62, 63
EtO ₂ C S HN N CCl ₃	80°, 16 h	$\begin{bmatrix} S \\ H \\ CO_2Et \end{bmatrix} + N \\ CI_3C \\ H \\ CI_3C \\ H \\ O \\ H \\ O \\ (80)$	438
SCO ₂ Et	110°	$\left[\begin{array}{c} S\\ \swarrow\\ CO_2Et \end{array}\right] + CP (-)$	439
R CO ₂ Et		$\begin{bmatrix} S \\ R & CO_2Et \end{bmatrix} + C_{10}H_{14}  ()$	439
$\kappa = me, El, Bn, or allyl S CO_2(CH_2)_nCH=CH_2n = 1-5$	FVP 500°	$\left[\begin{array}{c} S \\ \bigcirc \\ CO_2(CH_2)_nCH=CH_2 \end{array}\right] \longrightarrow \text{ ene and other products } + CP (-)$	440
S CO ₂ Et		$\left[\begin{array}{c} S\\ EtO_2C \end{array}\right] + CP (-)$	437
EtO ₂ C CO ₂ Et	t _{1/2} (100°) = 35 min	$\begin{bmatrix} S \\ E_{10}C \\ C_{02}E_{1} \end{bmatrix} + C_{10}H_{14}  (-)$	437

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
s,o	FVP, 650°	$\begin{bmatrix} s'^{O} \\ H_{11} \\ CH_{2} \end{bmatrix} + C_{14}H_{10}  (100)$	59
F ₃ C S _{CF3}	ca. 190°	$\begin{bmatrix} s'^{O} \\ CF_{3} & CF_{3} \end{bmatrix} + C_{14}H_{10}  ()$	441
CI SCF3 Cis	190°	$\begin{bmatrix} O_{S} \\ \parallel \\ CI \\ Z \end{bmatrix} + C_{14}H_{10}  ()$	442
CI SCCI3	150-180°	$\begin{bmatrix} 0\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	443
Sco ₂ Et +	60°	+ $C_{14}H_{10}$ ()	65
S ^{CO} 2Et +	80°	+ $C_{14}H_{10}$ ()	65
CO ₂ Et	111°	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	•) 437
EtO ₂ C CO ₂ Et	80°	$\begin{bmatrix} 0 \\ S \\ H \\ EtO_2C \\ CO_2Et \end{bmatrix} + C_{14}H_{10}  ()$	437
	-40°	$C_{1}$ + $C_{P}$ ()	444
SO ₂ CO ₂ Me	225°	$\begin{bmatrix} CH_2 = SO_2 \end{bmatrix} + \begin{bmatrix} CO_2Me \\ CO_2Me \end{bmatrix} + SO_2 + \begin{bmatrix} CO_2Me \\ CO_2Me \end{bmatrix} + CO_2Me $	-) 66
O ₂ S Ph CO ₂ Me CO ₂ Me	220°	$\begin{bmatrix} CH_2 = SO_2 \end{bmatrix}$ (>80) + $\begin{bmatrix} Ph \\ CO_2Me \\ CO_2Me \end{bmatrix}$	67, 68
O ₂ S Ph O O	Heat	$\begin{bmatrix} CH_2 = SO_2 \end{bmatrix} + \underbrace{Ph}_{I} O \\ I O \\ \hline I O \\ \hline 120^{\circ} 210 \min 16 \\ \hline 15 \\ \hline \end{bmatrix} \underbrace{Ph}_{I} O \\ + SO_2 \\ \hline II \\ \hline O \\ \hline O \\ \hline O \\ \hline II \\ \hline O \\ \hline \hline O \\ \hline \hline O \\ \hline \hline O \\ \hline O \\ \hline \hline \hline O \\ \hline \hline O \\ \hline \hline \hline O \\ \hline \hline O \\ \hline \hline \hline O \\ \hline \hline O \\ \hline \hline \hline O \\ \hline \hline \hline \hline$	445

TABLE II-D. THIONES (Continued)

TABLE II-E. OTHER C=X DIENOPHILES			
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} R^1 \\ Si \\ CF_3 \end{array}$	FVP, 350-650°	$\begin{bmatrix} CH_2 = Si \begin{pmatrix} R^1 \\ R^2 \end{bmatrix} \rightarrow \begin{bmatrix} R^2 \\ R^1 \end{pmatrix} Si \begin{pmatrix} Si \\ R^2 \end{pmatrix} R^2 + \begin{bmatrix} CF_3 \\ CF_3 \end{bmatrix}$ $= \begin{bmatrix} R^1 & R^2 & I(\%) & II(\%) \\ H & H & 85 & 20 \\ D & D & - & - \\ CI & CI & 79 & 36 \\ II & 65 & - \\ & Me & 39 & 28 \end{bmatrix}$	71, 446, 447
$CF_3$ $CF_3$ X = H, Me  or  CI H Me	FVP	$\left[\begin{array}{c} \mathbf{CH}_2 = \mathbf{Si} \begin{pmatrix} \mathbf{X} \\ \mathbf{H} \end{pmatrix}\right]^a + \mathbf{I}  ()$	72
$CF_3$ Me Me	FVP, 550°	$\begin{bmatrix} Me \\ CH_2 = Si \\ H \end{bmatrix} (35) + I (84)$	448
CF ₃	≥400°, flow	$\begin{bmatrix} Me \\ CH_2 = Si \begin{pmatrix} Me \\ Me \end{bmatrix} $ (94) + I (76)	449
Me _{no} Si CF ₃	FVP, 520°	$\begin{bmatrix} CH_2 = Si \\ Me \end{bmatrix} + I (83)$	448
Cl Si CO ₂ Me	FVP, 400°	$\begin{bmatrix} CH_2 = Si \begin{pmatrix} CI \\ CI \end{bmatrix} + \begin{pmatrix} CO_2Me \\ CO_2Me \end{pmatrix} ()$	447
$K_{Ph} = R = neopentyl$	FVP, 500°	$\begin{bmatrix} Me & Ph \\ Si & \\ U & \\ R \end{bmatrix} + CP \longrightarrow \begin{pmatrix} Si & Ph \\ Si & \\ K & \\ R &$	450
R = neopentyl	300°	$\begin{bmatrix} R \\ Si \\ Ph \end{bmatrix} (-) + C_{14}H_{10}$	73
R = neopentyl	'n	$\begin{bmatrix} R & Ph \\ S & Me \end{bmatrix} (-) + C_{14}H_{10}$	73
Me_TMS Si	_	$\begin{bmatrix} CH_2 = Si \begin{pmatrix} TMS \\ Me \end{bmatrix} \qquad ()  +  C_6H_6$	451
Me P CO ₂ Me CO ₂ Me	40°, 5 h	$\begin{bmatrix} CH_2 = P \end{bmatrix} (-) + \begin{bmatrix} CO_2Me \\ CO_2Me \end{bmatrix}$	74
Ph P	30°	$\begin{bmatrix} CH_2 = P' & \\ CH_2 = P' & \end{bmatrix}  ()  +  C_6 II_6$	74
P <i>endolexo</i> interconverted	≥100°		75. 452

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	110°	$ \begin{array}{c}                                     $	75
+	130°	(35)	75
Ph Ph Ph Ph		$ \begin{bmatrix} Ph \\ P \\ P \\ Ph \end{bmatrix}^{b} \xrightarrow{Ph} Ph \xrightarrow{Ph} Ph \xrightarrow{Ph} Ph \xrightarrow{Ph} Ph \xrightarrow{(-)} Ph \xrightarrow{Ph} Ph $	452
Ph CO ₂ Me S CO ₂ Me	PBu3, 150°	$(25) + CO_2Me \qquad (-)$	453
F P CF ₃	770°	$\begin{bmatrix} CF_2 = P'^{CF_3} \end{bmatrix} (-) + $	454
$ \underset{P_{CF_3}}{ }^{F} F $	610°	" (—) + CP	454
$F_{F}$	700°	" () +	454
$\mathbb{D}_{\mathbf{P}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}_{\mathbf{N}_{\mathbf{N}}_{\mathbf{N}}_{\mathbf{N}}}}}}}}}}$	rt, 3 d	$\begin{bmatrix} \swarrow \\ P \sim \bigwedge_{N \\ Ac}^{N} \end{bmatrix} + CP \longrightarrow \begin{bmatrix} \swarrow \\ P \sim \bigvee_{N \\ Ac}^{N} \end{bmatrix} (>46)$	455
Ph CO ₂ Me CO ₂ Me	112°	$\begin{bmatrix} CH_2 = P \\ Ph \end{bmatrix} (260) + CO_2 Me $ (100) Ph CO_2 Me	456
CF ₃ Se _{CF3} +	80°, 40 h	$Se = CF_3 (84) + C_{14}H_{10} CF_3$	457
Se	75°, CHCl ₃	$\begin{bmatrix} H \\ Ph \end{bmatrix}  (-)  +  C_{14}H_{10}$	76
Se CO ₂ Er	112°, 40 h	$\begin{bmatrix} H \\ EtO_2C \end{bmatrix} + CP \longrightarrow Se_{CO_2Et} K_{eq} (112^\circ) = 3.3$	458
Se CO ₂ Et +	100°	Se (85) + CP CO ₂ Et	458
EtO ₂ C Se	80°	$\begin{bmatrix} H \\ EIO_2C \end{bmatrix} = Se \begin{bmatrix} (264) + C_{14}H_{10} \end{bmatrix}$	459
+	80°, 64 h	$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	458
EtO ₂ C Se +	Heat	$Se$ () + $CO_2Et$	458

TABLE II-E. OTHER C=X DIENOPHILES (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
R Se + X	Heat	$Se = \frac{R}{PhCO} \frac{(\%)}{91} + $	458
LSb_Sb_	-20°	(-) ΔH° = 7.3; ΔS° = 23	77
Bi-Bi	-20°	$() \qquad \Delta H^{\circ} = 12; \Delta S^{\circ} = 23$	77, 460
BiBi	-10°	$() \qquad \Delta H^o = 9.9; \ \Delta S^o = 24$	77

TABLE II-E. OTHER C=X DIENOPHILES (Continued)

^{*a*} This intermediate is isolable at  $-263^{\circ}$ . ^{*b*} This intermediate was trapped by in situ dienophiles.

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV, Ar, -265°	$\square O \longrightarrow CO_2 + \Box (-)$	4
	UV	$\begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & $	461
	FVP, 400-850°	CO ₂ + ()	82
0 + Fe(CO) ₅	UV	$CO_2$ + $\overrightarrow{P}$ ()	462
$\square O + O + O Co(CO)_2$	"	$CO_2 + \overset{\frown}{CO}_{C0} (17)$	463
+ $CO_2Mc$ Co(CO) ₂	'n	$CO_2 + co (17)$	463
o o o o o o o	UV, Ar, -265°	$D \xrightarrow{O} UV CO_2 + D \xrightarrow{(-)}$	81
	n	$\bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} \bigcup_{D} (-)$	81
	"	$ \begin{array}{c} D \\ D \\ D \end{array} $ $ \begin{array}{c} D \\ D \\ D \end{array} $ $ \begin{array}{c} D \\ D \\ D \\ D \end{array} $ $ \begin{array}{c} D \\ D \\ D \\ D \\ D \end{array} $ $ \begin{array}{c} D \\ D \\$	81

TABLE III-A. CO2 FROM UNSUBSTITUTED PYRONES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV, Ar, -265°	D = D = D = D = (-)	81
	T	$D$ $UV$ $CO_2$ + $D$ $(-)$	81
	'n	$D \longrightarrow D \longrightarrow CO_2 + D \longrightarrow (-)$	81
NH ₂ CO ₂ H	NaNO2, HOAc, 0°	$\begin{bmatrix} 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ $	83
O O CO2Et	H ₂ O ₂ , HOAc, 0°	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	83
	180°, 5 d	$CO_2 + \underbrace{Ft}_{Ft} $ (12)	85
Ét <i>t-</i> Bu +     <i>t-</i> Bu	210°, 5 d	$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \longrightarrow CO_2 + Ph^{OO_2H} (-)$	85
$ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & $	≥10°	$N_2 + SO_2 + CO_2 + $ (36)	203
+ $()$	150-170° (OC)	CO ₂ + (4)	464
+ N Se		CO ₂ + (11)	464
+	rt	CO ₂ + (88)	464
+ N Se	150-170°	CO ₂ + " (74)	464
+ N Se		CO ₂ + (53)	464. 465
+ Se Nin	n	CO ₂ + (58)	464
+ N Se	150-170°	CO ₂ + (4)	464

TABLE III-A. CO₂ FROM UNSUBSTITUTED PYRONES (Continued)

TABLE III-A.	CO ₂ FROM UNSUBSTITUTED	PYRONES (Continued)
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TABLE III-A. CO2 FROM UNSUBSTITUTED PYRONES (Continued)									
Starting Material	Conditions				Produc	t(s) and Y	rield(s)	(%)	R
	150-170°	CO ₂ +				(60)			464
+ (CH ₂ ) ₁₀	DMF, 150°	CO ₂ +		(CH ₂ )	10		(10)		466
$\begin{array}{c} \mathbf{R}^{\mathbf{I}} \\ \mathbf{H} \\ \mathbf{R}^{2} \end{array}$	150°	CO ₂ +		$R^{1}$ $R^{2}$	+		+ 2	$R^1$ $R^2$ III	467
				" Me ₃ Sn TMS Me ₂ HSi Et	TMS " " Et	74 50 30 48 12	0 0 41 13 0	0 0 2 0 0	
$\begin{array}{c} R^{2} \\ R^{3} \\ R^{4} \end{array} \xrightarrow{O} \begin{array}{c} CO_{2}Me \\ + \\ R^{4} \end{array}$	200°	CO ₂ +	$R^2$ $R^3$		+ 2Me	$R^2$ $R^3$	$R^1$ $R^4$	,CO₂Me	468
			R ¹ H	R ² H	R ³ H	R ⁴	I:II	<u>(%)</u> 56	
			CO ₂ Me	н	"	"	68:32	95	
			Н	CO ₂ Me	"		65:35	56	
				н	CO ₂ Me	"	42:58	98	
					н "	сО ₂ Me	63:37	100	
			H	OMe		л "	74:26	45	
			"	"	Me		49:51	53	
			Me	"	н	"	58:42	95	
			Et	"	"	"	69:31	96	
			н	"	"	Me	88:12	44	
			"	"	"	CO ₂ Et	82:18	41	
				Me	CO-Ft	OMe Me	85:15	14 86	
				OFt	Н	н	23.05	64	
				OLI		11	23.11	<b>01</b>	



TABLE III-A. CO₂ FROM UNSUBSTITUTED PYRONES (Continued)

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
	115°	CO ₂ +	()	86
	180°	CO ₂ +	()	86
a market	220°	CO ₂ +	(91)	475
O O O O O O O O O O O O O O O O O O O	n	CO ₂ +	0 N (93)	475
0 McO ₂ C CO ₂ Mc	u	CO ₂ +	CO ₂ Me CO ₂ Me (95)	475
	275°	CO ₂ +		475
	-	CO ₂ +	0 (70)	475
	230°	CO ₂ +	0 + $0$ + $0$ + $0$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ + $1$ +	90
+	80°	CO ₂ +		88
+ $\mathbb{N}_0^0$	6.2 kbar, 25°			87
	140°	CO ₂ +		87
Br Br	Zn, DMF, 156°	CO ₂ +	(58)	476
	≥110°	CO ₂ +	(100)	476
	1. 65° (adduct) 2. 165°, vacuum	CO ₂ +	(80)	477
O O O O $CO_2Et$ O	140°	CO ₂ +	$(15) + (15) + CO_2Et$	478

## TABLE III-A. CO2 FROM UNSUBSTITUTED PYRONES (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Re
EtO ₂ C	125°	$CO_2$ + $CO_2Et$ $EIO_2C$ N (23) + $N$ (32)	478
	170°	$CO_2$ + $(21)$ + $C_4H_4O$ ()	478
	80°	CO ₂ + ()	479
+ N=R	112°	$CO_2 + C_6H_6 + $	(8) 480
$\mathbb{R}$	Heat	$CO_2 + C_6H_6 + \left[\begin{array}{ccc} R \\ \hline \\ R \\ R \end{array}\right] - \frac{R \text{ Temp }(\%)}{H  130^\circ - Me  150^\circ $	481, 482, 483
	Reflux	CO ₂ + (35)	91
+	140°	CO ₂ + ()	484
$R^{1}$ $R^{2}$ $R^{2}$ $R^{2}$ $R^{2}$ $R^{2}$	140°	$CO_2 + N^{-R^2} - R^2 + D + D + D + D + D + D + D + D + D + $	485
$ \bigcup_{i=1}^{n} O + \prod_{i=1}^{n} Ac $	157°	$CO_2$ + Ac (19) Ac endo, endo	486
+ (CO ₂ Me	90-178°	$CO_2$ + $MeO_2C$ $CO_2Me$ (27)	486
+ PhNO	n	$CO_2 + N-Ph$ (24) Ph N-OH	487
+ NPM	80°	$CO_2 + PhN \qquad (-)$	111
$R^2$ + NPM $R^3$ $R^4$	140°	$CO_{2} + PhN = R^{2} R^{1} R^{1} R^{2} R^{3} R^{4} = \frac{R^{1} R^{2} R^{3} R^{4}}{R^{1} R^{0} R^{1} R^{0} R^{1} R^{0} R^{1} R^{0} R^{1} R^{1} R^{0} R^{1} R^$	(%)           85           95         95           "           99           97           4         95           \$5
	196°. 0 1 h	CO ₂ + NPh (98)	488
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
-----------------------------------------------------------------------------------------------------------------------------------------------------	------------	------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	--------------------------------------------------------------------
$R^{3} \rightarrow 0 \qquad \qquad$	Heat	$CO_{2} + \begin{array}{c} R^{2} \\ R^{4} - N \\ O \end{array} \begin{pmatrix} R^{3} \\ R^{4} \\ O \\ O \\ \end{array} \begin{pmatrix} R^{2} \\ R^{1} \\ R^{4} \\ O \\ O \\ O \\ \end{array} \begin{pmatrix} R^{2} \\ $	489
0 + MA	112°, 10 h		490
0 + MA	150°	$CO_2 + O + O + O + O + O + O + O + O + O + $	490
С + МА	u	CO ₂ + " (—)	490
	60°	$CO_2$ + $O$ ()	491
	Heat	CO ₂ + ()	94
0	128-160°	$k (128^{\circ}) = 2.73 \times 10^{-5} s^{-1}$ $CO_2 +                                   $	92, 93
$R^2$ + MA $R^3$ $R^4$	160°	$CO_{2} + O_{1} = CO_{2} + O_{1} = CO_{$	%)           55           37         468           14           35
$\sim$ $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$ $^{\circ}$	160-170°	$CO_2 + $	492
+ ^{SO} 2	140°	$CO_2$ + PhCH ₂ SO ₃ H + BnSO ₂ SBn (—)	493
+ $N$ MeO ₂ CO ₂ Me	80°	$CO_2$ + $N^{CO_2Me}_{I}$ () + $MeO_2C_NN^{CO_2Me}_{N'CO_2Me}$ () + $MeO_2C_NN^{CO_2Me}_{N'CO_2Me}$ ()	26) 494
+ $N$ EtO ₂ C ⁻ N	u	$CO_2 + \bigvee_{i}^{N} \bigvee_{CO_2Et}^{CO_2Et} (-) + \underbrace{EtO_2C_N}_{EtO_2C-N} \bigvee_{i}^{N} \bigvee_{CO_2Et}^{N-CO_2Et} (-) + \underbrace{EtO_2C_N}_{N} \bigvee_{CO_2E_2E_1}^{N-CO_2E_2E_1} (-) + \underbrace{EtO_2C_N} (-) + \underbrace{EtO_2C_N}_{N} \bigvee_{CO_2E_2E_1}^{N-CO_2E_1}$	22) 494
+ N + N PhO ₂ C N	"	$CO_2 + \frac{PhO_2C_N}{PhO_2C-N} \bigwedge_{N-CO_2Ph}^{I} (60)$	494
	30°	$\operatorname{Co}_2$ + $\left[\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$	96
$ \begin{array}{c} 0 \\ R^3 \\ R^2 \\ R^2 \\ R^1 \\ 0 \end{array} $	80°	$CO_{2} + \begin{bmatrix} R^{4} \\ R^{3} \\ R^{2} \\ R^{1} \end{bmatrix} \xrightarrow{R}^{1} \\ R^{2} \\ R^{1} \end{bmatrix} \xrightarrow{R}^{1} \\ R^{2} \\ R^{2} \\ R^{1} \\ R^{2} \\ R^{1} \\ R^{2} \\ R^{1} \\ R^{2} \\ R^{1} \\ R^{2} \\ R^{2} \\ R^{1} \\ R^{2} \\ R^{$	<u>%)</u> 85 98 97 90 84

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
S + NPM	80°	COS +	PhN ()	111
	$100-140^{\circ}$ k (100^{\circ}) = 9.26 x 10^{-6}s^{-1}	CO ₂ +	(—)	98
o Fo	140°	CO ₂ +	0 (58)	495

TABLE III-A. CO₂ FROM UNSUBSTITUTED PYRONES (Continued)



TABLE III-B. CO₂ FROM ALKYL-SUBSTITUTED PYRONES



TADLE III D. CO. EDOM ALVAL CUDETITUTED DVDONEC (C. C.	
$-1$ A B L C 111-B $-1$ U $_{2}$ C K U M A L K T L-SU B ST U U 1 1 1 P U P T K U S E SU O D D D	ρđλ

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
O + CO ₂ Me	UV	$CO_2$ + $(-)$ + $[2+2]$ adducts	505
+ Br	Zn, DMF, 100°	CO ₂ + (37)	476
(CH ₂ ) ₁₁ 0 + N	240°	$CO_2$ + (CH ₂ ) ₁₁ (11)	466
o o o o o o o o o o o o o o o o o o o	90°	$CO_2 + $	491
CH ₂ Br ₂ O	120°	$CO_2$ + $CH_2Br$ $O$ $(-)$	491
0 1 1 1 1 1 1 1 1 1 1	140°	$CO_2$ + $O_1$ $CO_2Me$ (28) $O_2$ $CO_2Me$	506
+	140°	$CO_2 + 0$ (86)	506
+	v	$CO_2 + CP + O (40)$	506
O + NPM	138°	$CO_2 + \frac{O}{PhN} + \frac{O}{O} $ (76)	507
$\mathbf{R} \xrightarrow{\mathbf{O}} \mathbf{O} + \begin{array}{c} \mathbf{O} \\ \mathbf{CO}_2 \mathbf{E} \mathbf{t} \\ \mathbf{O} \\ \mathbf{O} \end{array}$	130-190°	$CO_2$ + R $CO_2Et$ $R (%)$ Pr = 90 $CO_2Et$ Bu 75 Et 73	508
$R$ $CO_2Me$ CO2Me $R = Me \text{ or } CH_2OAc$	100-120°	$CO_2$ + $CO_2Et$ $R$ $CO_2Et$ () R	509
R O + MA	140°	$CO_2$ + $O$ (80-85) O $R = Me, Et, Pr, or Bu$	510
$R^1$ $R^2$ $A$ $A$ $A$	112°	$CO_{2} + O + O + O + O + O + O + O + O + O + $	511

TABLE III-B. CO₂ FROM ALKYL-SUBSTITUTED PYRONES (Continued)

St	arting Material	Conditions			Product(s) and Yield(s) (%)	Refs
R CH ₂ OAc +	МА	140°	CO ₂	+	$O = \begin{bmatrix} 0 & R \\ 0 & \\ 0 & \\ 0 & \\ CH_2OAc \end{bmatrix} O = \begin{bmatrix} 0 & (100) \\ R & = Me, n-Pr, or Ph \end{bmatrix}$	512
CH ₂ Br +	МА		CO ₂	+		512
(CH ₂ ), +		200-240°	CO ₂	+	$(CH_2)_n (11) \begin{pmatrix} n & (\%) \\ 4 & 20 \\ 6 & 11 \\ 10 & 2 \end{pmatrix}$	466
$ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & $	+ $(CH_2)_n$ NR ₂ + $(CH_2)_n$ OF - $(CH_2)_2O(CH_2)_2$ -	Heat _	CO ₂	+	$(CH_2)_n \qquad \qquad \frac{n  (\%)}{4  50} \\ 5  13 \\ 6  4$	466
(CH ₂ ) _n +	$\mathbb{R}^{1}$	v	CO ₂	+	$(CH_{2})_{n} \parallel R^{1} \qquad \frac{n R^{1} R^{2}}{4 CO_{2}Me CO_{2}Me 85} \\ R^{2} \qquad \frac{6}{6} \qquad 95 \\ R^{2} \qquad Ac TMS 85 \\ CO_{2}Me t-Bu 56 \\ 4 TMS TMS 15 \\ 6 \qquad 24 \\ (CH_{2})_{10} - 55 \\ R^{2} \qquad 6 \\ R^{2} \qquad 85 \\ $	513
+	- MA	Heat	CO ₂	+	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	513
		112°	CO ₂	+	$\frac{n}{3} \frac{(\%)}{84}$	514
,	MA	140°	CO ₂	+	0 0 0 0 0 0 0 0 0 0 0 0 0 (69)	515, 516
+	$R = CO_2 Et \text{ or } Ac$	Heat	CO ₂	+	R m ()	516
	DMAD	145-190°	CO ₂	+	CO ₂ Me (80) CO ₂ Me	517
Et O +	$\mathbf{R}^{1}$	125-210°	CO ₂	+	Et $R^{2}(R^{1})$ $R^{1} = H \text{ or } n \cdot Pr$ (54-98) $R^{1}(R^{2})$ $R^{2} = CO_{2}Et, Ac, \text{ or } Bz$	502
Et to +	R ¹    R ²	100-75°	CO ₂	+	Et $R^{1}(R^{2})$ $R^{1} = H \text{ or } n \cdot Pr$ (85-95) $R^{2} = CO_{2}Et, Ac, \text{ or } Bz$	502

TABLE III-B. CO₂ FROM ALKYL-SUBSTITUTED PYRONES (Continued) Starting Material Conditions Product(s) and Yield(s) (%) Refs. CH₂OAc (---) + MA Heat  $CO_2$ 518 CH₂OAc ó 0  $R^{1}$  X = CI or OAc  $R^{2} \rightarrow O$   $R^{1} = Mc \text{ or } Pr$  (-)  $R^{2} = Me \text{ or } R^{1}, R^{2} = -(CH_{2})_{4} - CH_{2}$ CH₂X CO₂ + 0 MA 138° 519 CH₂X

"When  $R^1 = TMS$  in the reacting acetylene,  $R^1 = H$  in the product.

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
	565°	CO ₂ +	(81)	520
	FVP, 570°	CO ₂ +	" (—)	391
	FVP, 565°	CO ₂ +	" (85)	99
	FVP, 500°	CO ₂ +	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	521, 99
HO O	"	CO ₂ +	MeO HO	99
MeO R	u	CO ₂ +	$ \begin{array}{c}                                     $	99
MeO 0	n	CO ₂ +	MeO (21)	99
	FVP, 515-545°	CO ₂ +	(40) + (30); (71) at 570°	99
	FVP, 560°	CO ₂ +	CHO (65)	99

TABLE III-C. CO₂ FROM BENZO- AND ARYL-SUBSTITUTED PYRONES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	Heat	$CO_2 + \left[ \overbrace{H}^{NPh} R \right] \rightarrow \overbrace{H}^{NPh} R $ ()	522
$ \begin{array}{c}                                     $	157°	$CO_2 + \begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline & & & \\ & & & \\ \hline \hline & & & \\ \hline \hline & & & \\ \hline \hline \\ \hline & & & \\ \hline \hline & & & \\ \hline \hline \\ \hline \\$	523
(CH ₂ ),		H H 5 h 58 $CO_2Me$ " 26 h 19 H Me 1 h 50 $CO_2Me$ " 6 h 86 H $C_5H_{11}$ 0.5 h 78 $C(CH_2)_2$	
	FVP, heat	$CO_{2} + \underbrace{I \\ I \\ \frac{n }{3} \frac{\text{Temp}}{600^{\circ} - 30} \frac{I(\%)}{30} \frac{II(\%)}{30}$	524
CO ₂ H + DMAD CHO	Ac ₂ O, 138°	$\begin{array}{ccccccc} 430 & 302 & 23 & 33 \\ 4 & 600^{\circ} & - & 10 & 58 \\ & 410^{\circ} & SiO_2 & & 60 \end{array}$ $CO_2 + (51)$	100
CO ₂ H + DMAD	Ac ₂ O, 138°	$CO_2$ + $CO_2Me$ (100) $CO_2Me$	100
R = H, Me, or Ph	UV	$CO_2$ + $NMe$ ()	525
O NPh	PhNO ₂ . 210°	$CO_2$ + $(-)$	100
$ \begin{array}{c} 0 \\ 0 \\ -CN \\ -C$	140°	$CO_2$ + TCNE + $CO_2Me$ (55)	100
Ph Ph Ph Ph	n	$CO_2 + Ph$ ()	526
+ DMAD	140°	$CO_2$ + $CO_2Me$ (77) Ph $CO_2Me$ Ph	101

TABLE III-C. CO2 FROM BENZO- AND ARYL-SUBSTITUTED PYRONES (Continued)

TABLE III-	-C. CO ₂ FROM BENZO	ND ARYL-SUBSTITUTED PYRONES (Continued)	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
Ph O + $N=S$ $Ph$	BF ₃ •Et ₂ O, heat	CO ₂ + SO + Ph NPh () Ph	101
Ph $Bz$ $Ph$ $Bz$	≥mp (ca. 250°)	CO ₂ + Ph Ph Bz (20) + PhCHO ()	101
$MeO \longrightarrow CO_2H + O \longrightarrow MeO \longrightarrow Ac$	Ac ₂ O, 138°	CO ₂ + MeO (72)	527
O O Ph O Ph	80°, 6 h	$CO_2$ + $\begin{bmatrix} Ph \\ 0 \\ 0 \end{bmatrix} \rightarrow \begin{bmatrix} Ph \\ 0 \\ 0 \end{bmatrix} \begin{pmatrix} Ph \\ 0 \\ 0 \\ 0 \end{pmatrix}$	528
$\begin{array}{c} Ph \\ \hline \\ 0 \\ 0 \\ \end{array} + \begin{array}{c} Ph \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	210°	$CO_2 + I + I + I + I = II = II = II = II = $	: 2:1 (69) 529, 530
Ph $Ph$ $Ph$	N	$CO_2$ + <b>I</b> + <b>II</b> I: <b>II</b> = 1:9 (100)	529, 530
Ph O + MA	≥112°	$CO_2$ + $O$ $Ph$ $O$ $(-)$	531
$R^1$ $R^2$ $A$ $A$ $A$	140°	$CO_2 + O + O + O + O + O + O + O + O + O + $	R ² , H 532 Ph Me
$MeO + O_2Me + MeO + O_0 + MeO + O_0 + O_$	150°, 3 h	$CO_2$ + MeO $CO_2Me(H)$ () MeO $1:1 \text{ mixture}$ H(CO_2Me)	533
+ DMAD		$CO_2$ + MeO $CO_2Me$ (90) MeO $MeO$	533
+ 0 CH ₂	CI 175°	$CO_2 + MeO + CH_2Cl + MeO + O + O + O + O + O + O + O + O + O +$	534. 533. 535
MeO MeO MeO MeO O O	180°	$CO_2$ + $MeO$ $HeO$ $HeO$ $HeO$ $HeO$ $()$	533

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO MeO MeO O O	210°	$CO_2 + MeO $ $MeO $ $O$	536, 537
	HOAc, aqueous THF 100°	$CO_2 + MeO $ $MeO $ $MeO $ $MeO $ $(70)$	536
MeO MeO McO O	200°	$CO_2 + \begin{bmatrix} 0 & \ddots \\ 0 & 0 \end{bmatrix} + MeO & (-)$	537
Ph + CN	140°	$CO_2 + NC_{n}$ (10)	538
$R \rightarrow D + MA$ Ph	110°	$CO_2 + O + O + O + O + O + O + O + O + O + $	491
Ph	230°	$CO_2 + O_{O} Pli O_{O} (-)$	539
Ph O + MA	140°	$CO_2 + O Ph O (83)$	540
O + MA	u	$CO_2 + O_{O} Ph O_{O} (70)$	540
$AcOCH_2$ $Ph$ $CH_2OAc$ $+$ MA	'n	$CO_2 + O_1 + O_2 + P_h O_0 $ (70)	540
$\begin{array}{c c} Ph & Ph \\ \hline Ph & O \\ Ph & Ph \end{array} + \begin{array}{c} Ph \\ \hline Ph \\ I \\ Ph \end{array}$	300°	$CO_2$ + $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$	541
+ DMAD	150°	$CO_2$ + $Ph$ $CO_2Me$ (90) $Ph$ $CO_2Me$	542. 543
	UV	$\begin{bmatrix} P_{h} & & \\ P_$	CO ₂ 544
		+ Ph Ph Ph	

TABLE III-C. CO₂ FROM BENZO- AND ARYL-SUBSTITUTED PYRONES (Continued)



TABLE III-C. CO2 FROM BENZO- AND ARYL-SUBSTITUTED PYRONES (Continued)

" See also Table III-E.

	TABLE III-D. CO ₂ FF	ROM EWG-SUBSTITUTED PYRONES	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
Bz O NPh	140°	NPM + $O$ (-) + $CO_2$ + $NPh$ (15)	547
	210°	$CO_2 + H_2 + B_2 + O$	547
+ NPM	112°	$CO_2 + PhN \qquad O \qquad VPhN \qquad (58) \qquad O \qquad $	547
$HO_2C$ $\downarrow$ $O$ $+$ $\downarrow$ $N$ $N$ $N$ $O$ $N$ $O$ $N$ $O$ $O$ $V$ $N$ $O$	Cold	$CO_2 + HO_2C $ (15)	548
$HO_2C$ $O$	_	$CO_2 + O + O + O + O + O + O + O + O + O + $	539
HO ₂ C + Se	150-170°	CO ₂ + (30)	464
+	100°	HO ₂ C (≥70)	549
HO ₂ C + +	100°	HO ₂ C (15)	549
HO ₂ C + NN Se	150-170°	$CO_2$ + $CO_2H$ (49)	464
$\begin{array}{c} R^{1} \\ R^{2}O_{2}C \\ R^{1} \\ R^{1} \\ R^{1} \\ R^{1} \end{array}$	180-200°	$CO_2 + \begin{pmatrix} CO_2 R^2 \\ R^1 \\ R^1 \end{pmatrix} (25-30) \qquad \qquad$	550
$R^{1}$ $O$ $C$ $R^{2}O_{2}C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$ $C$	DMF, 153° (OC)	$CO_2 + \frac{R^1}{R^2O_2C} + \frac{R^1}{R^1} + \frac{R^2}{R^1} + \frac{R^2}{R^1} + \frac{R^2}{R^2}$	550
HO ₂ C + MA	140°	$CO_2 + O + O + O + O + O + O + O + O + O + $	490
$HO_2C$ + MA	Heat	$CO_2 + O + O + O + O + O + O + O + O + O + $	490
$CO_2Et$ O + $Ph$	210°	$CO_2 + \underbrace{I = 2:1 (60)}_{I = II = 2:1 (60)}$	529, 541

	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
CO ₂ Et	CO ₂ Me +	210°	CO ₂ +	I = I:4 (50)	529, 541
CO ₂ Me	+ $\left\  \right\ $	rt	CO ₂ +	$\bigvee_{i=1}^{CO_2Me} NEt_2 $ (79)	551
CO ₂ Et	$ \begin{array}{c} \mathbf{R}^{1} \\ + \\ \mathbf{R}^{2} \end{array} $	Heat	CO ₂ +	$\begin{array}{cccc} CO_2Et & CO_2Et \\ \hline & & & \\ I & R^2 & R^1 \\ \hline & & II \\ \hline R^1 & R^2 & Temp & I (\%) & II (\%) \\ \hline CO_2Et & H & 138^\circ & 10 & 40 \\ Ph & " & 300^\circ & 40 & 20 \\ \hline \end{array}$	541
CO ₂ Me	+ $\left  \begin{array}{c} \operatorname{NEt}_2 \\ R \end{array} \right $	rt	CO ₂ +	" Ph 250° 21 0 CO ₂ Mc R R R (%) R TMS 72 SiPh ₃ 32 SuMe ₃ 77 SnBu ₃ 70	552
	$ \begin{array}{c}     Me \\     N \\     + \\     Si(Me)_2Ph \end{array} $	rt	CO ₂ +	$ \begin{array}{c} CO_2Me & Me \\ N & Ph \\ Si(Me)_2Ph \end{array} $ (24)	552
	NPh ₂	_	CO ₂ +	MeO ₂ C (81) NPh ₂	553
$CO_2Et$ O R	+ C ₂ H ₄	3000 psig, 120-165°	CO ₂ +	$\begin{array}{c} & R & (\%) \\ \hline CO_2Et & H & 60 \\ \hline Me & 40 \\ \hline R & Ph & 10 \end{array}$	554
CO ₂ Me	+	150°	CO ₂ +	(33) + (2)	555
	+	6.2 kbar, 25°	CO ₂ +	MeO ₂ C 0 0 (84)	87
	+	150°	CO ₂ +	$\overset{McO_2C}{\longleftarrow} \overset{H}{\longleftarrow} (25-40)$	556, 557
Et.	$ = \frac{NEt_2}{=} +    $	rt, exotherm	CO ₂ +	$Et \underbrace{CO_2Me}_{NEI_2} (89)$	558

TABLE III-D. CO2 FROM EWG-SUBSTITUTED PYRONES (Continued)



TABLE III-D. CO₂ FROM EWG-SUBSTITUTED PYRONES (Continued)

Starting Material	Conditions		Product(s) and Yield(s) (%)	Ref
MeO ₂ C ^{CO2} Me MeO OM	e 120°	CO ₂ +	MeO ₂ C CO ₂ Me (80)	562
CO ₂ Me + I		CO ₂ +	OMe (78)	562
CO ₂ Me + I	140°	CO ₂ +	CO ₂ Me (59) OMe	562
MeO CO ₂ Me + I		CO ₂ +	MeO CO ₂ Me (75) OMe	563
MeO MeO O O		CO ₂ +	MeO MeO OMe (75)	562
$MeO \longrightarrow OMe \\ MeO \longrightarrow CO_2Me + 1 \\ N \longrightarrow O O O$	120°	CO ₂ +	MeO MeO N N N (83)	564, 560
MeO + OMe	1. 150°, 5 h 2. DBU, 100°	CO ₂ +	$MeO \qquad OMe \qquad (98)$ $MeO \qquad OMe \qquad (98)$ $MeO \qquad OMe \qquad (98)$	564
$R^1$ $O$ $R^2$ $R^3$	300°	CO ₂ +	$\begin{array}{c} R^2 & R^1 & 0 \\ R^2 & R^1 & 0 \\ R^3 & R^2 & R^3 & (\%) \\ \hline H & H & H & 58 \\ " & " & OMe & 61 \\ " & OMe & H & 51 \\ OMe & H & " & 47 \end{array}$	565
MeO ₂ C +	150°	CO ₂ +	$\frac{MeO_2C}{1.7:1 (38)}$	555
+		CO ₂ +	$(-) + MeO_2C \qquad (-)$	555
$\begin{array}{cccc} MeO_2C & & Ph \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ $	Heat	CO ₂ +	$\begin{array}{cccc} MeO_2C & MeO_2C & Ph \\ & & + & 3:2 (39) \\ & & CF_3 & CF_3 \end{array}$	566, 567
+ DMAE	ı "	CO ₂ +	$MeO_2C \longrightarrow CO_2Me $ $CO_2Me \qquad (67)$ $CF_3$	566, 567
NEt ₂			MeO ₂ C	

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IADLE III-D.	CO2 FROM EWO-SUBSTITUTED	FIRONES (Continuea)

Start	ing Material	Conditions	Product(s) and Yield(s) (%)	Refs.
MeO ₂ C O CF ₃	+ C ₂ H ₂	200°	$CO_2$ + (91) $CF_3$	566
	+	150°	CO ₂ + CP + " (87)	567
+		<u>30°</u>	adduct $\xrightarrow{180^\circ}$ CO ₂ + (90)	567
MeO ₂ C O MeO ₂ C O MeO ₂ C O MeO ₂ C		≥180°	$CO_2$ + AcOH + (100)	566
MeO ₂ C	Ph +	300°	$CO_2$ + $Ph$ (60) McO_2C (60)	541
EtO ₂ C	Ph +	210°	$CO_2$ + $Ph$ (60) EtO ₂ C (60)	529
MeO ₂ C	Ph +    Ph	250°	$CO_2$ + $Ph$ (43) MeO_2C Ph	541
	CO ₂ Me +	138°	$CO_2$ + (12) + (12) + (10) (10)	541
		210°	CO ₂ + " + " 3:2 (40)	529
	+ DMAD	80°	$CO_2$ + $MeO_2C$ $CO_2Me$ (59)	568
	+ $\left\  \right\ _{CO_2Et}$		$CO_2$ + $MeO_2C$ $CO_2Et$ (59)	568
EtO ₂ C	+ DMAD		$CO_2$ + $CO_2Me$ (59) EtO_2C $CO_2Me$	568
	+ $  $ CO ₂ Et	>155°	$CO_2$ + $EtO_2C$ $CO_2Et$ $()$	569
MeO ₂ C	siCl₃ +	175°	$CO_2$ + $MeO_2C$ + $MeO_2C$ + $MeO_2C$ + $SiCl_3$ + $MeO_2C$ + $SiCl_3$	570
	Me _∑ , ^{Ph} +     R	rt	$CO_2 + EtO_2C + CO_2Et + CO_2Et + CO_2Et + CO_2Et + SnMe_3 = 50 \\ SnBu_3 = 17 \\ DNDC = 14$	552
	SnMe ₃ +     SnMe ₃	142°	$CO_2$ + $SnMe_3$ $MeO_2C$ $SnMe_3$ (59)	474
	+	75°	$CO_2$ + (75)	568

TABLE III-D. CO2 FROM EWG-SUBSTITUTED PYRONES (Continued)



TABLE III-D. CO2 FROM EWG-SUBSTITUTED PYRONES (Continued)



TABLE III-D. CO2 FROM EWG-SUBSTITUTED PYRONES (Continued)



TABLE III-D. CO2 FROM EWG-SUBSTITUTED PYRONES (Continued)



	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
	CO O O R	180°, Pd/C	CO ₂ +	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	590
	0 + CO ₂ Me	150°	CO ₂ +	$HeO_2C$	555
	+	150°	CO ₂ +	$CO_2Et$ (7) + (12) MeO_2C	555
	$ \begin{array}{c} SO_2Ar \\ O \\ O \\ Ar = 4 \cdot MeC_6H_4 \end{array} $	105°	CO ₂ +	$\begin{bmatrix} SO_2Ar \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$	591
-	$EtO_2C$ $CO_2Et$ $Me$ $Ph$ R $R$	rt	CO ₂ +	$E_{tO_2C} \xrightarrow{CO_2Et} NMePh \qquad \frac{R \qquad (\%)}{Me} \\ R \qquad TMS \qquad 82 \\ SiPh_3 \qquad 67$	552

TABLE III-D. CO2 FROM EWG-SUBSTITUTED PYRONES (Continued)

NHAc O O O + MA	140°		Q NHACO	
Ph		CO ₂ +	O Ph (60)	592
$\begin{array}{c} R \\ \downarrow \\ EtO_2C \end{array} + \begin{array}{c} OEt \\ OEt \end{array}$	160°	CO ₂ +	$\begin{array}{c c} R \\ \hline \\ OEt \\ H \\ 73 \\ NO_2 \\ 28 \end{array}$	581
$EtO_2C + 0 + 0$	rt	CO ₂ +	$EtO_2C$ $NO_2 \\ NEt_2 \\ (57)$	581
$ \begin{array}{c}     Ph \\     Et_2N \\     \hline     O \\     Ph \\     Ph \\     Ph \\   \end{array} + \left[ \left[ \begin{array}{c} \\  \end{array}\right] \right] $	_	CO ₂ +	$ \begin{array}{c}                                     $	146
$E_{t_2N} \xrightarrow{Ph} O \\ + [\Box]$	_	CO ₂ +	$Et_2N \xrightarrow{Ph} (19)$ $Et_2N \xrightarrow{Ph} (19)$	146

TABLE III-E. CO2 FROM HETEROATOM-SUBSTITUTED PYRONES



TABLE III-E. CO₂ FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)



TABLE III-E. CO2 FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & $	Et 157° S	$CO_2 + N + CO_2Et + R + CO_2Et + CO_2$	605
+	Et "	$CO_2 + \underbrace{N_{H}}_{H} R + \underbrace{N_{H}}_{H} R$ major (23-78) minor	CO ₂ Et 606 R = H, alkyl
$ \begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & $	u	$CO_2 + N = R^{1}(R^2)$ $R^{1}(R^2)$ $R^{1} = Ph, CO_2Me, B$ $R^{2} = H, Me, alkyl, I$	606 z, Ph, or alkyl R(CO), or Ph
O N H R + DMAD		$CO_2$ + $CO_2Me$ $CO_2Me$ (25-89) R = H  or alkyl	606
	)] ] 83°	$CO_2$ + $N$ (45) + HN H	(10) 607
$ \begin{array}{c}                                     $	)   ] 81°	$CO_2$ + $N$ H (20) + $N$ H	N 105, (20)
$ \begin{array}{c}  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\  \\ $	157°	$CO_2 + \underbrace{\begin{pmatrix} R \\ H \end{pmatrix}}_{H} \underbrace{\begin{pmatrix} R \\ (CH_2)_n \end{pmatrix}}_{H} \begin{pmatrix} n & R \\ 3 & H \\ 3 & TMS \\ 4 & H \\ 4 & CO_2Me \\ 5 & H & 35 \end{pmatrix}$	
N C C	157°, Pd/C	$CO_2$ + $N_H$ (43)	608, 609
$ \begin{array}{c}                                     $	66° (OC)	$CO_2$ + $N_H$ (31)	607
excess + O	78°	$CO_2 + N + O + O + O + O + O + O + O + O + O$	0) 607
+	66° (OC)	$CO_2$ + $N_H$ (62)	607
+	Heat	$CO_2$ + $N$ $Z_2$ $R$ $(-)$ $R = CO_2Et \text{ or } SO_2Ph$	610

 TABLE III-E.
 CO2 FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)

Startir	ng Material	Conditions	Product(s) and Yield(s)	(%) Refs.
	+ R ³	ca. 110°	$CO_{2} + N = R^{4} R^{1} = H, M$ $R^{2} = H, M$ $R^{3} R^{3} = H, PI$ $R^{4} R^{3} R^{3} = H, PI$ $R^{4} = H$	e, Et, or Bn e, Et, i-Pr, or Bn a, Ac, CO ₂ Me b. 2-pyridyl, Ac, CN, CHO, Me or CO ₂ Et CONPhCO—; $-(CH_2)_nCO$ —; $O(CH_2)_n$ — (n = 2 or 3)
	+ R Cl	80°, collidine/THF	$CO_2$ + $N$ $R$ $CO_2$ $CO_2$ + $CO_2$ $CO$	(%)         85         612           76         78         612
	+	120°, (OC)	$CO_2 + \bigvee_{\substack{N \\ Me}} (9)$	93) 527
$ \bigvee_{\substack{N \\ R^1}} O $	+ ()OEt	80°	$CO_2 + \bigvee_{\substack{N \\   \\ R^1}} \frac{R^1}{R^2} + \frac{R^1}{R^2}$	X ² (%)       Me     44       527       Ph     45       CO ₂ Et     50
	+ OAc	120°	CO ₂ + (97)	527
N Me	+ Ac		$CO_2$ + $N$ $Ac$ + $(45)$ $Me$	527 N Me (18)
	+ (CH ₂ ) _n	120°	$CO_2$ + $(CH_2)_nOH$ $H_{c}$	n (%) 2 58 527 3 27
	+ Ph	100°	$CO_2$ + $N$ Me 1:1 (48)	N Me 527
	+ N 0	100°, Pd/C	$CO_2 + N O O$	27) 527
	+ N N	Heat	$CO_2 + $	(%) n 34 527 25
C H H	+ NC CO ₂ Et	60°	$CO_2$ + $N_H$ $CO_2Et$	(95) 613
	+ Ac Ac	"	$CO_2 + \bigvee_{\substack{N \\ Et}}^{Ac} Ac $ (67)	r) 613

TABLE III-E. CO₂ FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)

Star	ing Material	Conditions		Product(s) and Yield(s) (%)	Refs.
	+ Et	80°	CO ₂ +	$ \begin{array}{c}                                     $	613
	+ MeO ₂ C MeO ₂ C	100°	CO ₂ +	$CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $Me$ $(96)$	613
	+ NC CO ₂ Et	60°	CO ₂ +	(97)	613
	+ Ac Ac	60°	CO ₂ +	Ac $N$ $Ac$ $Ac$ $Ac$ $Ac$ $Ac$ $Ac$	613
	+ CH0	80°	CO ₂ +	Me CHO ()	613
	+	100°	CO ₂ +	(68) Me	613
C N H H	+ NPM	THF, rt	CO ₂ +	OHN OHN O I O (80)	614
		150°	CO ₂ +	I + $PhN$ () major 0 $NPh$ minor	614
C N H R	+ NPM or MA	п-65°	CO ₂ +	$\begin{array}{c} 0 \\ 0 \\ 0 \\ R \\ R$	522
N C C C C C C C C C C C C C C C C C C C	+ MA	rt	CO ₂ +	OHN O (41)	614
	+ TCNE	_	CO ₂ +	(-)	341

TABLE III-E. CO₂ FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)

	TABLE	III-E. CO ₂ FROM HET	EROATOM-SU	BSTITUTED PYRONES (Continued)	
	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
MeO MeO		PhNO ₂ , 210°	CO ₂ +	$MeO \xrightarrow{VO_2El}{N} MeO \xrightarrow{VO_2E}{N} MeO \xrightarrow{VO_2E}{N} MeO $	615
OH OH	+ DMAD	78°	CO ₂ +	OH CO ₂ Me (75) CO ₂ Me	469
		rt, 20 kbar	CO ₂ +	" (—)	616
	+    ^{CO} 2Me	170°	CO ₂ +	OH CO ₂ Me (56)	617
	+ CO ₂ Me	200°	CO ₂ +	OH CO ₂ Me (50)	617
	+ CO ₂ Me		CO ₂ +	$\bigcup_{CO_2Me}^{O}$ (85)	617
	+ NC CN		CO ₂ +	OH CN ()	617
	+ CO ₂ Me CO ₂ Me	115°	CO ₂ +	$\bigcup_{CO_2Me}^{OH} (73)$	617
	+	80°	CO ₂ +	$CO_2Et $ (68)	618
	+	Ac ₂ O	CO ₂ +	AcO OAc OAc OAc	617
	+ OR O OR O OR O	1. MeCN, 81° 2. PbO ₂	CO ₂ +	$\begin{array}{c ccc} OR & O & OH \\ \hline H & 27 \\ \hline H & 27 \\ \hline OR & O \end{array}$	619
	+ Cl + AcO O AcO O	1. MeCN, 81° 2. РьО ₂	CO ₂ +	$\begin{array}{c} OAc & O & OH \\ Cl & & & \\ & & \\ & & \\ AcO & O \end{array} \qquad (-)$	619
	+ AcO O AcO O	81°	CO ₂ +	$ \begin{array}{c}                                     $	619
НО	$\begin{array}{c} O & CO_2Et \\ 0 & + &    \\ & CO_2Et \end{array}$	170-200°	CO ₂ +	HO $CO_2Et$ ()	569

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c c} R^{1}O & R^{2} \\ & & \\ & & \\ & & \\ Ph & R^{3} \end{array}$	150°	CO ₂ +	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	620
$ \begin{array}{c} HO \\ \hline \\ O \\ Ph \end{array} \begin{array}{c} O \\ + \\ O \\ \end{array} \begin{array}{c} O \\ X \\ O \\ \end{array} $	150°	CO ₂ +	$\begin{array}{c} 0 \\ X \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ Ph \end{array} \begin{array}{c} 0 \\ X \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} X \\ 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 81 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 81 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 81 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 81 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \end{array} \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	620
$AcO \rightarrow O + DMAD O + DMAD$	Heat	CO ₂ +	$\begin{array}{c} OH \\ CO_2 Me \\ CO_2 Me \end{array} $ (20)	621
	530°	CO ₂ +		99, 622
$\begin{array}{c} \mathbf{R}^{I} \\ + & \left  \right  \\ \mathbf{R}^{2} \end{array}$	150°	CO ₂ +	$\begin{array}{c} OH \\ R^1 \\ R^2 \\ $	102
+ O O	200° (DC)	CO ₂ +	$\bigcup_{i=1}^{i} \bigcup_{j=1}^{i} \bigcup_{i=1}^{i} \bigcup_{j=1}^{i} \bigcup_{j$	102
+ O OH O OH	"	CO ₂ +	OH O OH (49)	102
+ O OH + O OH O OH	u	CO ₂ +	OH O OH (38) O OH	102
+ NPM	200°	CO ₂ +	PhN O O O O O O (48)	102
$\begin{array}{c} ONa \\ ONa \\ O \\ O \\ O \\ R^2 \end{array}$	rt, THF	CO ₂ +	$\begin{array}{c} OH \\ R^{1} \\ R^{2} \\ R^{2} \end{array} \begin{array}{c} R^{1} \\ CO_{2}Me \\ R^{2} \\ CO_{2}Et \\ CO_{2}Et \\ CO_{2}Me \\ CO_{2}Et $	103
OMe ONa O + DMAD	rt	CO ₂ +	$ \begin{array}{c} OMe & OH \\ \hline CO_2Me \\ CO_2Me \end{array} $ (79)	103
R ONa O + O O + O	rt (OC)	CO ₂ +	$\begin{array}{c c} R & OH & O \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	103

TABLE III-E. CO2 FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)

TABLE ]Starting Material	Conditions	OATOM-SUBSTITUTED PYRONES (Conti Product(s) and N	nued) Vield(s) (%)	Refs
ONa OH				
	rt (CO)	CO ₂ +	(85)	103
+ Br O OMe O	π, THF	CO ₂ +	(90)	103
+ Br	n	CO ₂ +	(73)	103
OMe ONa OMe ONa OMe ONa + "	"	CO ₂ +	(73) DMe	623
ONa ONe + "	T	CO ₂ + OH O OMe O O	(87) DMe	623
ONa $OONeO$ $OONe$ $Br$ $H$ $H$ $OONeO$ $OONe$ $O$	0°	CO ₂ + O OMe O OH	0 (78)	104, 624, 625
$\begin{array}{c} R & OLi \\ \hline \\ $	п	CO ₂ +	$ \begin{array}{c} R & (\%) \\ H & 95 \\ OMe & 62 \end{array} $	104, 624
R ONa O + "	0-25°	CO ₂ + CO ₂ + O	$\frac{\mathbf{R}  (\%)}{\mathbf{H}  92}$ $OMe  73$	104, 624
ONa OMe + "	0°	$CO_2$ + $OH O O O O O O O O O O O O O O O O O O$	0 (77)	104, 624
$ \begin{array}{c} R & ONa \\ \hline \\ \hline \\ \hline \\ OAc \end{array} + Cl + O \\ O$	THF	CO ₂ + CO ₂ + OAc O	$\begin{array}{c} R & (\%) \\ H & 75 \\ OMe & 62 \end{array}$	626
$ \begin{array}{c} NaO \\ O \\ N \\ N \\ Me \end{array} + \left\  \right\  $	65°	$CO_2$ + $N_{Me}$ $CO_2Et$	(21)	627
$ \begin{array}{c} NaO \\ O \\ NaO \\ O \\ N \\ Me \end{array} + \begin{array}{c} CO_2Et \\ O \\ CO_2Et \end{array} $	π	$CO_2$ + $N_{Me}$ $CO_2Et$	(45)	627

TABLE III-E. CO₂ FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)



Starting Mate	rial Conditions		Product(s) an	d Yield(s) (%)	R
$R^{2} + M$ $R^{3} + M$	A 140°	CO ₂ +	$ \begin{array}{c}                                     $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	468
MeO Ac	CO ₂ Et	CO ₂ +	Ac CO ₂ Et	$McO + CO_2Et = 3:2 (84)$	631, 632
MeO +	CO ₂ Et	CO ₂ +	MeO CO ₂ Et	(—)	633
$R^{2}O$ + $DN$ $R^{1}$	/AD "	CO ₂ +	$R^{2}O$ $CO_{2}Et$ $CO_{2}Et$ $CO_{2}Et$	$\frac{R^{1}}{Me} = \frac{R^{2}}{n-Pr} \frac{(\%)}{65}$	634
$R^1$ $R^2$ $R^3$ +	0       	CO ₂ +	$ \begin{array}{c} \mathbf{MeO} \\ \mathbf{R}^2 \\ \mathbf{R}^3 \\ \mathbf{O} \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	469
$R^2$ $+$ $MeO$ $R^3$ $+$ $R^4$	NMe ₂ 200°	CO ₂ +	$R^2$ $R^3$ $R^4$ $R^4$	R ¹ R ² R ³ R ⁴ (%)           H         OMe         H         CO ₂ Me         68           "         "         Me         30           "         Me         H         93           Me         "         H         39           Br         "         Me         10	469
MeO 0 +	O X 150° O	CO ₂ +	O N O Ph O O O Me O X X O O N O O O O O O O O O O O O O	X (%) O 84 NPh 82	620
MeO Ph Ph Ph Ph	1AD 200°	CO ₂ +	MeO Ph CO ₂ Me Ph	(72)	635
$\begin{array}{c} R^{1} \\ TMSO \\ R^{2} \\ R^{3} \end{array} + DM$	IAD I. 200° 2. H ₃ O+	CO ₂ +	HO $R^2$ $CO_2Me$ $R^3$ $CO_2Me$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	469
³⁷⁰ + MA	112°	CO ₂ +	OBz OBz	(—) 6	636






TABLE III-E.       CO2 FROM HETEROATOM-SUBSTITUTED PYRONES (Continued)				
Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
$CO_2H$	157° Ac ₂ O, 138°	$CO_2$ +	$\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array}{0} \\ & \end{array}{0} \\ & \end{array}{0} \\ $ \\  \\  \\ \\ 0{0} \\ \end{array}{0} \\ \end{array}{0} \\ \end{array}{0} \\ \end{array}{0} \\ \end{array}{0} \\ \end{array}{0} \\ \\  \\  \\ \\	654 654
$ \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & $	157°	CO ₂ + (	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	655
			"         H         CO ₂ Et         65         1:1           "         TMS         "         69         6:1           Me         CO ₂ Me         CO ₂ Me         93            "         H         CO ₂ Et         79         1.5:1           "         TMS         "         67         >20:1           "         MeCHOH         CO ₂ Me         46         >20:1           "         MeCHOH         CO ₂ Me         59         5:1           "         Ph         "         70         1.2:1           n-C ₅ H ₁₁ CO ₂ Me         "         68            "         H         CO ₂ Et         54         1:1           "         TMS         "         60         >20:1           "         MeCHOH         CO ₂ Et         55         >20:1           "         MeCHOH         CO ₂ Et         55         >20:1	
			" Ph " 70 1.6:1	
$E_{i} \rightarrow 0 \qquad R^{2} \qquad \qquad$	100-175°	CO ₂ +	Et $R^{2}(R^{1})$ $R^{1} = H \text{ or } n\text{-Pr}$ $R^{2} = CO_{2}Et, Ac, \text{ or } Bz$ Br	502
O Br O NPh	195°, 0.3 h	CO ₂ +	NPh (98)	488
MeO ₂ C + NPM	138°	CO ₂ +	$\begin{array}{c} CO_2 Me \\ O \\ PhN \\ O \\ Br \\ O \end{array} $ (60)	507
O O Br O + MA	195°, 0.3 h	CO ₂ +	O Br O C C C C C C C C C C C C C C C C C C C	531
Br O + MA	80°	CO ₂ +	" (—)	491
$R^1$ $R^2$ $+$ MA	138°	CO ₂ +	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	656

^a The starting material was prepared by a DA reaction at 110°.

^b This product was not isolated.

^c The major isomer is shown.





TABLE III-F.	CO ₂ FROM	OXAZINES	(AZAPYRONES)	& ANAL	OGS (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
N = 0 + EtO OEt	rt	$CO_2 + N$ (12)	664
$ \begin{array}{c}                                     $	65°	$CO_2$ + (65)	664
$O$ + Ph $CF_3$ + CF3	110°	$CO_2$ + $Ph$ (38) N $CF_3$	664
• • • • • • • • • • • • • • • • • • •		$CO_2$ + (38)	664
+	110° (OC)	$CO_2$ + $(30)$	664
$ \begin{array}{c}                                     $	80°	$CO_{2} + N = R^{2} + R^{1} + R^{2} + R^{1} + R^{2} +$	666
$+ \frac{R^2}{R^1}$	Heat	CO ₂ + "	666
$\begin{array}{c} 0 \\ \downarrow \\ N \\ R \end{array} + \begin{array}{c} NEt_2 \\ \downarrow \\ H \\ R \end{array}$ $+ \begin{array}{c} Et0 \\ \downarrow \\ NEt_2 \\ R^2 \\ R^2 \\ R^1 \end{array}$	П 	$\frac{R^{1}}{H}  \frac{R^{2}}{H}  \frac{X}{1}  \frac{\text{Temp}}{140^{\circ}}  \frac{(\%)}{56}$ $\stackrel{"}{}  "  OAc  164^{\circ}  58$ $\stackrel{"}{}  \frac{R}{1}  \frac{R^{2}}{R}  \frac{X}{164^{\circ}}  \frac{164^{\circ}}{58}$ $\stackrel{"}{}  \frac{R}{1}  \frac{R^{2}}{60}  \frac{R^{2}}{58}$ $\stackrel{"}{}  \frac{R}{1}  \frac{R^{2}}{60}  \frac{R^{2}}{58}$ $\stackrel{"}{}  \frac{R}{1}  \frac{R^{2}}{7^{2}}  \frac{R}{1}  \frac{R^{2}}{7^{2}}  \frac{R}{1}  \frac{R^{2}}{7^{2}}  \frac{R^{2}}{16}  \frac{R^{2}}{16}$ $\stackrel{"}{}  \frac{R^{2}}{16}  R^{2$	107 107 664
N = O R + $R$	120°	$CO_2 + CP + $ (31-84) OAc OAc	664
		$R = Ph$ , $\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma_{\gamma$	

TABLE III-F. CO2 FROM OXAZINES (AZAPYRONES) & ANALOGS (Continued)

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
$R^{2} \rightarrow 0 \qquad R^{3} \rightarrow X \qquad R^{4} \qquad R^{4$	0-20°, HCl	CO ₂ +	$R^{2} = \frac{R^{3}}{R^{2}} R^{4} = CF_{3}, i-Pr, i-Bu, or t-Bu$ $R^{2} = Me \text{ or } Ph$ $R^{3}, R^{4} = H, Et; -(CH_{2})_{3}, or -(CH_{2})_{4} - X$ $X = NEt_{2}; -N(CH_{2})_{n} - n$ $n = 3, 4, or 5$	664
+ $R_3 \rightarrow OEt$ $R_4$	115°	CO ₂ +	$R^{1} = CF_{3}, i-Pr, \text{ or } t-Bu$ $R^{2} = Me$ $R^{3}, R^{4} = H, H; -(CH_{2})_{3}-, \text{ or } -(CH_{2})_{4}-$ $X = NEt_{2}; -N(CH_{2})_{n}-$ $n = 3,4, \text{ or } 5$	664
N = 0 $CF_3$ $Ph$ Me Me	20°	CO ₂ +	$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$	664
+ N Ph	20°	CO ₂ +	$\bigvee_{\substack{N \\ CF_3}} F^{n} $ (70)	664
+ Ph	130°	CO ₂ +	$P_h \longrightarrow N (-)$ $R = unspecified$	664
N = 0 O =	25°	CO ₂ +	(86)	664
+	'n	CO ₂ +	(15) + (15) + (65)	664
+	·	CO ₂ +	$\begin{array}{c} CO_2Me \\ N \\ N \\ \end{array} (70) + \\ \end{array} (18)$	664
$ \begin{array}{c} 0 \\ + DMAD \\ N \\ Ph \end{array} $	200°	CO ₂ +	$CO_2Me$ $CO_2Me$ (36) N Ph	665
$\begin{array}{c} 0 \\ R^2 \\ R^3 \\ R^4 \end{array} + \left\  \right\ $	rt	CO ₂ +	$R^{2}$ $R^{3}$ $R^{4}$ $I$ $R^{4}$ $R^{4}$ $R^{2}$	667
			$\begin{array}{cccccccccccccccccccccccccccccccccccc$	

TABLE III-F. CO2 FROM OXAZINES (AZAPYRONES) & ANALOGS (Continued)

	Starting Material	Conditions		Produc	t(s) and Yield(s) (%)	Refs.
0 0 an	d/or 0 0	rt	CO ₂ +		and/or (—)	110
			CO ₂ +		(—)	110

^a The starting material was prepared at room temperature.

 b  The starting material was prepared at –80°.

 c  The starting materials decompose upon preparation.

	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs
Ph CO ₂ H	+ DMAD	(R ₂ CO) ₂ O, 100-130°	CO ₂ +	Ph $\stackrel{\text{H}}{\longrightarrow}$ R (60-98) MeO ₂ C CO ₂ Me R = Me, cyclohexyl, or aryl	127
$Ph \rightarrow 0$ N- $\langle N - \langle R \rangle$	CO ₂ Me +	110°	CO ₂ +	$\begin{array}{c} R \\ \swarrow \\ N \\ \swarrow \\ \downarrow \\ \downarrow$	127
	+ DMAD	100-130°	CO ₂ +	$R = Me \text{ or } Ar$ $MeO_2C \qquad CO_2Me \qquad Ar = various$	127
	+ $\left\  \begin{array}{c} CO_2 Me \\ R^2 \end{array} \right\ $	100°	CO ₂ +	$R^{1} \xrightarrow{N} Ar$ $R^{2} \xrightarrow{CO_{2}Me} (55-98) \qquad R^{1} = alkyl, aryl$ $R^{2} = H \text{ or } CO_{2}Me$	668
$\begin{array}{c} R^{1} \\ + \\ R^{2} \\ R^{3} \end{array} \xrightarrow{O^{-}} $	R ⁴ +     R ⁵	0-70°	CO ₂ +	$R^{1}$ $R^{5}$ $R^{4}$ $R^{n} = H.$ Me, Ph, alkyl, or CO ₂ Me	669
Ph O +N Me Ph	$+ \left\  \right\ _{R^2}^{R^1}$	0-110°	CO ₂ +	$\begin{array}{c} Me \\ Ph \\ N \\ R^{\dagger} \\ R^{2} \\ R^{2} \\ R^{1}, R^{2} = H, alkyl, aryl, CO_{2}H, or CO_{2}R' \end{array}$	670
	O V + DMAD	Ac ₂ O, 80°	CO ₂ +	$Me O_{2}C CO_{2}Me O $ (59)	671

TABLE IV-A. CO₂ FROM MESIONICS TO FORM PYRROLES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} Ph \underbrace{O}_{+N} O^{-} \\ +N \underbrace{O}_{-} Ph \end{array} + \underbrace{EtO}_{+} NHMe \ BF_{4}^{-} \\ Me \ Ph \end{array}$	I. п 2. Na ₂ CO ₃	$CO_2 + Ph $ $N $ $Ph$ $N$ $Ph$ $N$ $Ph$ $N$ $Ph$ $N$ $Ph$ $NMe$ $EtO$ $(89)$	672
$Ph$ $N$ $Co_2Et$ $N$	Ac ₂ O, 100°	$CO_2 + N $ $(49)$	673
$\begin{array}{cccc} Me & & & R^{1} \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$	Ac ₂ O, 130°	$CO_{2} + \bigvee_{R^{2} \\ R^{2} \\ R^{2} \\ R^{1} \\ R^{2} \\ $	674
$Me_{N} \xrightarrow{O} CO_2Me_{+} DMAD$	55°	$CO_2$ + $MeO_2C$ $CO_2Me$ (57)	675
$HN$ $CO_2Me$ + DMAD Ph $CO_2H$		$CO_2$ + $Ph$ $N$ $CO_2Me$ () $MeO_2C$ $CO_2Me$	675
$HO_{2}C \xrightarrow{N}_{R} \overset{H}{}_{Ar} + DMAD$ $R = 4 - O_{2}NC_{6}H_{4}$	Ac ₂ O, reflux	$CO_2 + \underbrace{\begin{pmatrix} R & (\%) \\ N & Ar & Heology \\ MeO_2C & CO_2Me & Ph & 79 \end{pmatrix}}_{MeO_2C}$	367
$ \begin{array}{c} R^{1} & O & CO_{2}Me \\ & +N & + & H \\ R^{2} & R^{3} & + & H \end{array} $	Ac ₂ O, 115°	$CO_{2} + \underbrace{\begin{array}{c} R^{1} \\ MeO_{2}C \\ I \end{array}}^{R^{2}} R^{3} + \underbrace{\begin{array}{c} R^{2} \\ N \\ R^{1} \\ R^{3} \\ R^{2} \\ R^{3} \\ R$	676
$\begin{array}{cccc} Ph & & Bz \\ & & & \\ +N & & + & \\ Me & Ph & & Bz \end{array}$	Ac ₂ O, heat	$CO_2 + Ph \xrightarrow{Me}_{J} Ph$ (63) Bz Bz T	677
+ $(N_{11})^{1}$ Ts CO ₂ Me	40°	$CO_2$ + $Ph$ $N$ $Ph$ (55) + $N$ (56) MeO_2C $CO_2Me$	383
+ $(0)$ $CO_2Me$ $CO_2Me$	rt	$CO_2$ + " (16) + $MeO_2C$ $CO_2Me$ Me + $Ph$ $N$ $Ph$ (24) + $O$	384, 385
⁰⁻ сно		$MeO_2C CO_2Me$ CHO	
	120°	$CO_2 + \bigvee_{N \to 0} (40)$	678
$ \begin{array}{c} & \begin{array}{c} & & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ $	Ac ₂ O, 138°	$CO_2 + (90)$	679

TABLE IV-A. CO₂ FROM MESIONICS TO FORM PYRROLES (Continued)

	Starting Material	Conditions	Product(s) and Yield(s) (%) Refs.
HO ₂ C KHO	CO₂Et +     H	140°, Ac ₂ O	$CO_2$ + $HCO_2$ (80) 680, $CO_2Et$ 681
	O ₂ Me + DMAD	65-115°	$CO_2 + \bigvee_{CO_2Me}^{(CH_2)_3CO_2Me} (<30) $ $CO_2Me (<30) $ $CO_2Me (<30)$
$\begin{array}{c} O \xrightarrow{R} \\ HO_2C \xrightarrow{N} \end{array}$	+ DMAD	Ac ₂ O, 120°	$CO_{2} + \begin{pmatrix} R & (\%) \\ \hline CF_{3} & 78 \\ \hline CO_{2}Me & 3,4-Cl_{2}C_{6}H_{3} & 91 \\ -CO_{2}Me & Ph & 87 \\ \hline 4-ClC_{6}H_{4} & 90 \\ Ph & 87 \\ -4-MeOC_{6}H_{4} & 82 \\ -4-FC_{6}H_{4} & 99 \end{pmatrix} $ $682$
	CO ₂ Me + DMAD R = H, OAc	Ac ₂ O, 135°	$CO_2 + R \sim N + CO_2Me = \frac{R}{H} (\%) + \frac{(\%)}{H} = \frac{683}{OAc} = \frac{683}$
$HO_2C$ $\xrightarrow{N}$ $S$	+ DMAD	Ac ₂ O, reflux	$CO_2 + S - CO_2Me$ (49) 684
HO ₂ C	CO ₂ Me + DMAD	65-115°	$CO_2$ + $(CH_2)_3CO_2Me$ $CO_2$ + $CO_2Me$ (<30) 675 $CO_2Me$
$R^{1}$ $O$ HO ₂ C $N$ $R$	$R^2$ + $   $ $R^3$	Ac ₂ O, 120°	CO ₂ + $R^3$ $R^1$ $R^1$ = H or Me (45-90) $R^2$ = H, Ph, or CO ₂ Et 685 $R^3$ = H or Ph
HO ₂ C N	+     Bz	Ac ₂ O, rt	$CO_2$ + $N$ $Bz$ (70) 128
	+ () 0	Ac ₂ O, 100°	$CO_2 + $ $O$ $(5)$ $128$
	+	Ac ₂ O, 100°	CO ₂ + (34) 128
HO ₂ C N	+     Bz	Ac ₂ O, 70°	$O \rightarrow Bz (10) + O \rightarrow Bz (45) $ $I = Bz $ $I = Bz $ $I = Bz$
	+     R	Ac ₂ O, 100°	$I \xrightarrow{138^{\circ}} CO_2 + II$ $CO_2 + \qquad $

TABLE IV-A. CO₂ FROM MESIONICS TO FORM PYRROLES (Continued)



Starting Material	Conditions		Product(s) and Yield(s) (%)		Refs.
CO ₂ H NH R H	1. Ac ₂ O 2. DMAD, 115°	CO ₂ +	MeO ₂ C CO ₂ Me	R         (%)           H         64           Bn         27           2-MeOC ₆ H ₄ 49	690
NH NH CO ₂ H	1. (RCO) ₂ 0 2. DMAD, 115°	CO ₂ +	$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	R         (%)           Me         75           Et         69	690
	1. Ac₂O 2. ≡−R ,115°	CO ₂ +		R         (%)           CO ₂ Et         51           Ph         34	690
	1. Ac ₂ O 2OAc, 110°	CO ₂ +	N N H (53)		690
	1. Ac ₂ O 2. O O	CO ₂ +		(85)	690
$EtS \xrightarrow{O} O^{-} + DMAD$ $Me^{+} \xrightarrow{O} CF_{3}$	120°	CO ₂ +	$CF_{3} \xrightarrow{N} SEt (6)$ $MeO_{2}C \xrightarrow{CO_{2}Me}$		691

TABLE IV-A. CO₂ FROM MESIONICS TO FORM PYRROLES (Continued)

	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs
Me_N_CO ₂ H	+ DMAD	Ac ₂ O, 130°	$CO_2 + Me$ MeO ₂ C CO ₂ Me (60)	674
N + N Ph	+	170°	$CO_2 + \underbrace{\bigvee_{l}^{N} N}_{l} (75)$	112
$N^{O}_{H^{+}N^{+}}$ $R^{2}$	$\begin{array}{c} \mathbf{R}^{3} \\ + & \left  \right  \\ \mathbf{R}^{4} \end{array}$	Heat	CO ₂ + $R^{1}$ $R^{1} = Me, Bn, or Ar$ $R^{2}$ $R^{1} = Me, Bn, or Ar$ $R^{2} = H, Me, or Ph$ $R^{3} = H, CO_{2}Me; R^{4} = H, Ph, CO_{2}Me$ (64 - 100)	692. 112
N +N Ph	+ $\left\  \right\ _{Ph}^{CO_2Et}$	$130-150^{\circ}$ $\Delta H^{\ddagger} = 18.4$ $\Delta S^{\ddagger} = -29$	$CO_2 + N $ () EtO_2C Ph	125
	+ DMAD	90-110° $\Delta H^{\ddagger} = 14.8$ $\Delta S^{\ddagger} = -31$	$CO_2 + MeO_2C + CO_2Me$	125
$R^{1}$ $R^{2}$ $R^{2}$	<b>R</b> ³ +	200°	$CO_{2} + R^{2} \bigvee_{R^{3}}^{N} N + R^{2} \bigvee_{N}^{N} N \text{ mixtures (14-60)}$ $R^{1} = NMe_{2} \text{ or } N\text{-morpholino}$ $R^{2} = H, Me, CH_{2}NR_{2}$ $R^{3} = aryl$	693

TABLE IV-B.  $CO_2$  FROM MESIONICS TO FORM PYRAZOLES

Starting Material	Conditions	s Product(s) and Yield(s) (%) R
$\begin{array}{c} N & O^{-} & Bz \\ + N & CH_2CO_2Me \end{array} + H \\ \end{array}$	_	$CO_2 + MeO_2CH_2C \bigvee_{N}^{N} N  (-) \qquad 694$
$ \begin{array}{c} N & O^{-} & CO_2 Me \\ \uparrow N & \downarrow N & \downarrow N \\ R^2 & R^1 & \downarrow \\ \end{array} $	AcO ₂ , 130°	$CO_2 + \frac{R^2}{I} + \frac{R^2}{I}$
		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
$\begin{array}{c} N \\ + N \\ + N \\ + N \\ R^2 \end{array} + \left  \right  \\ R^1 = aryl \end{array}$	п	$CO_2 + R^2 \bigvee_{CO_2Me}^{R^1} N + R^2 \bigvee_{MO_2C}^{R^1} N $ $MeO_2C$ mixtures (73.99)
$R^2 = H$ , Ph, SMe, SOMe, Ac, or CN		
+ DMAD	n	$CO_2 + \frac{R^2}{N}N$ (62-99) 695 MeO_2C CO_2Me
$ \begin{array}{c} & & & & & \\ N & & & & \\ + N & & & + & \\ Me & & & & & \\ \end{array} $	90-120°	$CO_2 + \underbrace{\bigvee_{k=1}^{N} N}_{EtO_2C} CO_2Et $ () 696
$N \rightarrow 0$ + N + DMAD Ph Ph	UV	$CO_2$ + $MeO_2C$ $N$ (81) 697, MeO_2C Ph 698
$N = \frac{1}{10000000000000000000000000000000000$		$CO_2 + \underbrace{MeO_2C}_{MeO_2C} \bigvee_{Ph}^{Ar} (80) $ $699$
$N$ $+ N$ $+ DMAD$ $R^2$	120°	$CO_2 + $ $R^2 + N_N (12-82)$ $R^1 = Me \text{ or } Ph 700$ $R^2 = Br \text{ or } Cl$ $MeO_2C + CO_2Me$
N = 0 + N = + DMAD 3n = X	_	$CO_2 + X + N (-) 701$ $MeO_2C + CO_2Me$
$ \sum_{\substack{N \\ +N \\ +N \\ Ph}}^{N O^{-}} + \left[ \left( \sum_{i=1}^{N} \right) \right] $	65°	$CO_2$ + NNPh (65) 702
	≤65°	CO ₂ + " (49) 703
$ \begin{array}{c} N & O \\ + N & + N \\ + N & R^2 \end{array} + \left[ \left( \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right) \right] $	_	$CO_{2} + N - R^{1} = N - R^{1} - R^{2} - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) - (\%) -$
$ \begin{array}{c} N_{n} & 0 \\ + N_{n} & + \\ P h \end{array} + \left[ \begin{array}{c} \\ N_{n} & 0 \end{array} \right] $	rt	$CO_2$ + N NPh +/or NPh (30) 705

TABLE IV-B. CO2 FROM MESIONICS TO FORM PYRAZOLES (Continued)



TABLE IV-B. CO2 FROM MESIONICS TO FORM PYRAZOLES (Continued)

" This product is not formed by an rDA reaction.

	TABLE IV-C.	CO ₂ FROM MESIONICS		
	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c} Ph & O \\ + N & \\ Me & Ph \end{array}$	+ RCN	rt-80°	$CO_{2} + \frac{Ph}{N} \underbrace{\bigvee_{N}^{N}}_{R} Ph = \frac{R}{CO_{2}Et} \frac{(\%)}{74} \\ Bz = 51 \\ R = 2,4-Me_{2}C_{6}H_{3}O = 41 $	30
OAc Ph CO ₂ H	+ DMAD	Ac ₂ O, reflux	$CO_2$ + $Ph$ (32) 70 MeO_2C CO_2Me	08
$Ar \underbrace{O}_{+} O^{-} \underbrace{O}_{+} Ph$	+ DMAD	rt	$CO_2 + \underbrace{Ar}_{MeO_2C} + \underbrace{CO_2Me}_{CO_2Me} + \underbrace{Ar}_{HeOC_6H_4} \frac{(\%)}{90}$	09
$\overset{Ph}{\swarrow} \overset{O}{\underset{+}{}} \overset{O^-}{\underset{Ph}{\overset{-}}}$	+ DMAD	80°	$CO_2$ + $Ph$ $Ph$ (11) 3 MeO_2C $CO_2Me$	79
N + S R ¹	+ $\left\  \right\ _{\mathbf{R}^3}^{\mathbf{R}^2}$	60-100°	CO ₂ + $R^1 = Ph \text{ or aryl}$ $R^2(R^3) = R^3(R^2)$ $R^1 = Ph \text{ or aryl}$ $R^2 = CO_2Me \text{ or } Ph$ 7 $R^3 = H, Ph, \text{ or } CO_2Me$ 7	10, 11
Ph O O +N Me Ph	+ Ph Ph Ph	rt	$CO_2 + \underbrace{Ph}_{Ph} Ph \\ Ph \\ Ph \\ Ph \\ Ph \\ Ne Ph \\ N$	31. 12
	+ Ph Ph Ph	u	$CO_2$ + $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$	12

TABLE IV-C. CO₂ FROM MESIONICS TO FORM OTHER HETEROCYCLES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs
$\begin{array}{c} Ph & O & O^{-} \\ & & & \\ & & & \\ & & & \\ Me^{-} & Ph & Ph \\ & & & Ph \end{array} + \begin{array}{c} Ph & \\ & & & \\ & & & \\ Ph & & \\ & & Ph \end{array}$	60-110°, Ac ₂ O	$CO_2 + \begin{pmatrix} R^1 & R^2 \\ Ph & Ph \\ Ph & Ph \\ Ph & Ph \\ Me \end{pmatrix} = R^1, R^2 = CN, Ac, CO_2Me$	713 , or Bz
$R^{1} \longrightarrow 0^{-} + R^{3} \longrightarrow X$ Me $R^{2} = R^{4}$		CO ₂ + $R^4$ $R^3$ (17-63) $R^1$ $R^2$ $R^1, R^2, R^3, R^4 = Me \text{ or } Ph$ Me $X = O \text{ or } S$	713
$Ph \underbrace{O}_{+X} \underbrace{O}_{Ph} + Ph \underbrace{Ph}_{Ph} Z$	-	$CO_2 + \frac{R^4}{R^1 - X} + \frac{R^3}{R^2} + \frac{(17-63)}{X = NMe \text{ or } S}$	714
$Ph \xrightarrow{O} \xrightarrow{O^-} + Ph \xrightarrow{Ph} Z$	_	$CO_{2} + \begin{array}{c} X \\ R^{4} \\ R^{1} \\ R^{1} \\ Me \end{array} \begin{array}{c} Z \\ C(CN)_{2} \\ R^{2} \\ C(CN)_{2} \\ R^{1} \\ C(CN)CO_{2}Et \\ 65 \end{array}$	715
+ Ph Ph Ph	rt	$CO_2 + Ph \qquad V \\ Ph \qquad N \qquad Ph \qquad (83)$	716
$R^{\dagger} \bigvee_{R^{2}}^{O} O^{-} + \square CN$	50°	$CO_2 + NC + R^1 = Me \text{ or } Ph$ $N-R^2 = H \text{ or } Me$ $R^3 = Me, Bn, \text{ or}$ $R^3 = Me, Bn, or$	717 Ph
$(CH_2)_n$ $N$ $O$ $+$ $CN$ $CN$ $R$ $CN$	Ac ₂ O, 95°	$CO_{2} + NC + (CH_{2})_{n} + R + (\%) = \frac{n - R - (\%)}{3 - H - 85}$ $R + 3 - Me - 52 = 3 - 86 - 56 - 36 - 56 - 56 - 56 - 56 - 56 - 5$	717
$\begin{array}{c} Ph & O \\ + N & + \\ Me & Ph \end{array} + \begin{array}{c} CO_2 Me \\ CO_2 Me \\ CO_2 Me \end{array}$	_	$CO_2 + MeO_2C$ Ph NMe (-) $MeO_2C$ Ph NMe (-)	131
+ [] CO ₂ Me	_	$CO_2 + Ph$ NMe (20)	131

TABLE IV-C. CO2 FROM MESIONICS TO FORM OTHER HETEROCYCLES (Continued)



	TABLE V. COS	S FROM MESIONICS (Continued)	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \begin{array}{c} R^2 \\ + S \\ R^1 \\ R^2 \\ R^1 \\ R^2 $	80°	$COS + \begin{array}{c} R^{1} \\ Bz \end{array} \begin{array}{c} R^{2} \\ Bz \end{array} (83) \\ R^{2} = R \\ R^{2} = N - piperidinyl \end{array}$	727
+ DMAD	'n	$COS + \frac{R^{1} - S}{MeO_{2}C} + \frac{R^{2}}{CO_{2}Me} + \frac{R^{2}}{R^{2}} + \frac{R^{2}}{R^{$	727
+ DMAD	130°	COS + " (67-98) $R^1 = Me \text{ or aryl}$ $R^2 = aryl$	726
+     R ⁴	Heat	$COS + \begin{pmatrix} R^{1} \\ R^{4} \end{pmatrix} \begin{pmatrix} R^{2} \\ R^{3} \end{pmatrix} \begin{pmatrix} R^{1} \\ R^{2} \\ R^{3} \\ R^{3} \end{pmatrix} = CO_{2}Me, Bz \text{ or } Ph$ $R^{4} = H, Ph \text{ or } CO_{2}Me$	728
$R \bigvee_{+S}^{S} O^{-} + DMAD$	rt	$COS + \frac{Ph}{MeO_2C} CO_2Me \frac{R}{S-allyl} \frac{(\%)}{43}$	729
S Ar O Ph	₽d/C	$H_2$ + COS + $Ph$ () Ph	730
$O = Ph CO_2Me CO_2Me$		$H_2$ + COS + $H_2CCCO_2Mc$ ()	730
S Ar	Pd/C	$H_2$ + COS + (-)	730
$O_{\text{S}} = N + \frac{1}{N} CO_2 Me$ $S_{\text{Ph}} = CO_2 Me$ $CO_2 Me$	80°	$COS + \frac{Ph}{\sqrt{S}} + \frac{S}{Ph} (67) + \frac{Ts}{MeO_2C} + CO_2Me (64)$	383
$CO_2Me$ S Ph $CO_2Me$ $CO_2Me$ Ph	140°	$COS + Ph \xrightarrow{S} Ph (92) + \underbrace{O}_{MeO_2C} CO_2Me (91)$	384, 385
$Ph \underbrace{S}_{+S} O^{-1} + \left[ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	_	COS + $PhS$ (36) Ph	132
$\begin{array}{ccc} Ph & S & O^{-} & Ph \\ + N & + & \\ Mc & Ph & Ph \end{array}$	п	$COS + \frac{Ph + Ph}{Ph + Ph} Ph \qquad (-)$	712
+ Ph Ph Ph	_	$COS + \frac{Z}{Ph} + \frac{Z}{N} + \frac{Ph}{Me} + \frac{Z}{Ph} + \frac{Z}{O} + \frac{(\%)}{55} + \frac{5}{55} + \frac{5}{56} + $	715

Conditions Starting Material Product(s) and Yield(s) (%) <u>z</u> 0 (%) Ph Ph COS + 38 715 z C(CN)₂ 19 Ph 150° COS (≥62) 731 +

cos

R


112-138°

^a The starting material shown here is a proposed intermediate.

 $Z = CH_2$ 

R

TABLE V. COS FROM MESIONICS (Continued)

Refs.

731

m n (%) 1 1 36

0 45

1 1 95

1 1 100

1 71

1

2

 $\frac{R^1}{R^2}$ 

Me Ph

"

н

"

Me

|| 0

	TABLE VI-A. N ₂ FROM A		
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{bmatrix} \begin{matrix} & \mathbf{N} \\ & \mathbf{N} \\ & \mathbf{N} \end{bmatrix}^{a}$	_	N ₂ + ()	732
NH NH	rt (OC)	$\begin{bmatrix} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & $	133
	n	N ₂ + ()	133
NH NH	u	N ₂ + (299)	133
NH NH	u	N ₂ + (298)	133
NH NH		N ₂ + ()	133
	HgO	N ₂ + (73)	733

TABLE VI-A. N2 FROM ALIPHATIC DIAZA COMPOUNDS

TABLE VI-A. N ₂ FROM ALIPHATIC DIAZA COMPOUNDS (Continued)			
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	Warm; $\Delta H^{\ddagger} = 15.4$ ; $\Delta S^{\ddagger} = -7$	$N_2$ + $\left[ \begin{array}{c} \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ \end{array} \right]$ ()	138
	UV, -196°	" + " ()	138
	≥ -40°	" + " ()	137
NH NH	π, HgO	" + " (≥34)	734
+ SO ₂	HgO	$N_2$ + $N_2$ + $N_2$ + $N_2$ + $N_2$ - $N_2$ - $Ca. 9/1$ ()	735
$\left[ \begin{array}{c} \boxed{\begin{matrix} \blacksquare \end{matrix} \\ \blacksquare \end{matrix} \\ N \end{array} \right]^{c}$	_	$N_2$ + $\begin{bmatrix} \square \end{bmatrix}$ $(-)$	736
	Heat	$N_2$ + $Cl$ $d$ $(-)$	737
R N OAc R N OAc Ph	<ul> <li>a) Zn•Cu, 90% HOAc (OC)</li> <li>b) <i>n</i>-Bu₄NF, THF (OC)</li> </ul>	$N_2 + CO_2 + OAc O Ph$	738
		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	
,NH NH	HgO, -10°°	$\left[ \begin{array}{c} \swarrow \\ N \end{array} \right] \longrightarrow N_2 + \begin{array}{c} \bigcirc \\ (-) \end{array}$	739
	-78°	N ₂ + ()	134
V N I	25°; $E_a = 18.9 \pm 1.5$ $k_{rel}$ (I/II) = 10 ¹¹	N ₂ + ()	740
	Heat; E _a = 37.3	$N_2$ + $\left[ \begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array} \right]$ ()	740
	Solvent, temperature varied $E_a = 22.1-24.3$ $\Delta S^{\ddagger} = 3.4-8.9$	N ₂ + ()	136
	Heat k _{rel} ( <b>III/V</b> ) = 10 ¹⁷	""()	135
N N N	Heat k _{rel} ( <b>IV/V</b> ) = 10 ⁵	$N_2 + \left[ \underbrace{ \frown }_{\bullet} \right] (-)$	135
V NN	Heat	$N_2$ + $\left[ \bigcirc \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	135
NH	Air oxidation	N ₂ + (70) semibullvalene	741

T	ABLE VI-A. N ₂ FROM ALIPHA	TIC DIAZA COMPOUNDS (Continued)	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
NH	МпО ₂ , гі	N ₂ + (73)	742
MeO ₂ C	UV	$N_2$ + (80) McO ₂ C	743
PhN I NH NH	HgO	$N_2$ + $N_1$ (50-70) Ph	744
$N = CO_2CH_2CCI_3$	l. Zn 2. CuCl ₂ 3. aqueous NH3, -40°	$ \begin{array}{c} 0 \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	745
O N N	0°	$N_2$ + (-)	139
A N N	≥180°	$N_2$ + $(-)$	139
NH NH H	MnO ₂ , -15°	$N_2$ + $10^{\circ}$ ()	746
NN-0	Si₂Cl ₆ , ≤0°	$\left[\begin{array}{c} \searrow \\ & \searrow \\ & N \end{array}\right] \xrightarrow{\leq -40^{\circ}} N_2 + \left(\begin{array}{c} & (-) \end{array}\right)$	140, 747
N ^N	n	N ₂ + ()	140
N ^N -O	n	N ₂ + ()	140
N-O	n	N ₂ + ()	140
	≤ -40°	N ₂ + ()	747
	140°	N ₂ + ()	748
	UV, ≥340 nm	N ₂ + ()	749
NH N, N, H H	200°	N ₂ + (-)	141

TABLE VI-A. N2 FROM ALIPHATIC DIAZA COMPOUNDS (Continued)

Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
N = N + N + N + N + N + N + N + N + N +	200°	N ₂ +	(35) NH NH	141
O S NH	aqueous Cl ₂	N ₂ +	О // S ОН (—)	750

^a This reaction is theoretical.

^b The starting material was prepared at  $-90^{\circ}$ .

^c This compound is a proposed intermediate.

^d The tetrachloro analog gives pyrazole (see Part I, Table IX, p. 209)¹.

	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs
$ \begin{array}{c} \mathbf{R}^{2} \\ \mathbf{R}^{3} \\ \mathbf{R}^{3} \\ \mathbf{R}^{4} \end{array} $	NEI2 +	Heat	N ₂ + $R^{1}$ NEt ₂ $R^{2}$ + $R^{1}$ NEt ₂ + $R^{2}$ + $R^{2}$ NEt ₂ NEt ₂ + $R^{3}$ R ⁴ II	142
			$\frac{\mathbf{R}^{1}}{\mathbf{R}^{2}} = \frac{\mathbf{R}^{3}}{\mathbf{R}^{4}} = \frac{\mathbf{R}^{2}}{\mathbf{I}(\%)} = \frac{\mathbf{I}(\%)}{\mathbf{I}(\%)}$	
			$CO_2Me$ H H H $138^{\circ}$ 23 —	
			$11  CO_2 MC  11  74 =$	
			Ph CO ₂ Et " " 138° 73 —	
			" " " 101° — 95	
			CO ₂ Me H " CO ₂ Me " — 75	
			"Ph """— 89	
			" CO ₂ Me " " — 85	
MeO ₂ C	+	_	HCN + $(-)$	751
McO ₂ C N MeO ₂ C N	•	_	$N_2$ + $MeO_2C$ () $MeO_2C$ NEt ₂	751

TABLE VI-B. N2 FROM PYRIDAZINES AND ANALOGS





TABLE VI-B. N2 FROM PYRIDAZINES AND ANALOGS (Continued)



$\begin{split} & \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\ \displaystyle + \end{array} \right) + \left( \begin{array}{c} \displaystyle \int_{-\infty}^{\mu} N \\$	Starting Material	Conditions	Product(s) and Yield(s) (%) Refs.
$ \begin{array}{c} + \underset{\mathbf{k}}{\mathbf{k}} + \underset{\mathbf{k}}{\mathbf{k}}{\mathbf{k}} + \underset{\mathbf{k}}{\mathbf{k}} + \underset{\mathbf{k}}{\mathbf{k}}{\mathbf{k}} + \underset{\mathbf{k}}{\mathbf{k}} + \underset{\mathbf{k}}{$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	120°	N ₂ + $R^1$ $R^3$ $R^1 = CN \text{ or } SO_2Me$ $R^2, R^3 = -(CH_2)_n -; n = 3 \text{ or } 4$ 764 $R^2$ $NR_2 = piperidinyl or morpholino$
$ \begin{array}{c} \left( \sum\limits_{k=1}^{N} & + & \left( \sum\limits_{k=1}^{N$	$+ \frac{R^{3}}{R^{2^{\mu^{\mu^{\mu}}h_{2_{n}}}}} NR_{2}$		$N_2$ + $R^3$ (63-74) 764 $R^2$ substituents as above
$ \begin{split} & \overset{R}{\overset{L}{\underset{k}{\mapsto}}} = \overset{R}{\overset{N}{\underset{k}{\mapsto}}} + \overset{N}{\overset{N}{\underset{k}{\mapsto}}} \stackrel{P}{\underset{k}{\stackrel{N}{\mapsto}}} + \overset{R}{\underset{k}{\stackrel{N}{\mapsto}}} \stackrel{P}{\underset{k}{\stackrel{N}{\mapsto}}} + \overset{R}{\underset{k}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\mapsto}}} = \overset{R}{\underset{k}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\mapsto}}} \stackrel{R}{\underset{k}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\mapsto}}} \stackrel{R}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{R}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\mapsto}}} \stackrel{NE}{\underset{k}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\stackrel{N}{\stackrel$	$ \begin{array}{c}                                     $	140°	$N_2$ + $N_2$ (21) 764
$\begin{split} & \overset{P_{1}}{\underset{N}{\overset{L}{\underset{N}{\overset{N}{\underset{N}{\overset{N}{\underset{N}{\overset{N}{\underset{N}{N$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Heat	$N_2 + N_1 + N_2 + N_2 + R = CN \text{ or } SO_2Me$
$\begin{split} P_{h}^{h} \xrightarrow{NO_{h}Me}_{h} + (-) \xrightarrow{NO_{h}} 101^{\circ} & N_{2} + \bigvee_{h}^{P_{h}} \xrightarrow{SO_{h}Me}_{h} (3) & 76^{\circ} \\ P_{h} \xrightarrow{N}_{h} \xrightarrow{V}_{h} \xrightarrow{N}_{h} + \bigvee_{h}^{NE_{2}} 00^{\circ} & N_{2} + \bigvee_{p_{h}} \xrightarrow{S}_{h} \xrightarrow{V}_{h} \xrightarrow{V}_{$	$Ph \qquad R^{1} \qquad \qquad$	140°	$N_{2} + N_{1} + N_{1} + R^{2} + R^{3} + (CH_{2})_{3} + (CH_{2})_$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c} Ph & SO_2Me \\ \\ N & N & N \\ N & N \end{array} + \\ N & N \end{array}$	101°	$N_2 + \bigvee_{N}^{N} \bigvee_{N}^{N} (53)$ (53)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Ph \xrightarrow{S}_{N} \stackrel{I}{\underset{N}{\overset{V}{\longrightarrow}}} N \xrightarrow{NEl_2}_{N} \stackrel{NEl_2}{\underset{Et}{\overset{H}{\longrightarrow}}} H$	90°	$N_2$ + $Ph - K_{Et}$ (75) 763
$+ = \bigvee_{NMe_{2}}^{OMe} \cdot N_{2} + \bigvee_{N}^{Ph} + \bigvee_{N}^{SO_{2}Me_{2}} (9) $ $+ (CH_{2})_{n} - N + \cdots + N_{2} + \bigvee_{N}^{Ph} + \bigcup_{N}^{SO_{2}Me} \frac{n - (%)}{3 - 47} $ $N_{2} + \bigvee_{N}^{N} + \bigcup_{N}^{C} + \bigcup_{N}^{C} + (CH_{2})_{n} - \frac{4 - 45}{4 - 45} $ $N_{2} + \bigvee_{N}^{Ph} + \bigcup_{N}^{C} + \bigcup_{N}^{C} + (S_{1}) + ($	$\begin{array}{c cccc} Ph & SO_2Me & NEt_2 \\ N & & N & + \\ N & & N & \\ N & & N & \\ \end{array}$	101°	$N_2 + N_1 + N_1 + N_2 + N_1 + N_1 + N_2 + N_1 + N_2 + N_1 + N_1 + N_2 + N_2 + N_1 + N_2 $
$+ (CH_{2})_{n} - N \qquad " \qquad N_{2} + \begin{pmatrix} P_{h} \\ N_{k} + \begin{pmatrix} 0 \\ -1 \end{pmatrix}_{n} & \frac{1}{3} & \frac{1}{47} \\ \frac{1}{4} & \frac{1}{45} \end{pmatrix} \qquad 767$ $+ \begin{pmatrix} -1 \\ N_{k} + \begin{pmatrix} -1 \\ -1 \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & N_{2} + \begin{pmatrix} P_{h} \\ N_{k} + \begin{pmatrix} -1 \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & N_{2} + \begin{pmatrix} P_{h} \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} \\ + \begin{pmatrix} -1 \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & N_{2} + \begin{pmatrix} P_{h} \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} \\ + \begin{pmatrix} -1 \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & N_{2} + \begin{pmatrix} P_{h} \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} \\ + \begin{pmatrix} -1 \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & N_{2} + \begin{pmatrix} P_{h} \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} & \frac{1}{40^{\circ}} \\ + \begin{pmatrix} -1 \\ N_{k} + \end{pmatrix}_{n} & \frac{1}{40^{\circ}} & \frac$	+ $\rightarrow NMe_2$	"	$N_2$ + $N_1$ $N_2$ $N_2$ $N_1$ $N_2$ (9) 767
Ph + Cl + N + N + N + N + N + N + N + N + N +	+ (CH ₂ ) _n N		$N_2$ + $N_1$ $N_2$ $N_1$ $(CH_2)_n$ $N_1$ $(CH_2)_n$
$+ \swarrow -N \qquad " \qquad N_2 + \qquad N_2 + \qquad N_1 \qquad (30) \qquad 767$	$\begin{array}{c} Ph & Cl \\ N & N \\ N & N \\ N & N \end{array} + N \end{array}$	140°	$N_2 + N_1 + N_1 + N_2 + N_1 + N_2 $
$ \begin{array}{c} O & a \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & $	+	r	$N_2 + N_1 + N_1 + N_2 + N_1 + N_2 $
		-30°	$N_2$ + $N_1$ (43) 548

TABLE VID N.







TABLE VI-B. N2 FROM PYRIDAZINES AND ANALOGS (Continued)



 a  The starting material was prepared at –50°.

	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\underset{N \in N}{\overset{R}{\longrightarrow}} $	NEt ₂	Pressure, rt	$N_2$ + $R$ $N$ $NEt_2$ $Ne$ $7.5$ kbar 36	773
+		rt	$N_2$ + (24) R = H or Me	773
N +	(CH ₂ )n N	100°	$N_2$ + (CH ₂ ) _n $\frac{n}{4} \frac{(\%)}{45}$ 6 69 8 27 10 34	774
+		60°	$N_2 + (16)$	774
+	-<->-N	n	N ₂ + (25)	774
+		100°	$N_2$ + (45) + (11)	774
+		100°, 2 h	N ₂ + (37)	148

TABLE VI-C. N₂ FROM 1,2,3-TRIAZINES (Continued)

	TABLE VI-C. N ₂ FROM	1 1,2,3-TRIAZINES (Continued)	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \underset{N \in N}{ \underset{N \in N}{ + } } + \underset{Pr-i}{ \underset{Pr-i}{ } } $	100°, 2 h	N ₂ + $r_i$ cis:trans = 1:2	(12) 775
$ \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & $	180°	$N_2$ + $R^2$ + $R^2$ $R^2$ + $R^2$ I II	149
$+ \qquad \begin{array}{c} R^2 \\ R^1 \end{array} \qquad $	n	$\frac{R^{1}}{NEt_{2}} \frac{R^{2}}{Me} \frac{I(\%)}{50} \frac{II(\%)}{3}$ $\frac{R^{1}}{Ph} \frac{R^{2}}{H} \frac{R^{3}}{38} \frac{I(\%)}{11} \frac{II(\%)}{11}$ $\frac{R^{1}}{H} \frac{R^{2}}{H} \frac{R^{3}}{50} \frac{I(\%)}{35} \frac{II(\%)}{11}$	149

TABLE VI-C. N₂ FROM 1,2,3-TRIAZINES (Continued)

Starting Material	Conditions	Product(s) and Vield(s) (%)	Refs
$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	45°	$N_2$ + $R^1$ (22-78) $R^1, R^2 = H, alkyl, aryl$	776
+ $R^1$ $R^2$	pyrrolidine catalyst, 45°	$N_2$ + $N_2$ (19-93)	154
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	100°	N ₂ + $R^{1}$ $R^{2}$ $R^{3}$ $R^{2}$ $R^{3}$ $R^{3}$ $R^{1}$ $R^{2}$ $R^{3}$ $R^{3}$ $R^{3}$ $R^{1}$ $R^{2}$ $R^{3}$ $R^{3}$	777
		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
$R^{1} \xrightarrow{R^{2}}_{N \xrightarrow{V}} R^{2} \xrightarrow{X \xrightarrow{Y}}_{O_{2}Me}$	40-100°	$N_2$ + $X_{MeO_2C}$ $R^2$ + $X_{MeO_2C}$ $R^2$ (19-100) $R^1 = H, Ph, or CO_2Me; R^2 = H, Ph, or CO_2Me$	778

TABLE VI-D. N₂ FROM 1,2,4-TRIAZINES

 $X = OEt \text{ or } NMe_2$ ; Y = OEt, SMe, or  $NMe_2$ 








TABLE VI-D. N2 FROM 1,2,4-TRIAZINES (Continued)



 TABLE VI-D.
 N2 FROM 1,2,4-TRIAZINES (Continued)





TABLE VI-D. N2 FROM 1,2,4-TRIAZINES (Continued)

HOH₂C

юн





TABLE VI-D. N2 FROM 1,2,4-TRIAZINES (Continued)



	TABLE VI-D. N ₂ FROM	1,2,4-TRIAZINE	S (Continued)	1.12 - 1.1(-) (0)	Dofe
Starting Material	Conditions		Product(s) a	and 1 (eld(s) (%)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	See Table	N ₂ +	R	R         Conditions         (%)           SBn $101^{\circ}$ 95           SOBn          <20	820
N N S	210°, 12 h	N ₂ +		(24)	810
$\mathbb{C}F_{3}$ $\mathbb{N}$ \mathbb{N} $\mathbb{N}$ \mathbb{N} $\mathbb{N}$ $\mathbb{N}$ \mathbb{N} \mathbb{N} $\mathbb{N}$ \mathbb{N} \mathbb{N} $\mathbb{N}$ \mathbb{N} $\mathbb{N}$ \mathbb{N} \mathbb{N} $\mathbb{N}$ \mathbb{N} \mathbb{N} \mathbb{N} \mathbb{N} $\mathbb{N}$ \mathbb{N} N	Heat	N ₂ +	CF3	n Temp (%) 2 132° 93 (CH ₂ ) _n 3 180° 78 4 210° 55	821
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	101°	N ₂ +	R ¹ S R ² N	(91-98) $R^1 = Me \text{ or } Bn$ $R^2 = Me, i-Pr, \text{ or } Ph$	813
$\begin{array}{c} O \\ S - R^{1} \\ R^{2} \\ N \\ N \\ N \\ N \\ N \end{array} + \\ N \\$	HOAc, 0°	N ₂ +	$R^{1}$ $R^{2}$ $N$	(68-92) $R^{1} = Me \text{ or } Bn$ $R^{2} = Me, i-Pr, \text{ or } Ph$	813
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	n	N ₂ +	R ¹ O ₂ S	(46-88) $R^{1} = Me \text{ or } Bn$ $R^{2} = Me, i-Pr, \text{ or } Ph$	813
$\begin{array}{cccc} Ph & & & & & \\ & & & & \\ N & & N & + & & \\ & & & XBn & & \\ \end{array}$	0°	N ₂ +	Ph N XBn	$\frac{X}{SO} = \frac{(\%)}{9}$ $SO_2 = 46$	813
$XR \qquad \qquad$	Heat	N ₂ +		$\begin{array}{c ccc} X & Temp & (\%) \\ \hline S & 101^{\circ} & 9 \\ SO & 0^{\circ} & 67 \\ SO_2 & " & 61 \\ \end{array}$	813
$Ph \underbrace{\downarrow}_{\substack{N \\ N \\ R}}^{Ph} + \underbrace{\downarrow}_{\substack{N \\ R}}^{Ph}$	112°	N ₂ +	CP + Ph Ph	$\begin{array}{c cccc} R & (\%) \\ \hline CO_2Et & 65 \\ H & 88 \\ \hline N & R & Me & 64 \\ Ph & 27 \\ SO_2Me & 66 \\ \end{array}$	822
$Ar \xrightarrow{Ar}_{N \xrightarrow{N}} + \qquad \qquad$	"	N ₂ +	CP + Ar	I 38 (68) $N = 4-MeOC_6$	822 H ₄
$R^{1} \xrightarrow{R^{2}} N \xrightarrow{N} N$	Heat	N ₂ +	$R^2$ $R^1$ N S	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	823

Starting Material	Conditions	Product(s) and Yield(s) (%)	Ref
$\begin{array}{c} R^2 \\ R^1 \\ N \\ N \\ S \\ S \\ \end{array} $	<i>m-</i> CPBA, rt	$N_2$ + $R^2$ $N_2$ + $R^1$ $R^2$ (%) $R^1$ $R^2$ (%) $R^2$ $R^2$ $R^$	823
Ar N N N N S	100°, 25 h (OC)	$N_2$ + (34) Ar N S Ar = 4-ClC ₆ H ₄	823
$ \begin{array}{c}                                     $	Heat	$N_2$ + $R^2$ $N_2$ + $R^1$ $R^2$	823
$Ph \bigvee_{\substack{N \\ N \\ O_2S}} N$	66°, 24 h	$N_2$ + $Ph$ $N$ $S_0$ (78)	823
$Ph \underbrace{ \begin{array}{c} & + & Et \\ & & & \\ N & & N \\ & & N \\ & & S \end{array}}_{S} \\ S \\ \end{array}$	54°, 7 h	$N_2 + C_2H_4 + \frac{Ph}{H}BF_4^- $ (56)	824
$\begin{array}{c} Ph \\ H \\ H \\ N \\ N \\ S \\ S \\ \end{array} \begin{array}{c} + & Et \\ BF_4^- \\ S \\ S \\ \end{array}$	1. 101°, 20 h 2. Aqueous base	$N_2 + C_2H_4 + N S $ (40)	824
	Heat, solvent	$N_{2} + \begin{pmatrix} R \\ \downarrow \\ H \\ H$	825, 826
$\begin{array}{c} CO_2E_1 \\ O \\ & \\ N \\ & \\ N \\ S \\ \end{array}$	POCl ₃ , 106°	$N_2$ + $EtO_2C$ Cl N S (88)	826
$R^{1} \xrightarrow{R^{2}}_{N \xrightarrow{N}} R^{3} \xrightarrow{R^{4}}_{N \xrightarrow{N}} R^{4}$	№н, rt-65°	$N_{2} + \begin{array}{c} R^{2} \\ R^{1} \\ R^{1} \\ R^{2} \\ R^{3} \\ R^{4} \\$	786, 787

TABLE VI-D. N₂ FROM 1,2,4-TRIAZINES (Continued)



4-MeC₆H₄ -(CH₂)₃--

н

"

--(CH₂)₄---

Et 22

57

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TABLE VI-D. N₂ FROM 1,2,4-TRIAZINES (Continued)



TABLE VI-D. N₂ FROM 1,2,4-TRIAZINES (Continued)

	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
$X \xrightarrow{X}_{\substack{N \\   \\ N \\ X}} N$	+	70°, 7 d	N ₂ +	X $X$ $Cl 95$ $F 52$ $X$	833. 834
	+ C ₂ H ₄	70°	N ₂ +		834
	+ $\left( \begin{array}{c} R^1 \\ R^2 \end{array} \right)$	70°, 1-7 d	N ₂ +	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	.) 833, 834

^{*a*} The relative rates for this reaction are:  $X = SO > SO_2 > S$ ; no details are given.

^b Other starting materials include Ph or *i*-Pr in place of Me. The rates of the reactions are analogous: sulfone > sulfoxide > sulfide.

						Keis.
+	R ² R ³	_	N ₂	+	$ \begin{array}{c} \overset{N}{R^{3}} \xrightarrow{N^{1}} R^{1} \\ \overset{R^{1}}{R^{2}} \\ \overset{R^{2}}{R^{2}} \\ \overset{R^{2}}{R^{2}} \\ \end{array} (-) $	169
					$R^1 = CO_2Me$ , $CO_2H$ , $CONH_2$ , $CN$ , $CH_2OH$ , $Br$ , $H$ , NHCO_2Et, NHCO ₂ Bn, Cl, or $CO_2Bu$ - <i>t</i> $R^2$ , $R^3 = H$ or Me	
+	R ³ R ⁴	_	N ₂	+	$R^{1} = Ph \text{ or } 2\text{-pyridyl}$ $R^{2} = H, Ph \text{ or } 2\text{-pyridyl}$ $R^{2} = H, Ph \text{ or } 2\text{-pyridyl}$ $R^{3}, R^{4}, R^{5} = H \text{ or } Me$ $R^{2}$	835
+	Ph R ² Ph	π	N ₂	+	$\begin{array}{c} R^{1} \\ Ph \\ R^{2} \\ N \\ R^{2} \\ Ph \\ R^{2} \end{array} (-) \qquad \begin{array}{c} R^{1} = Me, Ph, 4-p-MeC_{6}H_{4}, \\ or \ 3-FC_{6}H_{4} \\ R^{2} = H \ or \ Ph \\ R^{1} \end{array}$	836
		80°	N ₂	+	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	837
+	TMS    R		N ₂	+	$ \begin{array}{c} Ph \\ N \\ H \\ N \\ N$	838
	+ +	+ $R^2$ $R^3$ + $R^4$ $R^5$ + $Ph$ $R^2$ + $Ph$ $R^2$ + $R^4$ $R^5$	+ $R^{2}$ $R^{3}$ $-$ + $R^{4}$ $R^{5}$ $-$ + $R^{4}$ $R^{5}$ $-$ + $Ph$ $R^{2}$ $\pi$ 80° + $R^{1}$ $R^{2}$ $R^{3}$ $R$	$ + \frac{R^{2}}{P_{h}} R^{3} - N_{2} $ $ + \frac{R^{3}}{R^{5}} R^{5} - N_{2} $ $ + \frac{P_{h}}{P_{h}} R^{2} - N_{2} $ $ = \frac{80^{\circ}}{N_{2}} N_{2} $ $ + \frac{TMS}{R} - N_{2} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$+ \prod_{R}^{2} R^{3} - N_{2} + \prod_{R}^{3} \prod_{R^{1} R^{2} R^{2}}^{N} R^{3} (-)$ $R^{1} = CO_{3}Me, CO_{3}H, CONH_{2}, CN, CH_{2}OH, Br, H, NHCO_{2}Bn, CI, or CO_{2}Bu - r, R^{2}, R^{3} = H \text{ or } Me$ $+ \prod_{R^{4} R^{5}}^{N} R^{5} - N_{2} + \prod_{R^{4} R^{5}}^{N} R^{5} (280) = R^{2} = H, Ph \text{ or } 2-pyridyl$ $R^{2} = H \text{ or } Me$ $+ \prod_{R^{4} R^{5}}^{Ph} R^{2} (280) = R^{2} = H, Ph \text{ or } 2-pyridyl$ $R^{2} = H \text{ or } Me$ $+ \prod_{R^{4} R^{4}}^{Ph} R^{2} (-) = R^{1} = Me, Ph, 4p-MeC_{6}H_{4}, Ph + Ph $

TABLE VI-E. N2 FROM 1,2,4,5-TETRAZINES

	Starting Material	Conditions	Product(s) and Yield(s) (%) Refs.
	+ TMS———(CH ₂ ) ₄ ——	65°	$N_2$ + $N_1$ + $N_2$ + $N_1$ + $N_1$ + $N_2$ + $N_1$ + $N_2$ + $N_3$ + $N_4$
	+ TMS — (CH ₂ ) ₄ — TMS	80°	$N_{2} + N_{1} + N_{1} + M_{1} + M_{1} + M_{2} + M_{1} + M_{2} + M_{1} + M_{2} + M_{2$
$\mathbb{R}^{1}$ $\mathbb{N}$ $\mathbb{N}$ $\mathbb{R}^{2}$	+ $\left( \begin{array}{c} N(R^3)_2 \\ R^4 \end{array} \right)$	101°	$N_{2} + N_{2} + (R^{3})_{2}NH $ $\frac{R^{1}}{Ph} + (R^{3})_{2}NH $ $\frac{R^{1}}{Ph} + (R^{3})_{2}NH $ $\frac{R^{1}}{Ph} + (R^{3})_{2}NH + (R^{3})_{2}NH $ $\frac{R^{1}}{Ph} + (R^{2})_{2}NH + (R^{3})_{2}NH + (R^{3})_{2}N$
N N N N N Ar	Ме +	rt, 3 weeks	$N_2 + N_1 + N_1 + \frac{Ar}{N} + \frac{Ar}{Ph} + \frac{(\%)}{0} + \frac{640}{100} + 6$
	Ph +    	rt, 2 weeks	$N_{2} + N_{1} + N_{1$
	+    ^{Ph}	— (OC)	$N_2$ + $N_2$ + $N_1$ + $N_2$ + $N_1$ + $N_2$ + $N_1$ (-) 840
	+	20°	$N_2 + \underbrace{\begin{array}{c} R \\ N_2 \end{array}}^R (-) \\ N \\ $
$R \xrightarrow{N-N} R$	+	T	$N_2 + \underbrace{R_1}_R K_R + \underbrace{R_10^3 k (M^{-1}s^{-1})}_{4-MeOC_6H_4} 20.7 + 4-MeC_6H_4 32.0 156 - 3-MeC_6H_4 51.6 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7 + 20.7$

TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)

	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
N N N N Ph	+ Y +	rt	$N_{2} + N_{1} + N_{1$	778
	+ Me ₂ N NMe ₂	Solvent, 30°	$N_{2} + N_{1} + N_{1$	<b>I:II</b> 99:1 155 6:94
	+ XX	rt	N ₂ + N N ₂ + N N N X () Ar = Ph, 4-ClC ₆ H ₄ , 4-MeOO 4-Me ₂ NC ₆ H ₄ , or 2-CF ₃ X = OEt or SMe	C ₆ H ₄ , C ₆ H ₄ 155
R	+	ч	$N_2$ + (62)	172
	+	Warm	$N_2$ + $(-)$ $R$ $R = Mc, Ph, or CO_2Mc$	841
	+ Ph Ph	_	$N_2 + N_1 + Ph$ $N_2 + N_1 + Ph$ Ph $R = Me, Ph, CO_2Me, or 4-Ba$	842 •C ₆ H ₄
	+ [1] Fe(CO)3	Ce(IV), 0°	$N_2 + \begin{bmatrix} R \\ N \\ N \\ N \\ R \end{bmatrix} \longrightarrow \begin{bmatrix} N \\ N \\ N \\ R \end{bmatrix} \xrightarrow{N \\ R \\ R \\ CO_2 Me}$	
	+ Fe(CO)3	Fe(III), 0°	$N_2$ + $N_1 R$ $R$ $(\%)$ R $R$ $R$ $R$ $(\%)$ Me 63	170
N=N-N N=N-N	+	0°	$N_2 + U = N + (89)$	176
	+ [  ^R	_	$N_2 + N + N + N + N + N + N + N + N + N + $	(—) 176
	+	101°	$N_2 + $ $N_1 + O_1 + O$	176
	+ NH a	101°, 3 h	$N_2$ + $N_1$ $N_1$ $N_1$ $N_1$ $N_1$ $N_1$ $N_2$ $N_1$ $N_1$ $N_2$ $N_2$ $N_1$ $N_2$ $N_1$ $N_2$ $N_2$ $N_2$ $N_1$ $N_2$ $N_2$ $N_1$ $N_2$ $N_2$ $N_2$ $N_1$ $N_2$ $N_2$ $N_2$ $N_2$ $N_2$ $N_1$ $N_2$ $N_$	176
	+ MeO N	Heat	$N_2$ + $MeO$ $R$ $N$ $N$ $R$ $R$ $R$ $Me$ $R$ $R$ $Ph$ $100^{\circ}$ $CO_2Me$ $rt$	(%) 5 190 

TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)

	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	R' +	-	$N_2$ + $N_1$ $R$ $(-)$ $R = CHFCF_3 \text{ or } Ph$ $R^1 = not reported$	843
ĸ	+   ^{R1}	_	" + " (—) " ¹	843
CHFCF ₃ N N N N CHFCF ₃	+    	_	$N_2$ + $N_1$ (-)	165
	+ / ^R	rt	$N_2 + N_1 + CHFCF_3 = R - (\%)$ $N_2 + N_1 + i-BuO Viny1 - Viny1 Viny1 - Viny$	166
	+		$N_2$ + $N_1$ () CHFCF ₃ ()	166
	+	T	$N_2$ + $N_2$ + $N_1$ $N_2$ $N_2$ $N_1$ $N_2$ $N_1$ $N_2$ $(-)$	166
	+	138°	N ₂ + $R$ $R$ $R$ $R$ $R$ $R$ $R$ $R$ $CO_2Me$ $72$ $CF_3$ $12$	186
$\mathbf{R}^{\mathbf{N}} \xrightarrow{\mathbf{N}^{\mathbf{N}} \mathbf{N}}_{\mathbf{N}} \xrightarrow{\mathbf{N}^{\mathbf{N}} \mathbf{N}}_{\mathbf{R}^{\mathbf{N}}}$	+ $R^2$ $N$ $R^2$ $N$	n	$N_{2} + N_{1} + N_{1} + R^{2} + R^{2$	844
$\mathbb{N} \xrightarrow{\mathbb{N}} \mathbb{N} \xrightarrow{\mathbb{N}} \mathbb{N} \xrightarrow{\mathbb{N}} \mathbb{R}$	+ (S	n	N ₂ + $N \xrightarrow{R} S$ $N \xrightarrow{S} CO_2 Me^{b} 21$ R $CF_3 46$	844
$ \begin{array}{c} CF_{3} \\ N \\ \parallel \\ N \\ CF_{3} \end{array} $	+ N ^{Me} MeS	и	$N_2 + U_{CF_3} + CF_3 + (45)$	845
	+ (N SMe	n	$N_2$ + $N_2 + K_1 + K_2 + K_1 + K_1 + K_2 + K_1 + K_$	845
	+ N MeS	"	$N_2 + $ $N_2 + $ $N_2 + $ $N_1 + N_2 + N_1 + N_2 + N$	845

TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)





TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)

		IABLE VI-E. N2 FROM 1,2,4	4,J-1E1KAZIN	Product(s) and Yield(s) (%)	Refs.
	Starting Material	138°	N ₂ +	Ph $CO_2Me$ V $CO_2Me$ $CO_2Me$ $CO_2Me$	752. 848
$     Ph     R^{1}     N     N     N     N     R^{2}     R^{2}   $	+ $\begin{vmatrix} \mathbf{NEt_2} \\ \mathbf{R}^3 \end{vmatrix}$	20°	N ₂ +	$\begin{array}{c} \overset{P}{Ph} \\ & \\ E_{t_2N} & \overset{R^1}{\underset{R^3}{\overset{N}{\overset{N}{\overset{P}{}}}}} \\ & \overset{R^1}{\underset{R^2}{\overset{R^2}{\overset{R^3}{\overset{R^3}{\overset{(\%)}{\overset{P}{}}}}}} \\ & \overset{R^1}{\underset{R^2}{\overset{R^2}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R}}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R^3}{\overset{R}}{\overset{R^3}{\overset{R}}{\overset{R^3}{\overset{R}}{\overset{R^3}}{\overset{R^3}{\overset{R}}{\overset{R^3}}{\overset{R^3}}{\overset{R}}{\overset{R^3}}{\overset{R}}{\overset{R^3}}{\overset{R^3}}{\overset{R^3}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$	29
Ph N N N Ph	SnPh ₃ +     Ph	130-150°	N ₂ +	$ \begin{array}{c} Ph \\ Ph_3Sn \\ & N \\ Ph \\ & N \\ Ph \\ Ph \\ Ph \\ \end{array} $ (60)	848
	+	≥rt	N ₂ +	$\begin{bmatrix} Ph \\ N \\    \\ N \\ Ph \end{bmatrix} \xrightarrow{H_3O^*} \xrightarrow{N} \xrightarrow{Ph} (8)$	193
	+	ca. 40°	N ₂ +	$ \begin{array}{c} \mathbf{R} \\ \mathbf{N} \\ \mathbf{N} \\ \mathbf{R} \\ \mathbf$	173
N = N = N $N = N$ $N = N$ $Ph$	+	n	N ₂ +	Ph N N Ph Ph (84)	849
	+ dienophile	C ₆ H ₅ NO ₂ , 120°	rDA produc	cts ^e	167
	+ R ¹ R ²	_	N ₂ +	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	173
	+ Ph	120°, 20 h	N ₂ +	$ \begin{array}{c} Ph \\ N \\ I \\ HN \\ Ph  \end{array} $ (90)	850
	+ ^{R¹} R ²	112°	N ₂ +	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	850
	+ JOPr	112°, 55 h	N ₂ +	Ph N N Ph Ph	850
	+ X	75°, 0.5 h	N ₂ +	$ \begin{array}{c} Ph \\ N \\ HN \\ HN \\ Ph \\ Ph$	166
	+ [[	100°, 120 h	N ₂ +	HN + CN + CN + Ph + CN + C	166

TABLE VI-E.	N2 FROM 1,2,4,5-TETRAZINES (Continued)



TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)

TABLE VI-E.	N ₂ FROM	1,2,4,5-TETRAZINES (Continued)
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	Starting Material	Conditions	,2,4,J-1E1KAZ	Product(s) and Yield(s) (%)	Refs.
	+ N-TMS Ph-	112°	N ₂ +	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	854
$Ph \\ N \\ N \\ N \\ N \\ Ph$	+	rt	N ₂ +	Ph $N$ $Ph$ $Ph$ $Ph$ $(99)$	790, 855
$ \begin{array}{c} \mathbf{R}^{I} \\ \mathbf{N}^{II} \\ \mathbf{N}^{II} \\ \mathbf{R}^{I} \\ \mathbf{R}^{$	$+ \qquad R^2 \qquad R^4 \qquad R^4$	rt or heat	N ₂ +	$R^{1}$ $R^{2}$ $R^{4}$ $R^{3}$ $R^{4}$ $R^{3}$ $R^{4}$ $R^{4}$ $R^{3} = H \text{ or } Ph$ $R^{4} = H \text{ or } Me$ $R$	856
	+	40°	N ₂ +	N N N N N N N N N N N N N N N N N N N	857
Ŕ				R $R = CO_2Me, Pn, 3-U.U_6H_4, 3-MeOC_6H_4, -4-MeOC_6H_4, 4-MeC_6H_4, or 3-CF_3C_6H_4$	
		40-85°	N ₂ +	R (-) R R as above	857
$\begin{array}{c} R \\ R \\ R \\ N = N \\ R \\$	+ Ph N	112°	N ₂ +	R R (%) Ph 58 HN 2-pyridyl 63 R Ph 83	858
$R \rightarrow N \rightarrow R$	+ $R^2$ N $R^3$	115°	N2 +	$R^{i}$ $R^{i$	859, y) 860 2Me
$R \xrightarrow{N-N}_{R}$	+ Ph	112°	N ₂ +	$\begin{array}{c} \begin{array}{c} & & \\ & & \\ Ph & N \\ R & & \\ & & \\ & & \\ & & \\ Ph & R \end{array} \end{array} \xrightarrow{R} \begin{array}{c} (\%) \\ \hline & & \\ & 4 - MeC_6H_4 \\ \hline & & \\ & & \\ & & \\ & \\ Ph \end{array} \xrightarrow{R} \begin{array}{c} \\ & \\ & \\ & \\ & \\ & \\ \end{array}$	861
$Ph \\ N \\ N \\ N \\ Ph $	+ Ph N	'n	N ₂ +	$ \begin{array}{c}     Ph \\     HN \\     N \\     N \\     N \\     Ph \\     Ph \\     Ph \\   \end{array} $ (68)	862
		163°	N ₂ +	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 862 Yh
	+ Ph	80°	N ₂ +	MeCN + $Ph \xrightarrow{H} N$ (100)	862
$Ar \\ N \\ \parallel \\ N \\ Ar \\ Ar$	+ CO ₂ Me	Heat	N ₂ +	Ar Ar Ar Ar $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ Ph $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$ $CO_2Me$	863



 $N_2 + H_N + H_N$ 

rt or heat

 $\left( \right)$ 

+

	Sta	rting Material	Conditions			Pr	oduct(s) and Yi	ield(s) (%)	Refs.
	+		rt or heat	N ₂	+	CP (65) +		R Temp (%) CO ₂ Me rt 85 Ph heat 95	173
ĸ	+		-	N ₂	+	R	$\begin{pmatrix} R & R \\ N & C \\ N & P \end{pmatrix}$	(%) O2Me 87 h 93	867
	+		180-200°, (OC)	N ₂	÷		R =	(60-80) Ph or 2-pyridyl	550
Ph N N N N Ph	+		20°	N ₂	÷		$\sim N$ $\sim N$ $\sim N$ $\sim N$ $\sim N$ $\sim Ph$	(70)	868
	+ Me	$ \begin{array}{c} RO \\ N & & \\ OR \\ \langle CH_2 \rangle_{n} \end{array} $	π	N ₂	+	Ph N= N Ph	-(CH ₂ ) _n ( / ( NMe	90-98) R = Me or Et n = 1,2,or 3	805
	+ R´	R	160°	N ₂	+	Ph N N Ph	NH ₂	R (%) H 59 Me 78	869
	+	××××	160°	N ₂	+	Ph N N Ph	NH ₂ (26)	$+ \begin{array}{c} Ph \\ H \\ H \\ H \\ Ph \end{array} $ (23)	869
	+	$\downarrow_{N}$	"	N ₂	+			$+ \begin{array}{c} R \\ H \\ H \\ R \\ H \\ H \\ H \\ H \\ H \\ H \\$	869
	+	<b>X</b>	Heat	N ₂	+		Ph 2-thienyl	$\frac{R}{CO_2Me} = \frac{(\%)}{54}$ Ph 25	869
$\overset{R^{1}}{\underset{N}{\overset{N}{}}}_{R}^{N}$	+	R ² N	160°	N ₂	+	$R \\ R' \\ N \\ R' \\ R' \\ R' $	R ² NH ₂	R ¹ R ² (%)           Ph         H         69           2-thienyl         "         67           Ph         Me         35	869
Ph N II N Ph	+	×	_	N ₂	+		OH (90)		870
-	+		112°	N ₂	+	Ph N N N Ph	~~_отт	IP (72)	871



TABLE VI-E. N₂ FROM 1,2,4,5 TETRAZINES (Continued)

Starting M	laterial Conditi	ons	Product(s) and Yield	(s) (%)	Refs.
+ Ph	DMSO/CHCl ₃ ,	24° N ₂ +	Ph Pyr Ph Pyr	R         krel           OH         470           H         2.1           OMe         2.7           9-C=O         1.4	879
+ Ph	25°	N ₂ +	N Ph Ph Ph Pyr	$\begin{array}{c ccc} \underline{X} & \underline{Y} & 10^2  k  (M^{-1} s^{-1}) \\ \hline H & OMe & 729 \\ \hline & H & 26.7 \\ carbonyl & 1.2 \end{array}$	880. 881
+ ^{CO} 2Mo	e "	N ₂ +	NHCO ₂ Me	()	882
+	-20°	N ₂ +	$ \begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	178
+ OMe	r	N ₂ +	OMe Pyr N OMe Pyr	(—)	883
+ R ² R ¹	Solvent, 22°	N ₂ +	$ \begin{array}{c}                                     $		174
			$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	⁻¹ s ⁻¹ ) 260 <u>DMSO</u> 12.6 1.8 459 108 12.9 4.5	)
+	DMSO, 28.8°	N ₂ +	Pyr R Pyr R Pyr O	$\frac{k_{rel}}{2.4} = \frac{E_a}{8.2} = \frac{\Delta S^{\ddagger}}{-35.6}$ Me 0.2 11.8 -28.5	175
+ , , , , , , , , , , , , , , , , , , ,	״ "R ¹	N ₂ +	$\begin{array}{c c} & Pyr & \frac{R^{1}}{H} \\ & N & H \\ & Pyr & Cart \\ R^{2} & R^{1} & OH \\ & OMc \\ & H \end{array}$	$R^2$ $k_{rel}$ $E_a$ $\Delta S^{\ddagger}$ H         0.98         10.0         -30.8           OH         1             onyl         0.14         12.0         -28.0           H         35.7             e         ''         14.0         7.53         -33.9           OMc         0.35         9.01         -36.0	175
+		N ₂ +	Pyr N Pyr	$k_{rel} = E_a = \Delta S^{\ddagger}$ 0.28 10.4 -32.4	175
+ Cl cl cl cl cl cl	CI CI DDQ, 80°	N ₂ +	$\begin{array}{c} Cl & Ar \\ Cl & \downarrow \\ Cl & \downarrow \\ Cl & \downarrow \\ Cl & \downarrow \\ Cl & Ar \end{array} $	-)	770

TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)



TABLE VI-E. N ₂ FROM	1,2,4,5-TETRAZINES (Continued)
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70°

____

25°

110°



Conditions	Product(s) and Yield(s) (%)	Refs.
≥25°	$ \begin{array}{c}                                     $	179
rt-heat	N ₂ +  (93) + "	889, 893
50-55°	N ₂ + (98) + "	180
'n	N ₂ + (81) + "	180
n	N ₂ + (88) + "	180
	N ₂ + (83) + "	180
50-55°	N ₂ + (87) + "	180
	N ₂ + (78) + "	180
n	N ₂ + (88) + "	180

$$N_2$$
 +  $N_2$  (38) + " 894

$$N_2$$
 +   
 $V_2$  +   
 $V_1$  (70) + " 890,  
891  
Pyr

$$N_2 + N + N + N + O = O$$
 (95) 895  
Pyr

$$N_{2} + N_{yr} = (56)$$



n.

MeO

OMe

QAc

**X** 

=0

+



l CO₂Me

902

	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
CO ₂ Me	TMS			CO ₂ Me	
$N \sim N$ $N \sim N$ $N \sim N$ $CO_2Me$	R	Heat	N ₂ +	$\begin{array}{c c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$	903
002.00		100°	N ₂ +	$\frac{R}{Me} = \frac{(\%)}{69}$ Et 36 <i>n</i> -Pr 40 <i>n</i> -Bu 34 <i>n</i> -Am 31 <i>n</i> -hexyl 25 Bz 78	904
÷	TMS— <del>———</del> TMS	135°	N ₂ +	$CO_2Me$ $TMS$ $(2)$ $CO_2Me$ $TMS$	904
+	//TMS	65°	N ₂ +	$ \begin{array}{c} CO_2Me \\ N \\ I \\ CO_2Me \\ TMS \end{array} $ (57)	904
+	тмs	75°	N ₂ +	$MeO_2C$ $N$ $N$ $N$ $TMS$ $MeO_2C$ $(13)$	904
+	O CH ₂ R	85°	N ₂ +	$MeO_{2}C$ $N$ $N$ $H$ $MeO_{2}C$ $N$ $H$ $CH_{2}R$ $H$ $H$ $CO_{2}Me$ $CO_{2}Me$ $TMS$ $H$	904
+	R ¹ R ²	rt	N ₂ +	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	173
÷	I		N ₂ +	(98)	905
+	Ph	n	N ₂ +	$HN \xrightarrow{CO_2Me}_{Ph} (91)$	905
+	$\downarrow$	n	N ₂ +	$MeO_2C$ $N$ $HN$ $MeO_2C$ $(81)$	905

TABLE VI-E.	N ₂ FROM	1.2.4.5-TETRAZINES (Continued)
	1.71 1.000	1,2,1,5 TETTCES(COMMUC)

	Starting Material	Conditions		Product(s) and Yield(s) (%)	R
				$CO_2Me$ R (%)	
N N	R		N. (	$\mathbf{N}$ $\mathbf{R}$ $\mathbf{H}$ $-$	850
∕                                                                                                                                                                                                                                                                                                                                                     <td></td> <td>n</td> <td>N₂ +</td> <td>HN $Ph$ 100</td> <td>0.50</td>		n	N ₂ +	HN $Ph$ 100	0.50
CO ₂ Me				$CO_2Me$ 4-MeOC ₆ H ₄ 98	
2				4-O ₂ NC ₆ H ₄ 62	
				MeO ₂ C n-Bu (80°) 99	
	P Dh			N $\stackrel{R}{\longrightarrow}$ Ph $\stackrel{R}{\longrightarrow}$ Temp Time (%)	
+		rt or 101°	N ₂ +	Me rt 20 h 88	850
	11			Ph 101° 140 h "	
				MeO ₂ C CO ₂ Me	
+	≫∽∽он	25°	N ₂ +	(92)	900
				MeO ₂ C 0	
				CO ₂ Me	
	N			N (90)	006
+		rt	N ₂ +		900
				 CO ₂ Mc	
	<u> </u>		NT .	$\frac{n}{(\%)}$	906
+	$= \langle (CH_2)_n \rangle$		IN ₂ +	$(CH_2)_n$ 1 80	200
				3 96	
				MeO ₂ C	
				MeO ₂ C	
+	s		N ₂ +	N (77)	906
				IIN	
				MeO ₂ Ć	
				McOvC	
	DL			N S	
+	s, Ph	н	N ₂ +	$ \begin{array}{c} \stackrel{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}{\overset{\mathbf{N}}}}}}}}}}$	906
	$\checkmark$			Ph	
				McO ₂ C	
				MeO ₂ C S	
L		"	N2 +	N ()	906
т	,		2	HN Ph	
				MeO ₂ C	
	٨			$\bigwedge_{N'} \frac{N CO_2 Me}{\Lambda}$	
+		_	N ₂ +		867
				MeQ-C	
				CO ₂ Me	
				NMe2	
+	MNNMe,	rt	N ₂ +	1 N (71)	907
	····· 2				
				CO ₂ Me	
+	Ph N.	"	N ₂ +	$N \longrightarrow N \longrightarrow$	907
	$\sim$ $\sim$ NMe ₂		-	HN Ph HN Ph	
				CO ₂ Me CO ₂ Me	
				$CO_2Me$ R ¹ R ² X (%)	
				$\mathbf{R}^{1} \qquad \mathbf{M} \mathbf{e} \qquad \mathbf{M} \mathbf{e} \qquad \mathbf{OSiEt_{3}} \qquad 87$	
+	Ĭ	25°	N ₂ +	Et " N-morpholino 70	901
	R ² /			$\gamma$ K ⁻ —CH ₂ ) ₄ — <i>N</i> -pyrrolidinyl 85	
				" " <i>N</i> -morpholino 87	
				OMe "OMe 65	
				OBn "OTBDMS 33	
				OMe Ac OMe 71	

TABLE VI-E. N ₂ FROM	1.2.4.5-TETRAZ	ZINES (Continued)
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	Starting Material	Conditions		Produc	t(s) and Yield(s) (%)	Refs
$\begin{array}{c} \hline CO_2Me \\ N \\ N \\ N \\ CO_2Me \end{array}$	$R^1$ X $R^2$	25°	N ₂ +	$N = CO_2 Me$ $R^1$ $R^2$ $CO_2 Me$	R ¹ R ² X         (%)           Me         Me         OSiEt ₃ 87           Et         "         N-morpholino         70          (CH ₂ ) ₄ N-pyrrolidinyl         85           Ph         H         OTMS         92           OMe         "         OMe         65	902
+	TMS	— (CO)	N ₂ +	CO ₂ Me N N CO ₂ Me	OTBDMS " OBn 33 (82)	903
+	R ¹ CH ₂ R ²	65°	N ₂ +	$N \rightarrow R^{1}$ $N \rightarrow R^{2}$ $CO_{2}Me$	() $R^1, R^2 = H, Me;(CH_2)_3;$ or(CH_2)_4	908
+	N_OH	138°	N ₂ +	CO ₂ Me N N CO ₂ Me	(43) <b>R</b> ²	186
+	$R^2$ $N$ $NMe_2$ $R^1$ $N$	rt	N ₂ +	MeO ₂ C N ² N MeO ₂ C	$ \begin{array}{c} N \\ N \\ N \\ R^{1} \\ R^{1} \\ R^{1} \\ R^{2} \\ H \\ H \\ H \\ 66 \\ Me \\ 74 \\ " Me \\ 51 \end{array} $	321
+	MeO	'n	N ₂ +		$\frac{R}{Me} = \frac{(\%)}{29}$ $\frac{R}{Ph} = \frac{21}{21}$	909
+	R	·	N ₂ +		R (%) OEt 100 OAc —	850
+	₩ ^{OAc}	100°, 2h	N ₂ +	N CO ₂ Me CO ₂ Me	()	850
+	Ph V ^{OMe}	rt, ≤l h	N ₂ +	N N CO ₂ Me CO ₂ Me	(89)	850
+	OEt	rt, 15 h	N ₂ +	N N CO ₂ Me CO ₃ Me	(100)	850
+		_	N ₂ +	N N CO ₂ Me CO ₂ Me	(91)	850
+	MeO OMe	25°	N ₂ +		1e (94)	910

TABLE VI-E.       N2 FROM 1,2,4,5-TETRAZINES (Continued)							
	Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.			
CO ₂ Me N N II I N N CO ₂ Me	+ EtO VOEt	rt, ≤1 min.	$N_2 + N_1 + OEt $ $N_2 + OEt $ $N_1 + OEt $ $N_2 + OEt $ $N_1 + OEt $ $OO_2Me + OEE $ $OO_2M$	850			
	+ MeO HeO OMe	rt	$N_2$ + $N_2$ + $N_2$ + $N_2$ + $N_2$ OMe (95) CO ₂ Me OMe	911			
	+ *	80°	$N_{2} + N_{1} + CO_{2}Me + N_{1} + CO_{2}Me + N_{1} + CO_{2}Me + N_{1} + CO_{2}Me + CO$	911			
	MeO OMe Ac	60°, 21 h	$N_2$ + $N_2$ $N_2$ $N_1$ $N_2$ $N_1$ $N_2$ $Ac$ $(70)$	760			
		101°	$N_2$ + $N$ $OMe$ $N_2$ $Ac$ $CO_2Me$ $(71)$	902			
	McO McO MeO OMe	_	$N_2$ + $N_2$ $OMe$ $N_2$ $OMe$ $N_1$ $OMe$ OMe OMe OMe OMe OMe	912			
	R ₂ NCN	132°	$N_{2} + N_{1} = N_{1} = 0$	913			
	$R^{1}$ $R^{2}$	"	$N_{2} + \begin{matrix} CO_{2}Me \\ N \\ N_{2} \end{matrix} + \begin{matrix} CO_{2}Me \\ N \\ R^{1} \end{matrix} + \begin{matrix} R^{2} \\ OPh \\ $	(%) 31 41 914 3 (112°) 43			
+	R OEt	60-80°	$N_{2} + H_{1} = N + CO_{2}Me + K + K + K + K + K + K + K + K + K + $	871			
+		80°	$N_{2} + \begin{matrix} CO_{2}Me \\ N \\ H \\ N \\ CO_{2}Me \end{matrix} = \begin{matrix} Ar \\ Ph \\ 2-pyridyl \\ 2-quinolinyl \\ 2-quinolinyl \\ 2-(5-methoxyquinolinyl) \\ 2-(5-methoxy-4-nitroquinolinyl) \end{matrix}$	(%)         -           65         -           68         902           70         -           78         -           9         82			
·	$\mathbb{R}^{n^{p^{r}}}^{R^{2}}$		$N_{2} + N_{1} + N_{1} + N_{1} + N_{2} + R^{1} + R^{2} + M_{1} + R^{2} + M_{2} + M_{2$	%)           78           90         798           "           85           92           90			

TABLE VI-E. N ₂ FROM 1,2,4,5-TETRAZINES (Continued)								
		Starting Material	Conditions				Product(s) and Yield(s) (%)	Refs.
$CO_2Me$ N N N N $CO_2Me$	+	NMe ₂ R	rt	N	J2	+	$\begin{array}{ccc} CO_2Me & \underline{R} & (\%) \\ \hline Me & 81 \\ \hline H & Et & 79 \\ \hline N & NMe_2 & i-Pr & 76 \\ \hline CO_2Me & n-Pr & 56 \\ \hline Ph & 70 \\ \end{array}$	908
	+	NR2 	n	N	J2	+	$\begin{array}{ccc} CO_2Me & R, R \\ \hline Me, Me \\ (90-99) & -(CH_2)_5- \\ N \\ V \\ CO_2Me & -(CH_2)_2O(CH_2)_2- \end{array}$	915
	+		60-80°	N	N2	+	$ \begin{array}{cccc} CO_2Me \\ N & Ph \\ N & OEt 27 \\ N & SMe 64 \\ CO_2Me \end{array} $	916, 781
	+		80°	N	<b>1</b> 2	+	$MeO_2C$ $N$	916, 781
	+	$R^1$ $R^2$ $NH$ $SMe$	'n	N	N ₂	+	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	916, 795, 781
	+	N r OMe	80°		N ₂	+	$ \begin{array}{c} CO_2Me \\ N \\ H \\ N \\ CO_2Me \end{array} $ $ \begin{array}{c} CO_2Me \\ Ar = 4 \cdot Me_2NC_6H_4 \end{array} $	798
	+	S    N NMe2	132°	1	N ₂	+	$\begin{bmatrix} & CO_2Me \\ N & S \\ \parallel & \parallel \\ N & NR_2 \\ CO_2Me \end{bmatrix} \xrightarrow{MeO_2C} \xrightarrow{N}_{N-N} CO_2Me  (73)$	913
	+		80°	]	N ₂	+	$ \begin{array}{c} R \\ \hline R \\ \hline H \\ 23 \\ MeO_2C \\ \hline N \\ N-N \end{array} $ $ \begin{array}{c} R \\ \hline H \\ 29 \\ Et \\ 10 \\ \end{array} $	917
	+	$R^1$ $R^2$ $R^3$	rt	1	N ₂	+	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	790, 855
	+	$\bowtie$	80°	ľ	N ₂	+	$N = (64)$ $CO_2Me$	918
	+	excess		ľ	N ₂	+	$MeO_2C$ $N CO_2Me$ $(72)$	918

TABLE VI-E.       N2 FROM 1,2,4,5-TETRAZINES (Continued)								
		Starting Material	Conditions			Product(s) and Yield(s) (%)	Refs.	
$\begin{array}{c} CO_2Me \\ N \\ \parallel \\ N \\ CO_2Me \end{array}$	+	$\bowtie$	40°	N ₂	+	$R \xrightarrow{R} \xrightarrow{R} \xrightarrow{R} \xrightarrow{R} \xrightarrow{R} (12)$ $R = CO_2 Me$	918	
	+		rt	N ₂	+	$R = CO_2 Me$ (70)	919	
	+	Ph Ph Ph	rt; $10^5 k_2 = 3,400$	N ₂	+	$MeO_2C$ $Ph$ $Ph$ $Ph$ $Ph$ $MeO_2C$ $(-)$	173	
	+	Ph Ph Ph Ph	_	N ₂	+	$MeO_{2}C$ $Ph$ $Ph$ $Ph$ $Ph$ $N$ $N$ $Ph$ $Ph$ $CO_{2}Me$ $CO_{2}Me$ $CO_{2}Me$	841	
	+		rt	N ₂	+	$(02)^{N} (92)$	920	
	÷	Ph		N ₂	+	$\begin{array}{c} MeO_2C \\ N \\ i \\ N \\ NH \\ MeO_2C \end{array} Ph \qquad (67)$	921	
	+		rt	N ₂	+	$HN = CO_2Me $ (83) $CO_2Me$	905	
	+	Fe(CO) ₃	Ce(IV)	N ₂	+	$\begin{bmatrix} CO_2Me \\ N \\ N \\ N \\ CO_2Me \end{bmatrix} \longrightarrow \begin{bmatrix} N \\ N \\ MeO_2C \end{bmatrix} (-)$	922	
	+		п	N ₂	+	CO ₂ Me NH CO ₂ Me (ca. 55)	923	
	+			N ₂	÷	(ca.55)	923	
	+	A	-	N ₂	+	$ \begin{array}{c} CO_2Me \\ N \\ MeO_2C \end{array} $ (65)	924	
	+	Ph Ph	25°	N ₂	+	$MeO_{2C} \xrightarrow{Ph} Ph$ $N \xrightarrow{I}$ $HN \xrightarrow{I}$ $MeO_{2C}$ $(72)$	925	
	÷	Ph Ph	25°	N ₂	+	$MeO_2C \xrightarrow{Ph} Ph$ $N \xrightarrow{HN} (72)$ $MeO_2C$	92	
TABLE VI-E. N2 FROM 1,2,4,5-TETRAZINES (Continued)



	Starting Material	Conditions		Product(s) and Yield(s) (%)	Rcfs.
$\begin{array}{c} CO_2Me \\ N & N \\ H & H \\ N & N \\ CO_2Me \end{array} +$		101°	N ₂ +	$\begin{array}{c} CO_2 Me \\ N \\ N \\ CO_2 Me \end{array} (-)$	869
+	K K K K K K K K K K K K K K K K K K K	−75°-π	N ₂ +	(65)	929
+	Ne Me	-75° to -10°	N ₂ +	$MeO_2C$ $NH$ $N$ $CO_2Me$ $(-)$	929
+		c 100°	N ₂ +	$MeO_2C \qquad N \qquad N \qquad (8)$ $Me \qquad CO_2Me \qquad (8)$	929
+	OMe N Me	-75°-rt	N ₂ +	$MeO_2C \xrightarrow{N-N} CO_2Me $ (9)	929
÷	N Me	75°-rt	N ₂ +	( -)	929
+		n	N ₂ +	$ \begin{array}{c} CO_2Me \\ N \\ H \\ N \\ CO_2Me \end{array} $ (77)	871
+	0~0	·	N ₂ +	$ \begin{array}{c} CO_2Me \\ N \\ II \\ N \\ CO_2Me \end{array} $ (18)	871
+	L _o L	40°	N ₂ +	$ \begin{array}{c} CO_2Me \\ N \\ \parallel \\ N \\ CO_2Me \end{array} $ (83)	183
÷		-	N ₂ +	MeO ₂ C N N N (59)	928
+	$\langle s \rangle$	<b>.</b>	N ₂ +	(24)	183
+		Heat	N ₂ +	$\begin{array}{c} CO_{2}Me \\ N \\ N \\ N \\ N \\ CO_{2}Me \\ R^{2} \\ Cl \\ R^{2} \\ H \\ M \\ M$	184

 		TABLE VI-E. N ₂ FROM I	,2,4,5-TETRAZI	NES (Continued)	
 	Starting Material	Conditions		Product(s) and Yield(s) (%)	Refs.
+	$\sim$	40°	N ₂ +	$MeO_{2}C$ $N$ $HN$ $CO_{2}Me$ (57)	184
+	$\square$		N ₂ +	$ \begin{array}{c} CO_2Me \\ N \\ S \\ CO_2Me \end{array} $ (47)	928
+	N N Me	rt	N ₂ +	$N \rightarrow N - N Me CO_2 Me $ (90)	844
+	∑ N Me	40°	N2 +	$ \begin{array}{c} CO_2 Me \\ N \\ N \\ N \\ CO_2 Me \end{array} $ (36)	183, 184
+		п, МеОН	N ₂ +	$\begin{array}{c} MeO & CO_2Me \\ HN & & O \\ N & N & \\ CO_2Me \end{array} $ (35)	844
+	OMc	40°	N ₂ +	$MeO_2C$ $N$ $HN$ $CO_2Me$ $(15)$	184
÷	$\bigcirc$	r	N ₂ +	(71)	905
+	SO ₂ Ph	50°	N ₂ +	$MeO_2C$ $SO_2Ph$ (100)	930
+	CI N SO ₂ Ph		N ₂ +	MeO ₂ C N SO ₂ Ph (37)	930
+		20°	N ₂ +	CCl ₂ CO ₂ Me NH N N (55)	172
+	MeO ₂ C N N	25°	N ₂ +	(69)	901, 902
+		-	N ₂ +	$N = NHAc$ $N = NHAc$ $N = (73)$ $CO_{2}Me$	931
+	$\bigcirc$	п	N ₂ +	$CO_2Me$ N $CO_2Me$ OH (80) $CO_2Me$	871





Product(s) and Yield(s) (%) Refs. Starting Material Conditions R¹ R² Temp (%) SMe X . R¹ N-morpholino -(CH₂)₃-25° 97 N₂ + N-pyrrolidinyl " Heat 81 761 **P**² OTMS 150° 61 Ph Н 140° 78 N-morpholino 65° 65 ... Et Me 67 OMe OMe н 80° 85 100° 79 N-2-pyrrolidinyl H 130° 87 OEt ,, .. OAc 140° 86 Н ---(CH₂)₃-43° 19 (85) 762 1. rt  $N_2$ 2. HOAc

TABLE VI-E. N₂ FROM 1,2,4,5-TETRAZINES (Continued)

^a There is no analogous reaction with maleic anhydride.

^b The product was identified as the hydrate.

^c This reference gives k_{rel} = 4-methoxystyrene > cyclopentene > styrene > 4-nitrostyrene ca.= ethyl vinyl ether > α-methylstyrene > phenylacetylene > (*E*)-1-phenylpropene > cyclohexene.

 d  The order of reactivity is given as: X, R = 4-MeO, H > H, H >> 4-MeO, Me > 2-MeO, Me > H, Me. There is no reaction for X, R = 4-MeO, CO₂Me and H, Ph.

^e This is the proposed general structure for the unknown reported in the previous entry, ref. 860.

^f This reference gives  $k_{rel} = cyclopentene > ethylene > 4-methylstyrene > ethyl vinyl ether > styrene > 1-hexene > 4-nitrostyrene > <math>\alpha$ -methylstyrene > *E*-4-octene > cyclohexene > *E*-1-phenylpropene > methyl acrylate > phenylacetylene > (Z)-4-octene > acrylonitrile.

 g  This product decomposes upon chromatography.

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$ \underbrace{ \left( \begin{array}{c} N \\ I \\ N \\ N \\ CO_2 E_1 \end{array} \right) }^{CO_2 E_1} $	КОН, МеОН	$\left[ N_2 H^- \text{ or } N_2 H_2 \right]$ + CP ()	194
	Aqueous OH-	$\left[ \underbrace{ \left[ \underbrace{ \left[ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	195
		$\mathbf{R} = \mathbf{H}, \mathbf{CO}_2\mathbf{E}\mathbf{I}, \text{ or } \mathbf{CO}_2$	
	H ₃ O ⁺ , 100°	$\begin{bmatrix} N \\ I \\ N \\ CO_2Et \end{bmatrix} + CP \xrightarrow{N_2H_2} HN \\ HN \\ CO_2Et \end{bmatrix} (-)$	195
NH NH	Air, CDCl _{3,} rt	$\begin{bmatrix} N_2H_2 \end{bmatrix}$ + CP $\longrightarrow$ H ₂ O + N ₂ ()	196
	CDCl ₃ , norbornadiene scavenger k (45°) = $1.02 \times 10^{-4} \text{s}^{-1}$	$\begin{bmatrix} N_2H_2 \end{bmatrix}$ + CP (—)	196
$ \begin{array}{c} OH \\ \searrow N \\ \square \\ OH \end{array}  \begin{array}{c} H \\OH \end{array}  \begin{array}{c} H \\OH$	450-800°	$\begin{bmatrix} N_2 H_2 \end{bmatrix} + \begin{bmatrix} \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \end{bmatrix}  (-)$	940
NH HN I	≥ 50°	$\left[ N_{2}H_{2} \right]$ + $C_{14}H_{10}$ (—)	197
	k (45°) = 3.28 x $10^{-4}$ s ⁻¹	$\left[ N_{2}H_{2} \right]$ + $C_{14}H_{10}$ ()	196
N.Me N.Me	409°	Me M	198

TABLE VII-A. DIIMIDE AND DERIVATIVES

	I ABLE VII-A. DIIMIDE AN		Dafa
Starting Material	Conditions	Product(s) and Yield(s) (%)	Keis.
Me N Me	Heat	$Me \qquad Me \\ N \qquad Me \\ Me \qquad I \qquad I \qquad Me \qquad Me \qquad Me \qquad Me \qquad Me \qquad M$	198
	150°	$I + II + C_{10}H_{14}$ () I:II = 1.0:0.0	198
An-	250°	$Me^{N^{\prime}}$ + ()	199
	100°; t _{1/2} = 16 min	$ \underset{N}{\overset{N}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{\underset{Et}{Et}{t}{Et}{\underset{Et}{\\Et}{\underset{Et}{\\{Et}{\\{Et}{\\{Et}{Et}{Et}{\underset{Et}{Et}{Et}{Et}{Et}{Et}{Et}{Et}{Et}{Et}$	199
	rt, rapid H+	N    N + CP ()	199, 200
	$50^{\circ}$ ; $t_{1/2} = 5.5 \text{ h}$	$\begin{array}{c} N \\ \parallel \\ N \end{array} \qquad + \qquad (-)$	199, 200
ANA	50°; $t_{1/2} = 2.1 \text{ h}$	N + ()	199, 200
EtO ₂ C N	Vacuum, 150°-170°	$EtO_2C^{\prime}$	205
CO ₂ Et EtO ₂ C N	270° 112°, 7 h	$V'' = C_{10}H_{14}$ () EtO ₂ C' "DEAD"	204
	610°	$\begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & $	202
		$\left[\bigcirc \right] \rightarrow \bigcirc (40)$	
N N N N N N N N N N N N N N N N N N N	400°	$\begin{bmatrix} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & $	3) 202
N N N	75°	$\begin{bmatrix} O_2 \\ S_1 \\ N \end{bmatrix} + CP  \frac{-N_2}{-SO_2}  \begin{bmatrix} O \\ O \end{bmatrix}$	203
Ph o		<u>CP</u> (2 50)	

 $\begin{array}{c} Ph & & \\ O \stackrel{I}{\longrightarrow} & \\ Ph & \\ \end{array}$ 

Heat



Starting Material	Conditions	Product(s) and Yicld(s) (%)	Refs.
	Vacuum, 500°	$CP + \left[ \underbrace{ \begin{matrix} 0 \\ 1 \\ 0 \end{matrix} \right]_{N}}_{O} \xrightarrow{N_2} + \underbrace{ \begin{matrix} 0 \\ 1 \\ 0 \end{matrix} \right]_{O}}_{O} (88)$	202
	Pyrolysis	$MeO = \begin{pmatrix} 0 \\ MeO \end{pmatrix} (12) + CP + N_2$	942
RO NI	Vacuum, 500°	$ \begin{array}{c} OR \\ O \\ O$	943
	Vacuum, 450°	$R^{n} = 4-Cl; 4-MeO; 3,6-diCl; 4,5-diBr;4,5-diMe; 4,5-diMeO, or unsubstituted$	942
	-	$(71) + C_{14}H_{10} + N_2$	942
Ph = N $N$ $Ph = N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$	КОН/МеОН, 80°, 24 h	(64) + PTAD hydrol.	944
Ph - N + N + N + N + N + N + N + N + N + N	15 N KOH, 85° Dh	(61) + PTAD hydrol.	945
	Heat	$CI \qquad (-) \qquad + \qquad PTAD$	737
$\begin{array}{c} Cl \\ PhN \\ O \\ Cl \\ N \\ O \\ Cl \\ N \\ $	Heat	$ \begin{array}{c} CI \\ \leftarrow \\ CI \\ CI \end{array} + \begin{pmatrix} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	737
CN N-O NPh		CN () + PTAD	946

## TABLE VII-A. DIIMIDE AND DERIVATIVES (Continued)



N2H4, aqueous EtOH 85-100° 34 Furan

...

65° 99

30

LiAlH4, THF * * AcO --- OH



TABLE VII-A. DIIMIDE AND DERIVATIVES (Continued)



TABLE VII-A. DIIMIDE AND DERIVATIVES (Continued)

^a The relative rates of the rDA reaction are: rapid in acetonitrile, CHCl₃, CH₂Cl₂, slower in acetone, MeOH or pyridine.

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$\begin{array}{c c} O & & NEt_2 \\ \hline R^{1} & & Ph & + \\ N-N & + & \\ O & & R^2 \end{array}$	rt, exotherm	N ₂ O + $R^1$ $Ph$ () Et ₂ N $R^2$ $R^1$ , $R^2$ = Me or Ph	211
A N-O	Vacuum, 325°	N ₂ O + ()	959
DAN"	Vacuum, 400°	N ₂ O + ()	959
A.N.O	≥100°; k _{rel} = 1	N ₂ O + ()	140
N-O	≥100°; k _{rel} = 0.05	N ₂ O + ()	140
N ^N O	≥100°; k _{rel} = 0.026	N ₂ O + ()	140
An-o	≥100°; k _{rel} = 6	N ₂ O + ()	140
N.O	≥100°; k _{rel} = 150	N ₂ O + ()	140
N N N N N N N N N N N N N N N N N N N	≥35°; k _{rel} = 1.3 x 10 ⁶	N ₂ O + ()	140
V N N	≥175°; k _{rel} ≤2 x 10 ⁻⁴	N ₂ O + ()	140, 960
N, o	'n	N ₂ O + ()	140
N ^N -0	u	$N_2O + $ ()	140
OMe N + MA	UV, 350 nM (OC)	OMe O (45)	961
+		MeO 0 (35)	961
	Aqueous KOH H ₂ O ₂ , 30°	$\left[ \underbrace{\prod_{i=1}^{N} N^{i}}_{N} \right] \longrightarrow N_2 O + CP  (-)$	140
	Aqueous KOH H ₂ O ₂ , 50°	MTAD hydrolysate + N ₂ O + C ₁₄ H ₁₀ ()	140

TABLE VII-B. N₂O

[&]quot; The rate of loss of  $N_2$  is  $\ge 10^6$  times the rate of loss of  $N_2O$ .

	TABLE VII-C.	NO AND NS DERIVATIVES	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
HN K	70-100°	[HNO] + ()	962
R-N/	Heat	[RNO] + " H ≥65° ≥80 CHO 112° ≥95	214
$\mathbb{N}_{0}^{N}$	rt	$\begin{bmatrix} PhNO \end{bmatrix}$ + CP (—)	215. 216
$ \begin{array}{c}     Ph \\     \hline                               $		$\begin{bmatrix} ArNO \end{bmatrix} + \begin{pmatrix} Ph \\ O \\ Ph \end{pmatrix} \qquad (-) \qquad Ar = Ph \text{ or } 4\text{-}Me_2NC_9H_4$	218
$\mathbb{V}_{0}^{N}$	≥80°	[PhNO] + ()	215
Ph, N O' MeO ₂ C S	- 	$[PhNO]$ + $MeO_2C$ $S$ $(-)$	963
Ph, N O MeO ₂ C	[3,3]	$\begin{bmatrix} CO_2Me \\ S \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$	<del>96</del> 3
MeO O MeO O N R (0.5] _{init.}	35°, CHCl₃ ↔	$[ArNO] + \underbrace{MeO}_{O}_{O}_{O}_{O}_{O}_{O}_{O}_{O}_{O}_{$	964, 965
NC. 0 NK	$\frac{k (40^{\circ})}{400} = 6.8 \times 10^{-5} \mathrm{s}^{-1}$	[NCNO] +	966, 967
R N N	112°	$\begin{bmatrix} 0\\ R & N \end{bmatrix} + \begin{bmatrix} R & (\%)\\ CF_3 & \geq 30\\ H & -CO_2F_1 &$	968
	60°	$\begin{bmatrix} 0\\ R & 0\\ R & N \end{bmatrix} = \begin{bmatrix} \frac{R}{(\%)} \\ Me & - \\ Ph \geq 69 \end{bmatrix} + CP$	969
	80° or 111°	" + CP $R =$ various unsaturated alkyl or ether ^a	970
Me NL	80°	$\begin{bmatrix} 0\\ Me \end{bmatrix} (295) + \begin{bmatrix} 1\\ 1\\ 1\\ 1 \end{bmatrix}$	971, 972, 973
+ Ph Ph		$ \begin{array}{c}                                     $	219



	TABLE VII-C. NO	O AND NS DERIVATIVES (Continued)	
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
OBn OV OBn	Benzene, $60^{\circ}$ k = 4.3 x $10^{-4}$ s ⁻¹	$\begin{bmatrix} 0\\BnO N \end{bmatrix} (-) + (-)$	983
N OR	60°	$\begin{bmatrix} O \\ RO \end{bmatrix} (100) + " (-) R = Ph, CCl_3CH_2, t-Bu, or 2-TSCH_2CH_2$	982
AcO MeQ	$\underbrace{K_{eq}(80^\circ) = 9}_{\longleftarrow}$	Aco * ()	984
$MeO$ $N$ $CO_2Et$ $Ar = 4-CIC_6H_4$	80°	$\begin{bmatrix} Ar & & \\ & N & \\ EtO_2C & & N \end{bmatrix} (-) + the baine \\ R^1 R^2 R^3 R^4$	985
$R^{1} \qquad O$ $R^{2} \qquad N \qquad Ar$ $R^{3} \qquad K^{4} \qquad Ar = 4 - MeC_{6}H_{4}$	<b>-</b>	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	986
	5°	$\begin{bmatrix} Ph & Ts \\ + & S \\ & & O \end{bmatrix} \xrightarrow{80^{\circ}} \begin{bmatrix} Ph & Ph \\ + & S \\ & & N \\ & & & N \\ & & & Ts \end{bmatrix} (90)$	222, 223
	100°, CHCl ₃	$\begin{bmatrix} & & & & \\ & & & & \\ & & & & \\ & & & & $	987
N ^{SO2Ph} S O		$ \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{i=1}^{N} \frac{1}{10^{\circ}} \sum_{j=1}^{N} \frac{1}{10$	988, 989

^a This reference is a study of the intramolecular ene reaction.

 b  This intermediate was intercepted by reaction with  $Ph_{3}P.$ 

 c  This is the most stable adduct (decomposes at 150°).

^d This is the most labile adduct; at 15-35°,  $\Delta H^{\circ} = 3.9$  kcal/mole.

"Regioisomers are formed.

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ti ⁿ (low valent Ti)	Ti(O) _n + (35)	228
	Ti ⁿ	$Ti(O)_n + (34) + (32)$	228
	UV, 185 nm	³ O ₂ [‡] + ()	990
	Tïn	$Ti(O)_n$ + (42)	228
	n	$Ti(O)_n$ + $C_{14}H_{10}$ (48)	228
Ph O _O Ph + TCNE	UV	$^{3}O_{2}$ + $()$ $(CN)$ $(CN)$ $(CN)$ $(CN)$ $(Ph)$	991
	Heat, magnetic field	¹ $O_2$ (76) + R (%) H - Me -	229
Ph Ph Ph	Heat, magnetic field $\Delta S^{\ddagger} = \pm 3$	$^{1}O_{2}$ (290) ^{<i>a</i>} +	229
Ph	Heat, magnetic field $\Delta S^{\ddagger} = +10$	¹ O ₂ (23-32) ^{<i>b</i>} +	229, 230
	$80^{\circ}; t_{1/2} = 16 \text{ h}$	O ₂ + "	992
$\begin{array}{c} \overset{*}{} 0 \\ \overset{*}{} 0 \\ \overset{*}{} Ph \\ \overset{*}{} Ph \\ \overset{*}{} R^{3} \\ \overset{*}{} 0 \\ \overset{*}{} R^{1} \end{array}$	80°	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	993
	110°	$^{1}O_{2}$ $\frac{R}{Me} \frac{(\%)}{0}$ + $R$ Ph 22 +	994
Ph OMe Ph OMe Ph OMe	80°	$O_2$ + $Ph$ OMe Ph OMe Ph OMe Ph OMe	995
Ph Ph Ph Ph Ph Ph	Heat	$O_2$ + $(-)$ + light Ph Ph Ph rubrene	224, 225, 226

TABLE VII-D. DIOXYGEN

^a The yield of ¹O₂ is not affected by the magnetic field.

^b This reaction had the largest observed effect of the magnetic field on the yield of  $^{1}O_{2}$ .

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
Me-Si-Me Me-Si-Me	260°	$ \begin{bmatrix} Me_{Si} & Me \\ II \\ II \\ Me^{Si} & Me \end{bmatrix} + (-) $	232
+	u	$Me \sim Si^{-}Me$ $Me \sim Si^{-}Me$ (ca. 100) +	232
Me~Si-Me Me~Si-Me Ph	250°	$ \begin{bmatrix} Me_{Si}, Me \\ II \\ Me^{Si}, Me \end{bmatrix} + (-) $	996, 997
Me_Si-Me Me_Si-Me	360°	" + ()	232
	N ₂ flow, 480°	" <b>+</b> " (—)	996, 997
	UV, -263°	Me Me Me Si - Si - Me (-)	233
+	UV, rt	" (16) + $Me$ $Si-Me$ $Me$ $Me$	233
+	Heat	$Me_{Si} Me + (-)$	998
Me-Si-Me Me-Si-Me	500°	$ \begin{bmatrix} Me_{Si'}Me \\ II \\ He'^{Si}Me \end{bmatrix} + C_{14}H_{10}  () $	232
+ D	Heat	$ \begin{array}{c} Me \sim Si^{-}Me \\ Me \sim Si^{-}Me \\ \hline Me \\ \hline D \end{array} + C_{14}H_{10}  (-) $	998
$R \xrightarrow{Si} R$ $R \xrightarrow{Si} R$ $R = i - Pr$	500°	$ \begin{bmatrix} R_{Si}, R \\ II \\ R, Si_{R} \end{bmatrix} \xrightarrow{R} R^{Si} = R \xrightarrow{I} R \xrightarrow$	999
R = Ph	≥320°	" — polymer + $C_{14}H_{10}$ (—)	1000
$ \begin{array}{c} Me & CF_3 \\ Si_Me & + & He_2Si(OMe)_2 \\ O & CF_3 \end{array} $	65°	$Me_2Si(OMe)OSi(OMe)Me_2$ (76) + (72) CF ₃	235, 234
Me of of of of of of of of of of of of of	180°	Me O Me O O O O O O O O O O O O O O O O	235
	UV	" (13) + (87)	235
$Me_{Si} TMS \\ 0' \\ 0' \\ 0' \\ 0' \\ 0' \\ 0' \\ 0' \\ + Me_2Si(OMe)_2$	150°	$Me_2Si(OMe)OSi(OMe)(Me)SiMe_3 (29) + 0 (53)$	235

## TABLE VII-E. SILYLENES AND SIO ANALOGS

TABLE VII-F.	PHOSPHOROUS-CONTAINING DIENOPHILES



TABLE VII-F.	PHOSPHOROUS-CONTAINING DIENOPHILES (Continued)
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Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$EtO_{p_1} O = O$	110°	$\begin{bmatrix} 0 \\ EtO-P' \\ 0 \end{bmatrix} (-) + \begin{pmatrix} 0 \\ -N-Ph \\ 0 \end{pmatrix} (-)$	1009
$EtO_{p} S \rightarrow S \qquad + Q \qquad R$	120°	$\begin{bmatrix} EtO-P_{i}^{N} \\ O \end{bmatrix} (-) + O_{i}^{O} + C_{i}^{O} + R_{i}^{O} = alkyl$	1006
$ \begin{array}{c} R^{1}O \\ P \end{array} \\ \hline \\ P \end{array} \\ \hline \\ O \\ Ph \end{array} $	R ² OH, 110°; or UV, 254 nm	$R^{1}O = Et; R^{2} = Et, i-Pr, t-Bu, or 2-Bu*$ $R^{2}O = OH \qquad (mixture of diastergeomers)$ $R^{1} = 2-Bu*; R^{2} = Et (1:1 mixture of diastergeomers)$	236, 237
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ p \\ - \end{array} \\ S \\ P \\ P \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ P \\ P \\ \end{array} \\ \begin{array}{c} \end{array} \\ S \\ P \\ \end{array} $	Heat	$\begin{bmatrix} Ph & P & S \\ Ph & P & F \\ Ph & S & Ph \\ Ph & S & Ph \\ Ph & S & Ph \\ Ph & S \end{bmatrix} \xrightarrow{P} Ph \\ Ph & S \\ Ph$	239
$ \prod_{i=1}^{n} P^{N(TMS)_2} $	40°	P = P' + CP  (-) (TMS) ₂ N	1010

TABLE VII-G. SULFUR AND ITS OXIDES						
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.			
CH ₂ SOBu- <i>t</i> CH ₂ OH	NCS, 0°	$\begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ $	1011			
CH ₂ SOBu-r CHPhOH	NCS, 0°	SO ₂ + <u>Ph</u> ()	1011			
CH ₂ SOBu- <i>t</i> CHROH R = alkyl	SO ₂ Cl ₂ , 0°	$\begin{bmatrix} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ $	735			
$rac{1}{k^{1}}$	80°	$\begin{bmatrix} SO_2 + \left( \begin{array}{c} R^1 \\ R \end{array} \right) \\ R \end{bmatrix} \xrightarrow{300^\circ} \left( \begin{array}{c} SO_2 \\ R^1 \\ R^2 \end{array} \right) $ (-)	1011			
		$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
S ⁻⁰ ^b	80-100°	$\begin{bmatrix} SO_2 & + & & \\ & & & & \\ & & & & & \\ & & & &$	240			
$\bigcup_{OH}^{O} NH_2 + (imid)_2 SO$	rt	$\begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ $	) 1012			

TABLE VII-G. SULFUR AND ITS OXIDES



Starting Material	Conditions	Product(s) and Yield(s) (%).	Refs.
$R = Ph \text{ or } \alpha\text{-naphthyl}$	Chromatography, SiO ₂ or Al ₂ O ₃ , or In vacuo, 80°; or Wet organic solution	$\begin{bmatrix} S_2O \end{bmatrix}$ + $R$ ()	245
Ph S ⁰ Ph	Ir(DIPHOS) ⁺ Cl ⁻ ° <1 min	Ir(DIPHOS)*S ₂ O ⁺ Cl ⁻ + Ph (-) Ph	1016, 1017

TABLE VII-G. SULFUR AND ITS OXIDES (Continued)

^{*a*} For this reaction,  $t_{1/2} = 6$  h.

^b SeO₂ gives an analogous [4+2] kinetic control product, but it does not rearrange to the sclenone ( $\leq$ 180°).

^c The reagents AgFOD, Eu(FOD)₂, and TFA were also examined.



## TABLE VII-H. MISCELLANEOUS BIS-HETEROATOM DIENOPHILES

## References

- 1. Rickborn, B. Org. React., 1998, **52**, 1.
- 2. Maggini, M.; Prato, M.; Scorrano, G. Tetrahedron Lett., 1991, 32, 6957.
- 3. Griffiths, G. J.; Previdoli, F. E. J. Org. Chem., 1993, 58, 6129.
- Chapman, D. O.; McIntosh, C. L.; Pacansky, J. J. Am. Chem. Soc., 1973, 95, 614.
- Brown, R. F. C.; Choi, N.; Eastwood, F. W. Tetrahedron Lett., 1992, 33, 3787.
- Turchi, I. J., in *Oxazoles*; Turchi, I. J., Ed., Wiley, New York, 1986; pp. 1– 342.
- Grigg, R.; Hayes, R.; Jackson, J. L. J. Chem. Soc., Chem. Commun., 1969, 1167.
- Tagmazyan, K. T.; Mkrtchyan, R. S.; Babayan, A. T. Russ. J. Org. Chem. (Engl. Transl.), 1975, **10**, 1657.
- 9. Crank, G.; Khan, H. R. J. Heterocycl. Chem., 1985, 22, 1281.
- 10. Whitney, S. E.; Rickborn, B. J. Org. Chem., 1988, 53, 5595.
- 11. Whitney, S. E.; Winters, M.; Rickborn, B. J. Org. Chem., 1990, 55, 929.
- 12. Reddy, G. S.; Bhatt, M. V. Tetrahedron Lett., 1980, 3627.
- 13. Grigg, R.; Jackson, J. L. J. Chem. Soc. (C), 1970, 552.
- Ibata, T.; Nakano, S.; Nakawa, H.; Toyoda, J.; Isogami, Y. Bull. Chem. Soc. Jpn., 1986, **59**, 433.
- 15. Whitney, S. E.; Rickborn, B. unpub. UCSB; SEW Dissertation, 1991.
- Jacobi, P. A.; Blum, C. A.; DeSimone, R. W.; Udodong, U. E. S. J. Am. Chem. Soc., 1991, **113**, 5384.
- 17. Jacobi, P. A. Adv. Heterocycl. Nat'l. Prod. Synth., 1992, 2, 251.
- 18. Martin, J. C. J. Heterocycl. Chem., 1980, 17, 1111.
- 19. Marcelis, A. T. M.; van der Plas, H. C. Tetrahedron, 1989, 45, 2693.
- Marcelis, A. T. M.; van der Plas, H. C.; Harkema, S. J. Org. Chem., 1985, 50, 270.
- 21. Neunhoeffer, H.; Lehmann, B. Justus Liebigs Ann. Chem., 1975, 1113.
- Stolle, W. A. W.; Frissen, A. E.; Marcelis, A. T. M.; van der Plas, H. C. J. Org. Chem., 1992, **57**, 3000.
- 23. Davies, L. B.; Greenberg, S. G.; Sammes, P. G. J. Chem. Soc., Perkin Trans. 1, 1981, 1909.
- 24. Frissen, A. E.; Geurtsen, G.; Marcelis, A. T. M.; Van der Plas, H. C. Tetrahedron, 1990, **46**, 595.
- 25. Neunhoeffer, H.; Werner, G. Justus Liebigs Ann. Chem., 1972, 761, 39.
- 26. de Bie, D. A.; Ostrowicz, A.; Geurtsen, G.; van der Plas, H. C.

Tetrahedron, 1988, 44, 2977.

- 27. Guertsen, B.; de Bie, D. A.; van der Plas, H. C. Tetrahedron, 1989, **45**, 6519.
- 28. Neunhoeffer, H.; Freuhauf, H. W. Tetrahedron Lett., 1969, 3151.
- 29. Steigel, A.; Sauer, J. Tetrahedron Lett., 1970, 3357.
- 30. Neunhoeffer, H.; Freuhauf, H. W. Tetrahedron Lett., 1970, 3355.
- 31. Seitz, G.; John, R. Chem. Ber., 1989, 122, 1381.
- Boger, D. L.; Schumacher, J.; Mullican, M. D.; Patel, M.; Panek, J. S. J. Org. Chem., 1982, 47, 2673.
- Boger, D. L.; Menezes, R. F.; Honda, T. Angew. Chem., Int. Ed. Engl., 1993, 32, 273.
- 34. Figeys, H. P.; Mathy, A. Tetrahedron Lett., 1981, 22, 1393.
- 35. Boger, D. L.; Honda, T.; Dang, Q. J. Am. Chem. Soc., 1994, 116, 5619.
- 36. Boger, D. L.; Dang, Q. Tetrahedron, 1988, 44, 3379.
- 37. Boger, D. L. Chem. Rev., 1986, 86, 781.
- 38. Boger, D. L. Bull. Soc. Chim. Belg., 1990, 99, 599.
- 39. Boger, D. L.; Patel, M. Progress in Heterocyclic Chemistry, 1989, 1, 30.
- 40. Boger, D. L. in *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I. Eds., Vol. **5**, Pergamon, Oxford, 1991 pp. 451–512.
- 41. Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*, Academic Press, New York, 1987.
- Sidhu, S. S.; Kiefer, J. H.; Lifshitz, A.; Tamburu, C.; Walker, J. A.; Tsang, W. Int. J. Chem. Kinet., 1991, 23, 215.
- 43. Loudon, A. G.; Maccoll, A.; Wong, S. K. J. Chem. Soc. (B), 1970, 1733.
- 44. Braillon, B.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. Nouv. J. Chem., 1982, 6, 121.
- 45. Cherkasov, V. M.; Kapran, N. A.; Zavatskii, V. N. Chem. Heterocycl. Compd. (Engl. Transl.), 1969, **5**, 266.
- 46. Grieco, P. A.; Parker, D. T.; Fobare, W. F.; Ruckle, R. J. Am. Chem. Soc., 1987, **109**, 5859.
- 47. Grieco, P. A.; Bahsas, A. J. Org. Chem., 1987, 52, 5746.
- 48. Afarinkia, K.; Vinader, V.; Nelson, T. D.; Posner, G. H. Tetrahedron, 1992, **48**, 9111.
- 49. Heep, U. Tetrahedron, 1975, 31, 77.
- 50. Bhattacharjee, D.; Popp, F. D. J. Heterocycl. Chem., 1980, 17, 1035.
- 51. Paul, R.; Tchelitcheff, S. C. R. Seances Acad. Sci., Ser. C, 1947, **224**, 1722.
- 52. Salomon, R. G.; Burns, J. R.; Dominic, W. J. J. Org. Chem., 1976, **41**, 2918.

- 53. Funk, R. L.; Bolton, G. L. J. Am. Chem. Soc., 1988, **110**, 1290.
- 54. Funk, R. L.; Bolton, G. L. Tetrahedron Lett., 1988, 29, 1111.
- 55. Clemens, R. J.; Witzeman, J. S. J. Am. Chem. Soc., 1989, 111, 2186.
- 56. Wang, S. L. B.; Wulff, W. D. J. Am. Chem. Soc., 1990, **112**, 4550.
- 57. Linn, W. J. J. Org. Chem., 1964, 29, 3111.
- 58. Okazaki, R. Yuki Gosei Kagaku Kyokaishi, 1988, **46**, 1149; Chem. Abstr., 1989, **110**, 113837m.
- 59. Vallee, Y.; Ripoll, J. L.; Lafon, C.; Pfister-Guillouzo, G. Can. J. Chem., 1987, **65**, 290.
- 60. Baldwin, J. E.; Lopez, R. C. G. Tetrahedron, 1983, **39**, 1487.
- 61. Baldwin, J. E.; Lopez, R. C. G. J. Chem. Soc., Chem. Commun., 1982, 1029.
- 62. Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W.; Lochead, A. W.; McDougall, D. G. J. Chem. Soc., Chem. Commun., 1983, 423.
- Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W.; Lochead, A. W.; McDougall, D. G. J. Chem. Soc., Perkin Trans. 1, 1985, 1541.
- 64. Guemas, J. P.; Quiniou, H. Sulfur Lett., 1984, 2, 121.
- Freer, A. A.; Kirby, G. W.; Lewis, R. A. J. Chem. Soc., Chem. Commun., 1987, 718.
- 66. Fisher, N. M.; Lin, H. N. J. Org. Chem., 1973, 38, 3073.
- 67. King, J. F.; Lewars, E. G. J. Chem. Soc., Chem. Commun., 1972, 700.
- 68. King, J. F.; Lewars, E. G. Can. J. Chem., 1973, 51, 3044.
- 69. Hales, N. J.; Smith, D. J. H.; Swindler, M. E. J. Chem. Soc., Chem. Commun., 1976, 981.
- 70. Walsh, R. J. Chem. Soc., Chem. Commun., 1982, 1415.
- 71. Maier, G.; Mihm, G.; Reisenauer, H. P. Chem. Ber., 1984, 117, 2351.
- Reisenauer, H. P.; Mihm, G.; Maier, G. Angew. Chem., Int. Ed. Engl., 1982, 21, 854.
- 73. Jones, P. R.; Lee, M. E. J. Am. Chem. Soc., 1983, 105, 6725.
- 74. Quin, L. D.; Hughes, A. N.; Pete, B. Tetrahedron Lett., 1987, 28, 5783.
- 75. De Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F.; Fischer, J.; Mitschler, A. J. Chem. Soc., Chem. Commun., 1982, 1272.
- 76. Erker, G.; Hock, R.; Nolte, R. J. Am. Chem. Soc., 1988, 110, 624.
- 77. Ashe, A. J.; Diephouse, T. R.; El-Sheikh, M. Y. J. Am. Chem. Soc., 1982, **104**, 5693.
- Shusherina, N. P.; Dmitrieva, N. D.; Luk'yanets, E. A.; Levina, R. Y. Russ. Chem. Rev. (Engl. Transl.), 1967, 36, 175.
- 79. Shusherina, N. P. Russ. Chem. Rev. (Engl. Transl.), 1974, 43, 851.
- 80. Pirkle, W.; McKendry, L. Tetrahedron Lett., 1968, 5279.

- Chapman, O. L.; De La Cruz, D.; Roth, R.; Pacansky, J. J. Am. Chem. Soc., 1973, 95, 1337.
- Hedaya, E.; Miller, R. D.; McNeil, D. W.; D'Angelo, P. F.; Schissel, P. J. Am. Chem. Soc., 1969, **91**, 1875.
- 83. Pfaff, E.; Plieninger, H. Chem. Ber., 1982, 115, 1967.
- 84. Sakurai, H.; Eriyama, Y.; Hosomi, A.; Nakadaira, Y.; Kabuto, C. Chem. Lett., 1984, 595.
- 85. White, D.; Seyferth, D. J. Org. Chem., 1972, 37, 3545.
- Malpass, J. R.; Tweddle, N. J. J. Chem. Soc., Perkin Trans. 1, 1977, 874.
- 87. Boger, D. L.; Brotherton, C. E. Tetrahedron, 1986, 42, 2777.
- 88. Ginsburg, D. *Propellanes: Structure and Reactions*, Verlag Chemie, Weinheim, 1975.
- 89. Neidlein, R.; Kohl, M.; Kramer, W. Helv. Chim. Acta, 1989, 72, 1311.
- 90. Krantz, A.; Lin, C. J. Chem. Soc., Chem. Commun., 1971, 1287.
- 91. Akhtar, J. A.; Fray, G. I.; Yarrow, J. M. J. Chem. Soc. (C), 1968, 812.
- 92. Goldstein, M. J.; Thayer, G. L. J. Am. Chem. Soc., 1965, 87, 1925.
- 93. Goldstein, M. J.; Thayer, G. L. J. Am. Chem. Soc., 1965, 87, 1933.
- 94. Goldstein, M. J.; Thayer, G. L. J. Am. Chem. Soc., 1963, 85, 2673.
- 95. Nesterova, T. L.; Shusherina, N. P.; Shulishov, E. V. Russ. J. Org. Chem. (Engl. Transl.), 1985, 21, 387.
- 96. Adam, W.; Erden, I. Angew. Chem., Int. Ed. Engl., 1978, 17, 211.
- 97. Adam, W.; Erden, I. J. Am. Chem. Soc., 1979, 101, 5692.
- 98. Kopecky, K. R.; Lau, M. J. Org. Chem., 1978, 43, 525.
- Spangler, R. J.; Beckmann, B. G.; Kim, J. H. J. Org. Chem., 1977, 42, 2989.
- 100. Holland, L.; Jones, D. W. J. Chem. Soc. (C), 1970, 536.
- 101. Holland, L.; Jones, D. W. J. Chem. Soc. (C), 1970, 530.
- Tamura, Y.; Wada, A.; Sasho, M.; Kita, Y. Tetrahedron Lett., 1981, 22, 4283.
- 103. Tamura, Y.; Sasho, M.; Nakagawa, K.; Tsugoshi, T. Kita, Y. J. Org. Chem., 1984, 49, 473.
- 104. Tamura, Y.; Sasho, M.; Akai, S.; Wada, A.; Kita, Y. Tetrahedron, 1984, **40**, 4539.
- 105. May, C.; Moody, C. J. J. Chem. Soc., Chem. Commun., 1984, 926.
- 106. May, C.; Moody, C. J. J. Chem. Soc., Perkin Trans. 1, 1988, 247.
- 107. Steglich, W.; Buschmann, E.; Hollitzer, O. Angew. Chem., Int. Ed. Engl., 1974, **13**, 533.
- 108. Steglich, W.; Buschmann, E.; Gansen, G.; Wilschowitz, L. Synthesis,

1977, 252.

- 109. Freeman, J. P.; Grabiak, R. C. J. Org. Chem., 1976, 41, 3970.
- Buynak, J. D.; Chandrasakaran, R.; Barrett, A. G. M.; Attrill, R. P.; Betts, M. J. J. Org. Chem., 1985, **50**, 5362.
- 111. Shusherina, N. P.; Pilipenko, V. S. Russ. J. Org. Chem. (Engl. Transl.), 1978, **14**, 834.
- 112. Huisgen, R.; Gotthardt, H.; Grashey, R. Chem. Ber., 1968, 101, 536.
- 113. Ohta, M.; Kato, H. in *Nonbenzenoid Aromatics*, Snyder, J. P. Ed., Academic Press, New York, 1969, pp. 117–247.
- 114. Ollis, W. D.; Ramsden, C. A. Adv. Heterocycl. Chem., 1976, 19, 1.
- 115. Newton, C. G.; Ramsden, C. A. Tetrahedron, 1982, 38, 2965.
- 116. Gotthardt, H.; Huisgen, R. Chem. Ber., 1968, 101, 552.
- 117. Huisgen, R. Angew. Chem., Int. Ed. Engl., 1963, 2, 565.
- 118. Gotthardt, H.; Huisgen, R.; Schaefer, F. C. Tetrahedron Lett., 1964, 487.
- 119. Huisgen, R.; Gotthardt, H.; Bayer, H. O. Tetrahedron Lett., 1964, 481.
- 120. Huisgen, R.; Hauck, H.; Grashey, R.; Seidl, H. Chem. Ber., 1968, **101**, 2568.
- 121. Huisgen, R.; Hauck, H.; Grashey, R.; Seidl, H. Chem. Ber., 1969, **102**, 736.
- 122. Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. J. Am. Chem. Soc., 1973, **95**, 1945.
- 123. Gotthardt, H.; Huisgen, R. Chem. Ber., 1970, 103, 2625.
- 124. Huisgen, R.; Gotthardt, H.; Bayer, H. O. Chem. Ber., 1970, 103, 2368.
- 125. Huisgen, R.; Gotthardt, H. Chem. Ber., 1968, 101, 1059.
- 126. Knorr, R.; Huisgen, R.; Staudinger, G. K. Chem. Ber., 1970, 103, 2639.
- 127. Bayer, H. O.; Gotthardt, H.; Huisgen, R. Chem. Ber., 1970, 103, 2356.
- 128. Uchida, T.; Tsubokawa, S.; Harihara, K.; Matsumoto, K. J. Heterocycl. Chem., 1978, **15**, 1303.
- 129. Stille, J. K.; Harris, F. W.; Bedford, M. A. J. Heterocycl. Chem., 1966, **3**, 155.
- 130. Brunn, E.; Funke, E.; Gotthardt, H.; Huisgen, R. Chem. Ber., 1971, **104**, 1562.
- 131. Martin, H. D.; Hekman, M. Angew. Chem., Int. Ed. Engl., 1972, 11, 926.
- 132. Kato, H.; Nakazawa, S.; Kiyosawa, T.; Hirakawa, K. J. Chem. Soc., Perkin Trans. 1, 1976, 672.
- 133. Berson, J. A.; Olin, S. S. J. Am. Chem. Soc., 1969, 91, 777.
- 134. Rieber, N.; Alberts, J.; Lipsky, J. A.; Lemal, D. M. J. Am. Chem. Soc., 1969, **91**, 5668.
- 135. Allred, E. L.; Hinshaw, J. C. J. Chem. Soc., Chem. Commun., 1969,

1021.

- 136. Snyder, J. P.; Harpp, D. N. J. Am. Chem. Soc., 1976, 98, 7821.
- 137. Hersh, W. H.; Bergman, R. G. J. Am. Chem. Soc., 1983, 105, 5846.
- 138. Flynn, C. R.; Michl, J. J. Am. Chem. Soc., 1974, 96, 3280.
- 139. Liao, Y.; White, J. B. Tetrahedron Lett., 1990, 31, 5129.
- 140. Olsen, H.; Snyder, J. P. J. Am. Chem. Soc., 1977, 99, 1524.
- 141. Korat, M.; Ginsburg, D. Tetrahedron, 1973, 29, 2373.
- 142. Neunhoeffer, H.; Werner, G. Justus Liebigs Ann. Chem., 1973, 437.
- 143. Jojima, T.; Takeshiba, H.; Kinoto, T. Chem. Pharm. Bull., 1976, **24**, 1581.
- 144. White, E. H.; Zafiriou, O.; Kagi, H. H.; Hill, J. H. M. J. Am. Chem. Soc., 1964, **86**, 940.
- 145. Thalhammer, F.; Wallfahrer, U.; Sauer, J. Tetrahedron Lett., 1988, **29**, 3231.
- 146. Christl, M. Gazz. Chim. Ital., 1986, 116, 1.
- 147. Christl, M.; Lanzendorfer, U.; Peters, K.; Peters, E. M.; Von Schnoring, H. G. Tetrahedron Lett., 1983, 353.
- 148. Sugita, T.; Koyama, J.; Tagahara, K.; Suzuta, Y. Heterocycles, 1986, **24**, 29.
- 149. ltoh, T.; Ohsawa, A.; Okada, M.; Kaihoh, T.; Igeta, H. Chem. Pharm. Bull., 1985, **33**, 3050.
- 150. Seybold, G.; Jersak, U.; Gompper, R. Angew. Chem., Int. Ed. Engl., 1973, **12**, 847.
- 151. Adger, B. M.; Keating, M.; Rees, C. W.; Storr, R. C. J. Chem. Soc., Perkin Trans. 1, 1975, 41.
- 152. Neunhoeffer, H. in *The Chemistry of Heterocyclic Compounds*, Weissberger, A. and Taylor, E. C. Eds., Vol. **33**, J. Wiley & Sons, New York, 1978, p. 189.
- 153. Boger, D. L. Tetrahedron, 1983, 39, 2869.
- 154. Boger, D. L.; Panek, J. S.; Meier, M. M. J. Org. Chem., 1982, 47, 895.
- 155. Muller, K.; Sauer, J. Tetrahedron Lett., 1984, 25, 2541.
- 156. Balcar, J.; Chrisam, G.; Huber, F. X.; Sauer, J. Tetrahedron Lett., 1983, **24**, 1481.
- 157. Benson, S. C.; Li, J.; Snyder, J. K. J. Org. Chem., 1992, 57, 5285.
- 158. Sagi, M.; Amano, M.; Konno, S.; Yamanaka, H. Heterocycles, 1989, **29**, 2249.
- 159. Shorshnev, S. V.; Esipov, S. E.; Kuz'menko, V. V.; Gulevskaya, A. V.; Pozharskii, A. F.; Chernyshev, A. I.; Aleksandrov, G. G.; Doron'kin, V. N. Chem. Heterocycl. Compd. (Engl. Transl.), 1990, 26, 191.

- 160. Gockel, U.; Hartmannsgruber, U.; Steigel, A.; Sauer, J. Tetrahedron Lett., 1980, **21**, 599.
- 161. Taylor, E. C.; French, L. G. Tetrahedron Lett., 1986, 27, 1967.
- Wiley, P. F. in *The Chemistry of Heterocyclic Compounds*, Weissberger, A. and Taylor, E. C. Eds., Vol. **33**, J. Wiley & Sons, New York, 1978, p. 1075.
- 163. Kovalev, E. G.; Postovskii, I. Y.; Rusinov, L. G.; Shegal, I. L. Chem. Heterocycl. Compd. (Engl. Transl.), 1981, 17, 1063.
- 164. Geldard, J. F.; Lions, F. J. Org. Chem., 1965, **30**, 318.
- 165. Carboni, R. A. U. S. Patent 2,817,662; Chem. Abstr., 1958, 52, 7360.
- 166. Carboni, R. A.; Lindsey, R. V. J. Am. Chem. Soc., 1959, 81, 4342.
- 167. Sauer, J.; Lang, D. Angew. Chem., 1964, 76, 603.
- 168. Barlow, M. G.; Haszeldine, R. N.; Pickett, J. A. J. Chem. Soc., Perkin Trans. 1, 1978, 378.
- 169. Fuhlhuber, H. D.; Gousetis, C.; Troll, T.; Sauer, J. Tetrahedron Lett., 1978, 3903.
- 170. Paquette, L. A.; Short, M. R.; Kelley, J. F. J. Am. Chem. Soc., 1971, **93**, 7179.
- 171. Martin, H. D.; Hekman, M. Tetrahedron Lett., 1978, 1183.
- 172. Schuster, H.; Sauer, J. Tetrahedron Lett., 1983, 24, 4087.
- 173. Sauer, J.; Heinrichs, G. Tetrahedron Lett., 1966, 4979.
- 174. Paddon-Row, M. N.; Patney, H. K.; Warrener, R. N. J. Chem. Soc., Chem. Commun., 1978, 296.
- 175. Paddon-Row, M. N.; Patney, H. K.; Warrener, R. N. J. Org. Chem., 1979, **44**, 3908.
- 176. Skovianetz, W.; Kovats, E. S. Helv. Chim. Acta, 1971, 54, 1922.
- 177. Tobia, D.; Harrison, R.; Phillips, B.; White, T. L.; DiMare, M.; Rickborn, B. J. Org. Chem., 1993, 58, 6701.
- 178. Wilson, W. S.; Warrener, R. N. J. Chem. Soc., Chem. Commun., 1972, 211.
- 179. Warrener, R. N. J. Am. Chem. Soc., 1971, 93, 2346.
- 180. Moursounidis, J.; Wege, D. Aust. J. Chem., 1988, 41, 235.
- 181. Priestly, G. M.; Warrener, R. N. Tetrahedron Lett., 1972, 4295.
- 182. Ashe, A. J. III; Chan, W. T.; Smith, T. W. Tetrahedron Lett., 1978, 2537.
- 183. Seitz, G.; Kampchen, T. Chem.-Ztg., 1975, 99, 292.
- 184. Seitz, G.; Kampchen, T. Arch. Pharm. (Weinheim, Ger.), 1978, 311, 728.
- 185. Seitz, G.; Mohr, R. Chem.-Ztg., 1985, 109, 348.
- 186. Seitz, G.; Dhar, R.; Mohr, R. Chem.-Ztg., 1983, **107**, 172.
- 187. Haddadin, M. J.; Agha, B. J.; Salka, M. S. Tetrahedron Lett., 1984, 25,

2577.

- 188. Hunter, D.; Neilson, D. G. J. Chem. Soc., Chem. Commun., 1983, 1601.
- 189. Haddadin, M. J.; Firsan, S. J.; Nader, B. S. J. Org. Chem., 1979, **44**, 629.
- 190. Neunhoeffer, H.; Metz, H. Justus Liebigs Ann. Chem., 1983, 1476.
- 191. Imming, P.; Mohr, R.; Muller, E.; Overheu, W.; Seitz, G. Angew. Chem., Int. Ed. Engl., 1982, **21**, 284.
- 192. Seitz, G.; Mohr, R.; Overheu, W.; Allmann, R.; Nage, M. Angew. Chem. Int. Ed. Engl., 1984, **23**, 890.
- 193. Martin, J. C.; Bloch, D. R. J. Am. Chem. Soc., 1971, 93, 451.
- 194. Cohen, S. G.; Zand, R.; Steel, C. J. Am. Chem. Soc., 1961, 83, 2895.
- 195. Stille, J. K.; Anyos, T. J. Org. Chem., 1962, 27, 3352.
- 196. Wang, C.; Sheridan, R. S. Tetrahedron Lett., 1993, 34, 5673.
- 197. Corey, E. J.; Mock, W. L. J. Am. Chem. Soc., 1962, 84, 685.
- 198. Nelsen, S. F. J. Am. Chem. Soc., 1974, 96, 5669.
- 199. Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. Tetrahedron, 1986, **42**, 1769.
- 200. Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. J. Am. Chem. Soc., 1984, **106**, 3366.
- 201. Nelsen, S. F.; Scamehorn, R. G.; De Felippis, J.; Wang, Y. J. Org. Chem., 1993, **58**, 1657.
- 202. Forster, D. L.; Gilchrist, T. L.; Rees, C. W.; Stanton, E. J. Chem. Soc., Chem. Commun., 1971, 695.
- 203. Wittig, G.; Hoffmann, R. W. Chem. Ber., 1962, 95, 2718.
- 204. Diels, O.; Schmitt, S.; Witte, W. Chem. Ber., 1938, 71, 1186.
- 205. Harley-Mason, J.; Tims, J. C. W. Proc. Chem. Soc., 1963, 345.
- 206. Tada, M.; Oikawa, A. J. Chem. Soc., Perkin Trans. 1, 1979, 1858.
- 207. Tada, M.; Oikawa, A. J. Chem. Soc., Chem. Commun., 1978, 727.
- 208. Gassman, P. G.; Bailey, T. F.; Hoye, R. C. J. Org. Chem., 1980, **45**, 2923.
- 209. Askani, R.; Schneider, W. Chem. Ber., 1983, 116, 2355.
- 210. Gardlik, J. M.; Paquette, L. A. Tetrahedron Lett., 1979, 3597.
- 211. Freeman, J. P.; Grabiak, R. C. J. Org. Chem., 1976, 41, 1887.
- 212. Freeman, J. P.; Duthie, E. G.; O'Hare, M. J.; Hansen, J. F. J. Org. Chem., 1972, **37**, 2756.
- 213. Freeman, J. P.; Kassner, J. A.; Grabiak, R. C. J. Org. Chem., 1975, **40**, 3402.
- 214. Ensley, H. E.; Mohadevan, S. Tetrahedron Lett., 1989, 30, 3255.
- 215. Kresze, G.; Schulz, G. Tetrahedron, 1961, 12, 7.

- 216. Hamer, J.; Ahmad, M. in *1,4-Cycloaddition Reactions*, Hamer, J., Ed., Academic Press, New York, 1967, pp. 419– 452.
- 217. Griffin, C. E.; Hepfinger, N. F.; Shapiro, B. L. J. Am. Chem. Soc., 1963, **85**, 2683.
- 218. Mustafa, A. J. Chem. Soc., 1949, 256.
- 219. Kirby, G. W.; Sweeny, J. G. J. Chem. Soc., Perkin Trans. 1, 1981, 3250.
- 220. Keck, G. E.; Webb, R. R. II J. Org. Chem., 1982, 47, 1302.
- 221. Keck, G. E. Tetrahedron Lett., 1978, 4767.
- 222. Kresze, G.; Wucherpfennig, W. Angew. Chem. Int. Ed. Engl., 1967, 6, 149.
- 223. Kresze, G.; Wagner, U. Justus Liebigs Ann. Chem., 1972, 762, 93.
- 224. Moureu, C.; Dufraisse, C.; Dean, P. M. C. R. Hebd. Seances Acad. Sci., 1926, **182**, 1440.
- 225. Moureu, C.; Dufraisse, C.; Dean, P. M. C. R. Hebd. Seances Acad. Sci., 1926, **183**, 101.
- 226. Moureu, C.; Dufraisse, C.; Butler, C. L. C. R. Hebd. Seances Acad. Sci., 1926, **183**, 101.
- 227. Gollnick, K.; Schenck, G. O. in *1,4-Cycloaddition Reactions*, Hamer, J., Ed., Academic Press, New York, 1967, p. 255–344.
- 228. Riguera, R.; Quinoa, E.; Castedo, L. J. Chem. Soc., Chem. Commun., 1984, 1120.
- 229. Turro, N. J.; Chow, M. F. J. Am. Chem. Soc., 1979, 101, 3701.
- 230. Turro, N. J.; Chow, M. F. J. Am. Chem. Soc., 1980, 102, 1190.
- 231. Wasserman, H. H.; Druckrey, E. J. Am. Chem. Soc., 1968, 90, 2440.
- 232. Roark, D. N.; Peddle, G. J. D. J. Am. Chem. Soc., 1972, 94, 5837.
- 233. Rich, J. D.; Drahnek, T. J.; West, R.; Michl, J. J. Organomet. Chem., 1981, **212**, C-1.
- 234. Barton, T. J.; Wulff, W. D. J. Am. Chem. Soc., 1979, 101, 2735.
- 235. Hussman, G.; Wulff, W. D.; Barton, T. J. J. Am. Chem. Soc., 1983, **105**, 1263.
- 236. Quin, L. D.; Sadanani, N. D.; Wu, X. J. Am. Chem. Soc., 1989, **111**, 6852.
- 237. Bodalski, R.; Jankowski, S.; Glowka, M. L.; Filipiak, T.; Quin, L. D. J. Org. Chem., 1994, **59**, 5173.
- 238. Sigal, I.; Loew, L. J. Am. Chem. Soc., 1978, 100, 6394.
- 239. Kawashima, T.; Shimamura, M.; Inamoto, N. Nippon Kagaku Kaishi, 1987, 1231; Chem. Abstr., 1988, **109**, 6601n.
- 240. Heldeweg, R. F.; Hogeveen, H. J. Am. Chem. Soc., 1976, 98, 2341.
- 241. Weidinger, H.; Sturm, H. J. Justus Liebigs Ann. Chem., 1968, 716, 143.

- 242. Gilchrist, T. L.; Wood, J. E. J. Chem. Soc., Chem. Commun., 1992, 1460.
- 243. Gilchrist, T. L.; Wood, J. E. J. Chem. Soc., Perkin Trans. 1, 1992, 9.
- 244. Ando, W.; Sonobe, H.; Akasaka, T. Tetrahedron Lett., 1987, 28, 6653.
- 245. Dodson, R. M.; Srinivasan, V.; Sharma, K. S.; Sauers, R. F. J. Org. Chem., 1972, **37**, 2367.
- 246. Hersh, W. H.; Hollander, F. J.; Bergman, R. G. J. Am. Chem. Soc., 1983, **105**, 5834.
- 247. Sakurai, H.; Nakadaira, Y.; Tobita, H. Chem. Lett., 1982, 1855.
- 248. Bleckmann, P.; Minkwitz, R.; Neumann, W. P.; Schriewer, M. Tetrahedron Lett., 1984, **25**, 2467.
- 249. Erker, G.; Petrenz, R. J. Chem. Soc., Chem. Commun., 1989, 345.
- 250. Gokou, C. T.; Pradere, J. P.; Quiniou, H. J. Org. Chem., 1985, 50, 1545.
- 251. Pfeifer, K. P.; Himbert, G. Tetrahedron Lett., 1990, 31, 5725.
- 252. Himbert, G.; Pfeifer, K. P.; Finkele, C. E. Phosphorus, Sulfur Silicon Relat. Elem., 1991, **59**, 419.
- 253. Sasaki, T.; Kojima, A. Tetrahedron Lett., 1971, 4593.
- 254. Frissen, A. E.; Marcelis, A. T. M.; Geurtsen, B.; de Bie, D. A.; van der Plas, H. C. Recl. Trav. Chim. Pays-Bas, 1987, **106**, 547.
- 255. Hafner, K.; Haring, J.; Jakel, W. Angew. Chem., Int. Ed. Engl., 1970, **9**, 159.
- 256. McNeil, D. W.; Kent, M. E.; Hedaya, E.; D'Angelo, P. F.; Schissel, P. O. J. Am. Chem. Soc., 1971, 93, 3817.
- 257. Yamazaki, C.; Katayama, K.; Suzuki, K. J. Chem. Soc., Perkin Trans. 1, 1990, 3085.
- 258. Abe, N.; Nishiwaki, T.; Komoto, N. Chem. Lett., 1980, 223.
- 259. Abe, N.; Nishiwaki, T.; Komoto, N. Bull. Chem. Soc. Jpn., 1980, **53**, 3308.
- Medvedskaya, L. B.; Makarov, M. G.; Kondrat'eva, G. Y. Bull. Acad. Sci., USSR, Div. Chem. Sci. (Engl. Transl.), 1973, 1267.
- 261. Novak, J. J. K. Collect. Czech. Chem. Commun., 1975, 40, 2855.
- 262. Kondrat'eva, G. Y.; Medvedskaya, L. B.; Ivanova, Z. N.; Shmelev, L. V. Proc. Acad. Sci., USSR, Ser. Chem., (Engl. transl.), 1971, **200**, 862.
- 263. Kondrat'eva, G. Y.; Medvedskaya, L. B.; Ivanova, Z. N. Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1971, 20, 2148.
- 264. Medvedskaya, L. B.; Kondrat'eva, G. Y.; Bykanova, N. V. Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1979, **28**, 1490.
- 265. Kawada, K.; Kitagawa, O.; Kobayashi, Y. Chem. Pharm. Bull., 1985, **33**, 3670.

- 266. Graf, F.; Koenig, H. German Offen., 1971, 1,935,009; Chem. Abstr., 1971, **74**, 64201.
- 267. Boll, W.; Konig, H. J. Liebigs Ann. Chem., 1979, 1657.
- 268. Jaworski, T.; Mizerski, T.; Krokilowska, A. Pol. J. Chem., 1979, **53**, 1799.
- 269. Konig, H.; Graf, F.; Weberndorfer, V. Justus Liebigs Ann. Chem., 1981, 668.
- 270. Kondrat'eva, G. Y.; Medvedskaya, L. B.; Ivanova, Z. N.; Shmelev, L. V. Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.), 1971, 20, 1278.
- 271. Jaworski, T.; Mizerski, T. Rocz. Chem., 1976, 50, 359.
- 272. Gorgues, A.; Le Coq, A. Tetrahedron Lett., 1979, 4829.
- 273. Stepanova, S. V.; L'vova, S. D.; Filippova, T. M.; Gunar, V. I. Russ. J. Org. Chem. (Engl. Transl.), 1976, **12**, 1544.
- 274. Gotthardt, H.; Huisgen, R.; Bayer, H. O. J. Am. Chem. Soc., 1970, **92**, 4340.
- 275. Hutton, J.; Potts, B.; Southern, P. F. Synth. Commun., 1979, 9, 789.
- 276. Liotta, D.; Saindane, M.; Ott, W. Tetrahedron Lett., 1983, 24, 2473.
- 277. Song, Z. Z.; Ho, M. S.; Wong, H. N. C. J. Org. Chem., 1994, 59, 3917.
- 278. Ohlsen, S. R.; Turner, S. J. Chem. Soc. (C), 1971, 1632.
- 279. Ansell, M. F.; Caton, M. P. L.; North, P. C. Tetrahedron Lett., 1981, **22**, 1727.
- 280. Nakazawa, T.; Ishihara, M.; Jinguji, M.; Miyatake, R.; Sugihara, Y.; Murata, I. Tetrahedron Lett., 1994, **35**, 8421.
- 281. Potts, K. T.; Marshall, J. L. J. Chem. Soc., Chem. Commun., 1972, 1000.
- 282. Jacobi, P. A.; Walker, D. G.; Odeh, I. M. A. J. Org. Chem., 1981, **46**, 2065.
- 283. Jacobi, P. A.; Walker, D. G. J. Am. Chem. Soc., 1981, 103, 4611.
- 284. Jacobi, P. A.; Craig, T. A.; Walker, D. G.; Arrick, B. A.; Frechette, R. F. J. Am. Chem. Soc., 1984, **106**, 5585.
- 285. Jacobi, P. A.; Craig, T. J. Am. Chem. Soc., 1978, 100, 7748.
- 286. Jacobi, P. A.; Kaczmarek, C. S. R.; Udodong, U. E. Tetrahedron Lett., 1984, **25**, 4859.
- 287. Jacobi, P. A.; Kaczmarek, C. S. R.; Udodong, U. E. Tetrahedron, 1987, 43, 5475.
- 288. Jacobi, P. A.; Selnick, H. G. J. Am. Chem. Soc., 1984, 106, 3041.
- 289. Jacobi, P. A.; Selnick, H. G. J. Org. Chem., 1990, 55, 202.
- 290. Selnick, H. G.; Brookes, L. M. Tetrahedron Lett., 1989, 30, 6607.
- 291. Jacobi, P. A.; Touchette, K. M.; Selnick, H. G. J. Org. Chem., 1992, 57,

6305.

- 292. Jacobi, P. A.; Egbertson, M.; Frechette, R. F.; Miao, C. K.; Weiss, K. T. Tetrahedron, 1988, **44**, 3327.
- 293. Jacobi, P. A.; Weiss, K. T.; Egbertson, M. Heterocycles, 1984, 22, 281.
- 294. Jacobi, P. A.; Frechette, R. F. Tetrahedron Lett., 1987, 28, 2937.
- 295. Robert, A.; Ferrey, M.; LeMarechal, A. Tetrahedron, 1980, 36, 1571.
- 296. Neunhoeffer, H.; Werner, G. Justus Liebigs Ann. Chem., 1974, 1190.
- 297. Marcelis, A. T. M.; van der Plas, H. C. J. Org. Chem., 1986, 51, 67.
- 298. Charushin, V. N.; van der Plas, H. C. Tetrahedron Lett., 1982, 23, 3965.
- 299. van der Plas, H. C.; Marcelis, A. T. M.; van dem Ham, D. M. W.; Verhoeven, J. W. J. Org. Chem., 1986, **51**, 4070.
- 300. Charushin, V. N.; van der Plas, H. C. J. Org. Chem., 1983, 48, 2667.
- 301. de Bie, D. A.; Geurtsen, B.; van der Plas, H. C. J. Org. Chem., 1986, **51**, 71.
- 302. Charushin, V. N.; van der Plas, H. C. Recl. Trav. Chim. Pays-Bas, 1983, 102, 373.
- 303. Stolle, W. A. W.; Frissen, A. E.; Marcelis, A. T. M.; van der Plas, H. C.; Wang, Y.; Haming, L.; Stam, C. H. J. Org. Chem., 1991, 56, 2411.
- 304. Frissen, A. E.; Marcelis, A. T. M.; Melger, W. C.; van der Plas, H. C. Tetrahedron, 1989, **45**, 6891.
- 305. Frissen, A. E.; Marcelis, A. T. M.; van der Plas, H. C. Tetrahedron Lett., 1987, **28**, 1589.
- 306. Frissen, A. E.; Marcelis, A. T. M.; van der Plas, H. C. Tetrahedron, 1989, 45, 803.
- 307. Frissen, A. E.; Marcelis, A. T. M.; Geurtsen, B.; de Bie, D. A.; van der Plas, H. C. Tetrahedron, 1989, **45**, 5151.
- 308. Jojima, T.; Takeshiba, H.; Kinoto, T. Heterocycles, 1979, 12, 665.
- 309. Stolle, W. A. W.; Marcelis, A. T. M.; Koetsier, A.; van der Plas, H. C. Tetrahedron, 1989, **45**, 6511.
- 310. Frissen, A. E.; Marcelis, A. T. M.; Buurman, D. G.; Pollmann, C. A. M.; van der Plas, H. C. Tetrahedron, 1989, **45**, 5611.
- Gotou, H.; Kurata, K.; Tominaga, Y.; Matsuda, Y. J. Org. Chem., 1985, 50, 4028.
- 312. Stolle, W. A. W.; Marcelis, A. T. M.; Van der Plas, H. C. Tetrahedron, 1992, **48**, 1657.
- 313. Stolle, W. A. W.; Veurink, J. M.; Marcelis, A. T. M.; Van der Plas, H. C. Tetrahedron, 1992, **48**, 1643.
- 314. Haider, N.; van der Plas, H. C. Tetrahedron, 1990, **46**, 3641.
- 315. Biedrzycki, M.; de Bie, D. A.; van der Plas, H. C. Tetrahedron, 1989, 45,
6211.

- 316. Neunhoeffer, H.; Freuhauf, H. Justus Liebigs Ann. Chem., 1972, **758**, 125.
- 317. Boger, D. L.; Patel, M.; Mullican, M. D. Tetrahedron Lett., 1982, 4559.
- 318. Taylor, E. C.; Pont, J. L. J. Org. Chem., 1987, 52, 4287.
- 319. Sagi, M.; Wada, K.; Konno, S.; Yamanaka, H. Heterocycles, 1990, **30**, 1009.
- 320. Adler, J.; Bohnisch, V.; Neunhoeffer, H. Chem. Ber., 1978, 111, 240.
- 321. Neunhoeffer, H.; Bachmann, M. Chem. Ber., 1975, 108, 3877.
- 322. Taylor, E. C.; Fletcher, S. R.; Fitzjohn, S. J. Org. Chem., 1985, 50, 1010.
- 323. Boger, D. L.; Kochanny, M. J. J. Org. Chem., 1994, 59, 4950.
- 324. Kurata, K.; Matsuo, M.; Awaya, H.; Tominaga, Y.; Matsuda, Y.; Kobayashi, G. Chem. Pharm. Bull., 1975, **23**, 1629.
- 325. Boger, D. L.; Dang, Q. J. Org. Chem., 1992, 57, 1631.
- 326. Boger, D. L.; Honda, T.; Menezes, R. F.; Colletti, S. L.; Dang, Q.; Yang, W. J. Am. Chem. Soc., 1994, **116**, 82.
- 327. Boger, D. L.; Menezes, R. F.; Dang, Q. J. Org. Chem., 1992, 57, 4333.
- 328. Srinivasan, R.; Studebaker, J.; Brown, K. H. Tetrahedron Lett., 1979, 1955.
- 329. Carroll, W. A.; Grieco, P. A. J. Am. Chem. Soc., 1993, 115, 1164.
- 330. Benincori, T.; Brenna, E.; Sannicolo, F. J. Chem. Soc., Perkin Trans. 1, 1991, 2139.
- 331. Le Coz, L.; Veyrat-Martin, C.; Wartski, L.; Seyden-Penne, J.; Bois, C.; Philoche-Levisalles, M. J. Org. Chem., 1990, **55**, 4870.
- 332. Bouaiziz, Z.; Fillion, H.; Pinatel, H. J. Heterocycl. Chem., 1993, 30, 41.
- 333. Grieco, P. A.; Clark, J. D. J. Org. Chem., 1990, 55, 2271.
- 334. Lasne, M. C.; Ripoll, J. L.; Thuillier, A. J. Chem. Res., Synop., 1982, 214.
- 335. Mariano, P. S.; Huesmann, P. L.; Beamer, R. L.; Dunaway-Mariano, D. Tetrahedron, 1978, **34**, 2617.
- 336. Acheson, R. M.; Paglietti, G. J. Chem. Soc., Perkin Trans. 1, 1979, 591.
- 337. Eisch, J. J.; Noels, A. F. J. Org. Chem., 1976, 41, 1461.
- 338. Biehler, J. M.; Fleury, J. P. J. Heterocycl. Chem., 1971, 8, 431.
- 339. Shatzmiller, S.; Eschenmoser, A. Helv. Chim. Acta, 1973, 56, 2975.
- 340. Koch, T. H.; Higgins, R. H.; Schuster, H. F. Tetrahedron Lett., 1977, 431.
- 341. Erfanian-Abdoust, H.; Pindur, U. Heterocycles, 1989, 29, 1709.
- 342. Acheson, R. M.; Tasker, P. A. J. Chem. Soc. (C), 1967, 1542.
- 343. Gisby, G. P.; Royall, S. E.; Sammes, P. G. J. Chem. Soc., Chem. Commun., 1979, 501.

- 344. Gisby, G. P.; Royall, S. E.; Sammes, P. G. J. Chem. Soc., Perkin Trans. 1, 1982, 169.
- 345. Birkhofer, L.; Wahle, B. Chem. Ber., 1983, **116**, 3309.
- 346. Bauer, L.; Bell, C. L.; Wright, G. E. J. Heterocycl. Chem., 1966, 3, 393.
- 347. Davies, L. B.; Leci, O. A.; Sammes, P. G.; Watt, R. A. J. Chem. Soc., Perkin Trans. 1, 1978, 1293.
- 348. Porter, A. E. A.; Sammes, P. G. J. Chem. Soc., Chem. Commun., 1970, 1103.
- 349. Cobo, J.; Melguizo, M.; Sanchez, A.; Nogueras, M. Synlett, 1993, 297.
- 350. Davies, L. B.; Sammes, P. G.; Watt, R. A. J. Chem. Soc., Chem. Commun., 1977, 663.
- 351. Potts, K. T.; Sorm, M. J. Org. Chem., 1972, 37, 1422.
- 352. Cobo, J.; Garcia, C.; Melguizo, M.; Sanchez, A.; Nogueras, M. Tetrahedron, 1994, **50**, 10345.
- 353. Machin, P. J.; Porter, A. E. A.; Sammes, P. G. J. Chem. Soc., Perkin Trans. 1, 1973, 404.
- 354. Tutonda, M. G.; Vanderzande, D.; Hendrickx, M.; Hoornaert, G. Tetrahedron, 1990, **46**, 5715.
- 355. Tutonda, M. G.; Vanderzande, D.; Vekemans, J.; Toppet, S.; Hoornaert, G. Tetrahedron Lett., 1986, 27, 2509.
- 356. Tutonda, M. G.; Vandenberghe, S. M.; Van Aken, K. J.; Hoornaert, G. J. Org. Chem., 1992, 57, 2935.
- 357. Potts, K. T.; Marshall, J. L. J. Org. Chem., 1979, 44, 626.
- 358. Robert, A.; Ferrey, M.; Foucaud, A. Tetrahedron Lett., 1975, 1377.
- 359. Maier, M. E.; Schoeffling, B. Chem. Ber., 1989, 122, 1081.
- 360. Padwa, A.; Hertzog, D. L.; Nadler, W. R.; Osterhart, M. H.; Price, A. T. J. Org. Chem., 1994, **59**, 1418.
- 361. Doyle, M. P.; Pieters, R. J.; Tauton, J.; Pho, H. G.; Padwa, A.; Hertzog, D. L.; Precedo, L. J. Org. Chem., 1991, 56, 820.
- 362. Abe, N.; Takehiro, T. Bull. Chem. Soc. Jpn., 1988, 61, 1225.
- 363. McEwen, W. E.; Grossi, A. V.; MacDonald, R. J.; Stamegna, A. P. J. Org. Chem., 1980, **45**, 1301.
- 364. Singh, G.; Pande, P. S. Tetrahedron Lett., 1974, 2169.
- 365. Hamaguchi, M.; Ibata, T. Chem. Lett., 1975, 169.
- 366. Potts, K. T.; Chen, S. J. J. Org. Chem., 1977, 42, 1639.
- 367. Clerin, D.; Meyer, B.; Fleury, J. P.; Fritz, H. Tetrahedron, 1976, 32, 1055.
- 368. McEwen, W. E.; Mineo, I. C.; Shen, Y. H.; Han, G. Y. Tetrahedron Lett., 1968, 5157.
- 369. McEwen, W. E.; Kanitkar, K. B.; Hung, W. M. J. Am. Chem. Soc., 1971,

**93**, 4484.

- 370. McEwen, W. E.; Stott, P. E.; Zepp, C. M. J. Am. Chem. Soc., 1973, **95**, 8452.
- 371. McEwen, W. E.; Mineo, I. C.; Shen, Y. H. J. Am. Chem. Soc., 1971, **93**, 4479.
- 372. McEwen, W. E.; Cabello, C. C.; Calabro, M. A.; Ortega, A. M.; Stott, P. E.; Zapata, A. J.; Zepp, C. M.; Lubinkowski, J. J. J. Org. Chem., 1979, 44, 111.
- 373. Potts, K. T.; Husain, S. J. Org. Chem., 1972, 37, 2049.
- 374. Potts, K. T.; Husain, S. J. Org. Chem., 1970, 35, 3451.
- 375. Potts, K. T.; Husain, S.; Husain, S. J. Chem. Soc., Chem. Commun., 1970, 1360.
- 376. Ibata, T.; Hamaguchi, M.; Kiyohara, K. Chem. Lett., 1975, 21.
- 377. Potts, K. T.; Houghton, E.; Singh, U. P. J. Org. Chem., 1974, 39, 3627.
- 378. Potts, K. T.; McKeough, D. J. Am. Chem. Soc., 1973, 95, 2750.
- 379. Potts, K. T.; Chen, S. J.; Kane, J.; Marshall, J. L. J. Org. Chem., 1977, 42, 1633.
- 380. Potts, K. T.; Houghton, E.; Singh, U. P. J. Chem. Soc., Chem. Commun., 1969, 1129.
- 381. Potts, K. T.; Ehrlinger, R.; Nichols, W. M. J. Org. Chem., 1975, 40, 2596.
- 382. Baudy, M.; Robert, A.; Guimon, C. Tetrahedron, 1982, 38, 2129.
- 383. Matsukubo, H.; Kato, H. Bull. Soc. Chem. Jpn., 1976, 49, 3314.
- 384. Matsukubo, H.; Kato, H. J. Chem. Soc., Perkin Trans. 1, 1976, 2565.
- 385. Matsukubo, H.; Kato, H. J. Chem. Soc., Chem. Commun., 1975, 840.
- 386. Kappe, T.; Lube, W. Angew. Chem., Int. Ed. Engl., 1971, 10, 925.
- 387. Coburn, R. A.; Glennon, R. A. J. Heterocycl. Chem., 1973, 10, 487.
- 388. Potts, K. T.; Sorm, M. J. Org. Chem., 1971, 36, 8.
- 389. Potts, K. T.; Hsia, R. C. J. Org. Chem., 1973, 38, 3485.
- 390. Potts, K. T.; Husain, S. J. Org. Chem., 1971, 36, 3368.
- 391. Schiess, P.; Rutschmann, S.; Toan, V. V. Tetrahedron Lett., 1982, **23**, 3665.
- 392. Hardegger, B.; Shatzmiller, S. Helv. Chim. Acta, 1976, 59, 2765.
- 393. Lidor, R.; Shatzmiller, S. J. Am. Chem. Soc., 1981, **103**, 5916.
- 394. Groth, U.; Schoellkopf, U.; Tiller, T. Tetrahedron, 1991, 47, 2835.
- 395. Sakamoto, T.; Kondo, Y.; Yamanaka, H. Tetrahedron Lett., 1992, **33**, 6845.
- 396. Baxter, G. J.; Brown, R. F. C. Aust. J. Chem., 1978, 31, 327.
- 397. Toussaint, W. J. U. S. Pat. 2,387,356 (1942), as quoted in: Needleman,
  S. B.; Chang Kuo, M. C. Chem. Rev., 1962, 62, 405.

- 398. Giordano, C.; Belli, A.; Abis, L. Tetrahedron Lett., 1979, 1537.
- 399. Schiess, P.; Chia, H. L. Helv. Chim. Acta, 1970, 53, 485.
- 400. Schiess, P.; Radimerski, P. Helv. Chim. Acta, 1974, 57, 2583.
- 401. Riediker, M.; Graf, W. Chimia, 1980, **34**, 461.
- 402. Faragher, R.; Gilchrist, T. L. J. Chem. Soc., Perkin Trans. 1, 1979, 258.
- 403. Faragher, R.; Gilchrist, T. L. J. Chem. Soc., Chem. Commun., 1977, 252.
- 404. Gygax, P.; Das-Gupta, T. K.; Eschenmoser, A. Helv. Chim. Acta, 1972, **55**, 2205.
- 405. Reichardt, C.; Yun, K. Tetrahedron Lett., 1982, 23, 3163.
- 406. Johansson, E.; Skramstad, J. J. Org. Chem., 1981, 46, 3752.
- 407. Diment, J. A.; Ritchie, E.; Taylor, W. C. Aust. J. Chem., 1969, 22, 1721.
- 408. Sandermann, W.; Casten, R. Tetrahedron Lett., 1963, 1267.
- 409. Sandermann, W.; Simatupang, M. Chem. Ber., 1964, 97, 588.
- 410. Sandermann, W.; Simatupang, M. Tetrahedron Lett., 1963, 1269.
- 411. Matsugo, S.; Takamizawa, A. Synthesis, 1983, 852.
- 412. Jager, G.; Wenzelburger, J. Justus Liebigs Ann. Chem., 1976, 1689.
- 413. Sato, M.; Ogasawa, H.; Yoshizumi, E.; Kato, T. Chem. Pharm. Bull., 1983, **31**, 1902.
- 414. Clemens, R. J.; Hyatt, J. A. J. Org. Chem., 1985, 50, 2431.
- 415. Hyatt, J. A.; Feldman, P. L.; Clemens, R. J. J. Org. Chem., 1984, **49**, 5105.
- 416. Sato, M.; Kanuma, N. Kato, J. Chem. Pharm. Bull., 1982, **30**, 1315.
- 417. Chen, C.; Quinn, E. K.; Olmstead, M. M.; Kurth, M. J. J. Org. Chem., 1993, **58**, 5011.
- 418. Wentrup, C.; Gross, G.; Berstermann, H.; Lovencak, P. J. Org. Chem., 1985, **50**, 2877.
- 419. Cuong, N. G.; Fournier, F.; Basselier, J. Bull. Soc. Chim. Fr., 1974, 2117.
- 420. Cuong, N. G.; Fournier, F.; Basselier, J. C. R. Seances Acad. Sci., Ser. C, 1970, **271**, 1626.
- 421. Fournier, F.; Altenburger-Combrisson, S.; Nguyen, K. C.; Basselier, J. J. Tetrahedron, 1979, **35**, 2633.
- 422. Burger, K.; Penninger, S.; Greisel, M.; Daltrozzo, E. J. Fluorine Chem., 1980, **15**, 1.
- 423. Hart, H.; Chen, S.; Lee, S. J. Org. Chem., 1980, 45, 2096.
- 424. Gilchrist, T. L.; Harris, C. J.; Peek, M. E.; Rees, C. W. J. Chem. Soc., Chem. Commun., 1975, 962.
- 425. Shalom, E.; Zenou, J.; Shatzmiller, S. J. Org. Chem., 1977, 42, 4213.

- 426. Bock, H.; Mohmand, S.; Hirabayashi, T.; Semkow, A. J. Am. Chem. Soc., 1982, **104**, 312.
- 427. Bock, H.; Mohmand, S.; Hirabayashi, T.; Semkow, A. Chem. Ber., 1982, **115**, 1339.
- 428. Moriyama, S.; Karakasa, T.; Motoki, S. Bull. Chem. Soc. Jpn., 1990, **63**, 2540.
- 429. Schonberg, A.; Konig, B. Chem. Ber., 1968, 101, 725.
- 430. Arnaud, R.; Pelloux-Leon, N.; Ripoll, J. L.; Vallee, Y. Tetrahedron Lett., 1994, **35**, 8389.
- 431. Lakshmikantham, M. V.; Levinson, M.; Menachery, M.; Cava, M. P. J. Org. Chem., 1986, **51**, 411.
- 432. Tamaru, Y.; Satomi, H.; Kitao, O.; Yoshida, Z. Tetrahedron Lett., 1984, **25**, 2561.
- 433. Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. J. Chem. Soc., Chem. Commun., 1984, 922.
- 434. Pfister-Guillouzo, G.; Gracian, F.; Senio, A.; Bourdon, F.; Vallee, Y.; Ripoll, J. L. J. Am. Chem. Soc., 1993, **115**, 324.
- 435. Friedrich, K.; Zamkanei, M. Tetrahedron Lett., 1977, 2139.
- 436. Kirby, G. W.; Lochead, A. W. J. Chem. Soc., Chem. Commun., 1983, 1325.
- 437. Kirby, G. W.; McGregor, W. M. J. Chem. Soc., Perkin Trans. 1, 1990, 3175.
- 438. Lee, L. F.; Dolson, M. G.; Howe, R. K.; Stults, B. R. J. Org. Chem., 1985, **50**, 3216.
- 439. Kirby, G. W.; Mahajan, M. P.; Rahman, M. S. J. Chem. Soc., Perkin Trans. 1, 1991, 2033.
- 440. Choi, S. S. M.; Kirby, G. W.; Mahajan, M. P. J. Chem. Soc., Chem. Commun., 1990, 138.
- 441. Elsasser, A.; Sundermeyer, W. Chem. Ber., 1985, **118**, 4553.
- 442. Fritz, H.; Sundermeyer, W. Chem. Ber., 1989, 122, 1757.
- 443. Maletzo, C.; Sundermeyer, W. Chem. Ber., 1991, **124**, 1311.
- 444. Zwanenburg, B.; Thijs, L.; Strating, J. Tetrahedron Lett., 1969, 4461.
- 445. King, J. F.; Enanoza, R. M.; Lewars, E. G. Can. J. Chem., 1974, **52**, 2409.
- 446. Maier, G.; Mihm, G.; Reisenauer, H. P.; Littman, D. Chem. Ber., 1984, **117**, 2369.
- 447. Maier, G.; Mihm, G.; Reisenauer, H. P. Angew. Chem., Int. Ed. Engl., 1981, **20**, 597.
- 448. Barton, T. J.; Burns, S. A.; Burns, G. T. Organometallics, 1982, 1, 210.
- 449. Barton, T. J.; Kline, E. A. J. Organomet. Chem., 1972, 42, C-21.

- 450. Jones, P. R.; Lee, M. E. J. Organomet. Chem., 1984, 271, 299.
- 451. Burns, S. A.; Burns, G. T.; Barton, T. J. J. Am. Chem. Soc., 1982, **104**, 6140.
- 452. Charrier, C.; Bonnard, H.; de Lauzon, G.; Mathey, F. J. Am. Chem. Soc., 1983, **105**, 6871.
- 453. Alcaraz, J. M.; Mathey, F. Tetrahedron Lett., 1984, 25, 4659.
- 454. Binnewies, M.; Grobe, J.; Van, D. L. Z. Naturforsch., B: Anorg. Chem., Org. Chem., 1985, **40B**, 927.
- 455. Yeung Lam Ko, Y. Y. C.; Carrie, R.; Toupet, L.; De Sarlo, F. Bull. Soc. Chim. Fr., 1986, 115.
- 456. Deschamps, E.; Mathey, F. J. Chem. Soc., Chem. Commun., 1984, 1214.
- 457. Haas, A.; Limberg, C.; Spehr, M. Chem. Ber., 1991, **124**, 423.
- 458. Kirby, G. W.; Trethewey, A. N. J. Chem. Soc., Perkin Trans. 1, 1988, 1913.
- 459. Kirby, G. W.; Tretheway, A. N. J. Chem. Soc., Chem. Commun., 1986, 1152.
- 460. Ashe, A. J. III Tetrahedron Lett., 1976, 415.
- 461. Lin, C. Y.; Krantz, A. J. Chem. Soc., Chem. Commun., 1972, 1111.
- 462. Rosenblum, M.; Gatsonis, C. J. Am. Chem. Soc., 1967, 89, 5074.
- 463. Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. J. Am. Chem. Soc., 1972, **94**, 1239.
- 464. Meier, H.; Molz, T.; Merkle, U.; Echter, T.; Lorch, M. Justus Liebigs Ann. Chem., 1982, 914.
- 465. Echter, T.; Meier, H. Chem. Ber., 1985, **118**, 182.
- 466. Markl, G.; Fuchs, R. Tetrahedron Lett., 1972, 4695.
- 467. Seyferth, D.; White, D. L. J. Organomet. Chem., 1972, 34, 119.
- 468. Effenberger, F.; Ziegler, T. Chem. Ber., 1987, **120**, 1339.
- 469. Ziegler, T.; Layh, M.; Effenberger, F. Chem. Ber., 1987, 120, 1347.
- 470. Seyferth, D.; Blank, D. R.; Evnin, A. J. Am. Chem. Soc., 1967, 89, 4793.
- 471. Ishikawa, M.; Sakamoto, H.; Kanetani, F.; Minato, A. Organometallics, 1989, **8**, 2767
- 472. Sakurai, H.; Nakadaira, Y. Hosomi, A.; Eriyama, Y. Chem. Lett., 1982, 1971.
- 473. Kyba, E. P.; Rines, S. P.; Owens, P. W.; Chou, S. P. Tetrahedron Lett., 1981, **22**, 1875.
- 474. Evnin, A.; Seyferth, D. J. Am. Chem. Soc., 1967, 89, 952.
- 475. Swarbrick, T. M.; Marko. I. E.; Kennard, L. Tetrahedron Lett., 1991, **32**, 2549.

- 476. Barton, J. W.; Lee, D. V.; Shepherd, M. K. J. Chem. Soc., Perkin Trans. 1, 1985, 1407.
- 477. Anatassiou, A. G.; Reichmanis, E.; Elliott, R. L. Tetrahedron Lett., 1973, 3805.
- 478. Anastassiou, A. G.; Reichmanis, E; Girgenti, S. J.; Schaefer-Ridder, M. J. Org. Chem., 1978, **43**, 315.
- 479. Battiste, M. A.; Visnick, M. Tetrahedron Lett., 1978, 4771.
- 480. Sasaki, T.; Manabe, T.; Nishida, S. J. Org. Chem., 1980, 45, 476.
- 481. Fieser, L. F.; Haddadin, M. S. J. Am. Chem. Soc., 1964, 86, 2081.
- 482. Fieser. L. F.; Haddadin, M. S. Can. J. Chem., 1965, 43, 1599.
- 483. Haddadin, M. J.; Agha, B. J.; Tabri, R. F. J. Org. Chem., 1979, 44, 494.
- 484. Anastassiou, A. G.; Libsch, S. S.; Griffith, R. C. Tetrahedron Lett., 1973, 3103.
- 485. Anastassiou, A. G.; Badri, R. Tetrahedron Lett., 1977, 4465.
- 486. Zimmerman, H. E.; Grunewald, G. L.; Paufler, R. M.; Sherwin, M. A. J. Am. Chem. Soc., 1969, **91**, 2330.
- 487. Becker, Y.; Bronstein, S.; Eisenstadt, A.; Shvo, Y. J. Org. Chem., 1976, 41, 2496.
- 488. Shusherina, N. P.; Nesterova, T. L.; Polyakova, O. V. Russ. J. Org. Chem. (Engl. Transl.), 1980, **16**, 1111.
- 489. Shimo, T.; Hiroyuki, Y.; Takaaki, S.; Kenichi, S. Nippon Kagaku Kaishi, 1988, 1984; Chem. Abstr. 1989, **111**, 23339s.
- 490. Diels, O.; Alder, K.; Muller, K. Justus Liebigs Ann. Chem., 1931, **490**, 257.
- 491. Shusherina, N. P.; Vashakidze, E. Y.; Levina, R. Y. Russ. J. Org. Chem. (Engl. Transl.), 1968, **4**, 1242.
- 492. Darms, R.; Threlfall, T.; Pesaro, M.; Eschenmoser, A. Helv. Chim. Acta, 1963, **46**, 2893.
- 493. McCaskie, J. E.; Nelson, T. R.; Dittmer, D. C. J. Org. Chem., 1973, **38**, 3048.
- 494. Arora, P.; Mackay, D. J. Chem. Soc., Chem. Commun., 1969, 677.
- 495. Boger, D. L.; Brotherton, C. E. J. Am. Chem. Soc., 1986, **108**, 6695.
- 496. Murakami, N.; Tanase, T.; Nagai, S.; Sato, Y.; Ueda, T.; Sakakibara, J.; Ando, H.; Hotta, Y.; Takeya, K. Chem. Pharm. Bull., 1991, **39**, 1962.
- 497. Hakimi, M. G. Moscow Univ. Chem. Bull. (Engl. Transl.), 1975, **30** (5), 93.
- 498. Panizzi, L.; Nicoletti, R. Ann. Chimica, 1961, **51**, 1256.
- 499. Nicoletti, R. Ann. Chimica, 1961, 51, 1260.
- 500. Lur'e, M. Y.; Trubnikov, I. S.; Shusherina, N. P.; Levina, R. Y. J. Gen.

Chem. USSR (Engl. Transl.), 1958, 28, 1410.

- 501. Novitskii, K. Y.; Yur'ev, Y. K.; Zhingareva, V. N. J. Gen. Chem. USSR (Engl. Transl.), 1962, **32**, 3245.
- 502. Dieter, R. K.; Balke, W. H.; Fishpaugh, J. R. Tetrahedron, 1988, **44**, 1915.
- 503. Shimo, T.; Yoshimura, H.; Uemura, H.; Somekawa, K.; Tsuge, O. Heterocycles, 1986, **24**, 3031.
- 504. de Mayo, P.; Yip, R. W. Proc. Chem. Soc., 1964, 84.
- 505. Shimo, T.; Somekawa, K.; Kumamoto, S. Nippon Kagaku Kaishi, 1983, 394.
- 506. Shusherina, N. P.; Vashakidze, E. Y.; Gapeeva, M. V.; Levina, R. Y. Russ. J. Org. Chem. (Engl. Transl.), 1969, **5**, 1457.
- 507. Gapeeva, M. V.; Stepanyants, A. U.; Schusherina, N. P.; Knirel, Y. A.; Levina, R. V. Russ. J. Org. Chem., (Engl. transl.), 1971, **7**, 2519.
- 508. Shusherina, N.; Levina, R.; Shostakovskii, V. J. Gen. Chem. USSR (Engl. Transl.), 1959, **29**, 3200.
- 509. Shusherina, N. P.; Vashakidze, E. Y.; Levina, R. Y. Vestnik Moskov. Gos. Univ., 1971, *no.* **4**, 473.
- 510. Shusherina, N. P.; Levina, R. Y.; Sidenko, Z. S.; Lur'e, M. Y. J. Gen. Chem. USSR (Engl. Transl.), 1959, **29**, 405.
- 511. Shusherina, N. P.; Luk'yanets, E. A.; Levina, R. Y. J. Gen. Chem. USSR (Engl. Transl.), 1964, **34**, 18.
- 512. Shusherina, N. P.; Luk'yanets, E. A.; Levina, R. Y. Russ. J. Org. Chem. (Engl. Transl.), 1965, **1**, 1521.
- 513. Markl, G.; Fuchs, R. Tetrahedron Lett., 1972, 4691.
- 514. Shusherina, N. P.; Lur'e, M. Y.; Levina, R. Y. Proc. Acad. Sci. USSR (Engl. Transl.), 1956, 367.
- 515. Dreiding, A. S.; Tomasewski, A. J. J. Am. Chem. Soc., 1954, 76, 6388.
- 516. Russell, R. K.; Wingard, R. E. Jr.; Paquette, L. A. J. Am. Chem. Soc., 1974, **96**, 7483.
- 517. Dmitrieva, N. D.; Shil'nikova, A. G.; Shusherina, N. P.; Levina, R. Y. J. Gen. Chem. USSR (Engl. Transl.), 1964, **34**, 2868.
- 518. Shusherina, N. P.; Dmitrieva, N. D.; Levina, R. Y. J. Gen. Chem. USSR (Engl. Transl.), 1961, **31**, 2606.
- 519. Shusherina, N. P.; Dmitrieva, N. D.; Levina, R. Y. Proc. Acad. Sci., USSR (Engl. Transl.), 1962, **146**, 912.
- 520. Spangler, R. J.; Kim, J. H. Synthesis, 1973, 107.
- 521. Spangler, R. J.; Beckmann, B. G. Tetrahedron Lett., 1976, 2517.
- 522. Plieninger, H.; Muller, W.; Weinerth, K. Chem. Ber., 1964, 97, 667.
- 523. Fray, E. G.; Moody, C. J.; Shah, P. Tetrahedron, 1993, 49, 439.

- 524. Hodgetts, I.; Noyce, S. J.; Storr, R. C. Tetrahedron Lett., 1984, 25, 5435.
- 525. Jones, D. W.; Kneen, G. J. Chem. Soc., Perkin Trans. 1, 1975, 175.
- 526. Moerck, R. E.; Battiste, M. A. J. Chem. Soc., Chem. Commun., 1972, 1171.
- 527. Van Broeck, P. I.; Van Doren, P. E.; Toppet, S. M.; Hoornaert, G. J. Chem. Soc., Perkin Trans. 1, 1992, 415.
- 528. Smith, J. P.; Schuster, G. B. J. Am. Chem. Soc., 1978, 100, 2564.
- 529. Kohl, R. T.; Katto, T.; Braham, J. N.; Stille, J. K. Macromolecules, 1978, **11**, 340.
- 530. VanKerckhoven, H. F.; Gilliams, Y. K.; Stille, J. K. Macromolecules, 1972, **5**, 541.
- 531. Shusherina, N. P.; Gapeeva, M. V.; Stepanyants, A.; Mondishka, D. M.; Levina, R. Y. Russ. J. Org. Chem. (Engl. Transl.), 1971, **7**, 1429.
- 532. Shusherina, N. P.; Levina, R. Y.; Trubnikov, I. S. J. Gen. Chem. USSR (Engl. Transl.), 1959, **29**, 2903.
- 533. Eschenmoser, A.; Schreiber, J.; Leimgruber, W.; Pesaro, M.; Schudel, P.; Threlfall, T. Helv. Chim. Acta, 1961, **44**, 540.
- 534. Schreiber, J.; Leimgruber, W.; Pesaro, M.; Schudel, P.; Threlfall, T.; Eschenmoser, A. Helv. Chim. Acta, 1961, **44**, 540.
- 535. Schreiber, J.; Leimgruber, W.; Pesaro, M.; Schudel, P.; Eschenmoser, A. Angew. Chem., 1959, **71**, 637.
- 536. Boger, D. L.; Brotherton, C. E. J. Org. Chem., 1985, 50, 3425.
- 537. Boger, D. L.; Brotherton, C. E. J. Am. Chem. Soc., 1986, 108, 6713.
- 538. Zakharkin, L. I.; Sorokina, L. P. Bull. Acad. Science USSR, Chem. Series (Engl. Transl.), 1965, 840.
- 539. Branchini, R.; Casini, G.; Gulinelli, S. Ann. Chimica, 1959, 49, 1850.
- 540. Dmitrieva, N. D.; Moiseeva, A. D.; Shusherina, N. P.; Shumakova, V. D.; Levina, R. Y. Russ. J. Org. Chem. (Engl. Transl.), 1968, **4**, 1420.
- 541. Reed, J. A.; Schilling, C. L. Jr.; Tarvin, R. F.; Rettig, T. A.; Stille, J. K. J. Org. Chem., 1969, **34**, 2188.
- 542. Padwa, A.; Hartman, R. J. Am. Chem. Soc., 1966, 88, 1518.
- 543. Padwa, A. Tetrahedron Lett., 1964, 813.
- 544. Padwa, A.; Hartman, R. J. Am. Chem. Soc., 1964, **86**, 4212.
- 545. Markl, G.; Jin, G. Y.; Silbereisen, E. Angew. Chem., Int. Ed. Engl., 1982, **21**, 370.
- 546. Schilling, C. L.; Reed, J. A.; Stille, J. K. Macromolecules, 1969, 2, 85.
- 547. Shusherina, N. P.; Hakimi, M. G.; Murakhovskaya, A. S.; Stepanyants, A. U. Moscow Univ. Chem Bull. (Engl. Transl.), 1974, **29**(6), 67.
- 548. Kealy, T. J. J. Am. Chem. Soc., 1962, 84, 966.

- 549. Imagawa, T.; Nakagawa, T.; Kawanisi, M.; Sisido, K. Bull. Chem. Soc. Jpn., 1979, **52**, 1506.
- 550. Sasaki, T.; Kanematsu, K.; Hiramatsu, T. J. Chem. Soc., Perkin Trans. 1, 1974, 1213.
- 551. Bryson, T. A.; Donelson, D. M. J. Org. Chem., 1977, 42, 2930.
- 552. Himbert, G.; Brunn, W. Justus Liebigs Ann. Chem., 1986, 1067.
- 553. Feustel, M.; Himbert, G. Tetrahedron Lett., 1983, 24, 2165.
- 554. Baker, F. W.; Stock, L. M. J. Org. Chem., 1967, 32, 3344.
- 555. Imagawa, T.; Haneda, A.; Nakagawa, T.; Kawanisi, M. Tetrahedron, 1978, **34**, 1893.
- 556. Watt, D. S.; Corey, E. J. Tetrahedron Lett., 1972, 4651.
- 557. Corey, E. J.; Watt, D. S. J. Am. Chem. Soc., 1973, 95, 2303.
- 558. Ireland, R. E.; Anderson, R. C.; Badoud, R.; Fitzsimmons, B.; McGarvey, G. J.; Thaisrivongs, S.; Wilcox, C. S. J. Am. Chem. Soc., 1983, **105**, 1988.
- 559. Ireland, R. E.; McGarvey, G. J.; Anderson, R. C.; Badoud, R.; Fitzsimmons, B.; Thaisrivongs, S. J. Am. Chem. Soc., 1980, **102**, 6178.
- 560. Boger, D. L.; Mullican, M. D. J. Org. Chem., 1984, 49, 4033.
- 561. Boger, D. L.; Mullican, M. D. Tetrahedron Lett., 1983, 24, 4939.
- 562. Boger, D. L.; Mullican, M. D. Tetrahedron Lett., 1982, 23, 4551.
- 563. Boger, D. L.; Mullican, M. D. Tetrahedron Lett., 1982, 23, 4555.
- 564. Boger, D. L.; Brotherton, C. E. J. Org. Chem., 1984, 49, 4050.
- 565. Kraus, G. A.; Pezzanite, J. O.; Sugimoto, H. Tetrahedron Lett., 1979, 853.
- 566. Martin, P.; Streith, J.; Rihs, G.; Winkler, T.; Bellus, D. Tetrahedron Lett., 1985, **26**, 3947.
- 567. Martin, P.; Steiner, E.; Streith, J.; Winkler, T.; Bellus, D. Tetrahedron, 1985, **41**, 4057.
- 568. Bahl, A. K.; Kemp, W. J. Chem. Soc. (C), 1971, 2268.
- 569. Alder, K.; Rickert, H. F. Chem. Ber., 1937, 70, 1354.
- 570. Tamao, K.; Yoshida, J.; Akita, M.; Sugihara, Y.; Iwahara, T.; Kumada, M. Bull. Chem. Soc. Jpn., 1982, **55**, 255.
- 571. Matsushita, Y.; Sakamoto, K.; Murakami, T.; Matsui, T. Synth. Commun., 1994, **24**, 3307.
- 572. Hatsui, T.; Hashiguchi, T.; Takeshita, H. Chem. Express, 1993, 8, 581.
- 573. Imagawa, T.; Sueda, N.; Kawanisi, M. Tetrahedron, 1974, **30**, 2227.
- 574. Imagawa, T.; Sueda, N.; Kawanisi, M. J. Chem. Soc., Chem. Commun., 1972, 388.
- 575. Matsui, T.; Matsushita, Y.; Nakayama, M. Heterocycles, 1992, 34, 723.

- 576. Harano, K.; Aoki, T.; Eto, M. Hisano, T. Chem. Pharm. Bull., 1990, **38**, 1182.
- 577. Shimo, T.; Nagahama, H.; Yorozu, K.; Somekawa, K. J. Heterocycl. Chem., 1992, **29**, 801.
- 578. Gingrich, H. L.; Roush, D. M.; Van Saun, W. A. J. Org. Chem., 1983, **48**, 4869.
- 579. Verma, S. M.; Maurya, H. Indian J. Chem., Sect. B, 1985, 24, 447.
- 580. Jaworski, T.; Kwiatkowski, S. Rocz. Chem., 1970, 44, 691.
- 581. Behringer, H.; Heckmaier, P. Chem. Ber., 1969, 102, 2835.
- 582. Jung, M. E.; Hagenah, J. A. J. Org. Chem., 1987, 52, 1889.
- 583. Jung, M. E.; Hagenah, J. A. Heterocycles, 1987, 25, 117.
- 584. Jaworski, T.; Kwiatkowski, S. Rocz. Chem., 1970, 44, 555.
- 585. Wenkert, E.; Johnston, D.; Dave, K. J. Org. Chem., 1964, 29, 2534.
- 586. Martin, S. F.; Rueger, H.; Williamson, S. A.; Grzejszczak, S. J. Am. Chem. Soc., 1987, **109**, 6124.
- 587. Ciganek, E. J. Am. Chem. Soc., 1981, 103, 6261.
- 588. Yamaguchi, R.; Otsuji, A.; Utimoto, K.; Kozima, S. Bull. Chem. Soc. Jpn., 1992, **65**, 298.
- 589. Noguchi, M.; Kakimoto, S.; Kajigaeshi, S. Chem. Lett., 1985, 151.
- 590. Noguchi, M.; Kakimoto, S.; Kawakami, H.; Kajigaeshi, S. Heterocycles, 1985, **23**, 1085.
- 591. Posner, G. H.; Nelson, T. D. Tetrahedron, 1990, 46, 4573.
- 592. Shusherina, N. P.; Dmitrieva, N. D.; Komarovskaya, G. V.; Levina, R. Y. Russ. J. Org. Chem. (Engl. Transl), 1968, **4**, 1976.
- 593. Andrews, J. F. P.; Jackson, P. M.; Moody, C. J. Tetrahedron, 1993, **49**, 7353.
- 594. Moody, C. J.; Rahimtoola, K. F. J. Chem. Soc., Perkin Trans. 1, 1990, 673.
- 595. Moody, C. J.; Rahimtoola, K. F.; Porter, B.; Ross, B. C. J. Org. Chem., 1992, **57**, 2105.
- 596. Moody, C. J.; Rahimtoola, K. F. J. Chem. Soc., Chem. Commun., 1990, 1667.
- 597. Opitz, G.; Zimmermann, F. Chem. Ber., 1964, 97, 1266.
- 598. Jackson, P. M.; Moody, C. J. J. Chem. Soc., Perkin Trans. 1, 1990, 2156.
- 599. Pindur, U.; Eitel, M.; Erfanian-Abdoust, H. Heterocycles, 1989, 29, 11.
- 600. Pindur, U.; Erfanian-Abdoust, H. Justus Liebigs Ann. Chem., 1989, 227.
- 601. Moody, C. J. J. Chem. Soc., Perkin Trans. 1, 1985, 2505.
- 602. Moody, C. J. J. Chem. Soc., Chem. Commun., 1984, 925.

- 603. Moody, C. J.; Shah, P. J. Chem. Soc., Perkin Trans. 1, 1989, 2463.
- 604. Jackson, P. M.; Moody, C. J. Synlett, 1990, 521.
- 605. Moody, C. J.; Shah, P. J. Chem. Soc., Perkin Trans. 1, 1989, 376.
- 606. Moody, C. J.; Shah, P. J. Chem. Soc., Perkin Trans. 1, 1988, 1407.
- 607. Pindur, U.; Erfanian-Abdoust, H. Justus Liebigs Ann. Chem., 1988, 803.
- 608. Moody, C. J.; Shah, P.; Knowles, P. J. Chem. Soc., Perkin Trans. 1, 1988, 3249.
- 609. Moody, C. J.; Shah, P.; Knowles, P. Tetrahedron Lett., 1988, 29, 2693.
- 610. Pindur, U.; Erfanian-Abdoust, H. Heterocycles, 1990, 31, 1751.
- 611. Van Doren, P.; Vanderzande, D.; Toppet, S. M.; Hoornaert, G. Tetrahedron, 1989, **45**, 6761.
- 612. Navasimhan, N. S.; Gokhale, S. M. J. Chem. Soc., Chem. Commun., 1985, 86.
- 613. Van Doren, P.; Compernolle, F.; Hoornaert, G. Tetrahedron, 1990, **46**, 4023.
- 614. Pindur, U.; Erfanian-Abdoust, H. Chimia, 1988, 42, 180.
- 615. Perez, D.; Guitian, E.; Casteda, L. Tetrahedron Lett., 1992, 33, 2407.
- 616. Gladysz, J. A.; Lee, S. J.; Tomasello, J. A. V.; Yu, Y. S. J. Org. Chem., 1977, **42**, 4170.
- 617. Corey, E. J.; Kozikowski, A. P. Tetrahedron Lett., 1975, 2389.
- 618. Kozikowski, A. P.; Floyd, W. C.; Kuniak, M. P. J. Chem. Soc., Chem. Commun., 1977, 582.
- 619. Cano, P.; Echavarren, A.; Prados, P.; Farina, F. J. Org. Chem., 1983, 48, 5373.
- 620. Tanyeli, C.; Tarhan, O. Synth. Commun., 1989, 19, 2453.
- 621. Kozikowski, A. P.; Schmiesing, R. Tetrahedron Lett., 1978, 4241.
- 622. Spangler, R. J.; Kim, J. H. Tetrahedron Lett., 1972, 1249.
- 623. Tamura, Y.; Fukata, F.; Sasho, M.; Tsugoshi, T.; Kita, Y. J. Org. Chem., 1985, **50**, 2273.
- 624. Tamura, Y.; Wada, A.; Sasho, M.; Fukunaga, K.; Maeda, H.; Kita, Y. J. Org. Chem., 1982, **47**, 4376.
- 625. Tamura, Y.; Akai, S.; Sasho, M.; Kita, Y. Tetrahedron Lett., 1984, **25**, 1167.
- 626. Tamura, Y.; Sasho, M.; Akai, S.; Kishimoto, H.; Sekihachi, J.; Kita, Y. Tetrahedron Lett., 1986, **27**, 195.
- 627. Tamura, Y.; Mohri, S.; Maeda, H.; Tsugoshi, T.; Sasho, M.; Kita, Y. Tetrahedron Lett., 1984, **25**, 309.
- 628. Profitt, J. A.; Jones, T.; Watt, D. S. Synth. Commun., 1975, **5**, 457.
- 629. Warren, J. D.; Lee, V. J.; Angier, R. B. J. Heterocycl. Chem., 1979, 16,

1617.

- 630. Bosshard, P.; Fumagalli, S.; Good, R.; Treub, W.; von Philipsborn, W.; Eugster, C. H. Helv. Chim. Acta, 1964, **47**, 769.
- 631. Ichihara, A.; Murakami, K.; Sakamura, S. Agric. Biol. Chem., 1984, **48**, 833.
- 632. Ichihara, A.; Murakami, K.; Sakamura, S. Tetrahedron, 1987, 43, 5245.
- 633. Bu'Lock, J. D.; Smith, H. C. J. Chem. Soc., 1960, 502.
- 634. Tam, T. F.; Coles, P. Synthesis, 1988, 383.
- 635. Padwa, A.; Hartman, R. J. Am. Chem. Soc., 1966, 88, 3759.
- 636. Iguchi, S.; Inoue, A. Chem. Pharm. Bull., 1962, 10, 1070.
- 637. Ahmed, S. A.; Bardshiri, E.; Simpson, T. J. Tetrahedron Lett., 1988, **29**, 1595.
- 638. Jung, M. E.; Lowe, J. A. J. Chem. Soc., Chem. Commun., 1978, 95.
- 639. Ahmed, S. A.; Bardshiri, E.; Simpson, T. J. J. Chem. Soc., Chem. Commun., 1987, 883.
- 640. Jung, M. E.; Brown, R. W. Tetrahedron Lett., 1981, 20, 3355.
- 641. Jung, M. E.; Lowe, J. A. III; Lyster, M. A.; Node, M.; Pflueger, R. W.; Brown, R. W. Tetrahedron, 1984, **40**, 4751.
- 642. Jung, M. E.; Node, M.; Pfluger, R. W.; Lyster, M. A.; Lowe, J. A. III J. Org. Chem., 1982, **47**, 1150.
- 643. Tamura, Y.; Fukata, F.; Tsugoshi, T.; Sasho, M.; Nakajima, Y.; Kita, Y. Chem. Pharm. Bull., 1984, **32**, 3259.
- 644. Mehta, G.; Venkateswarlu, Y. J. Chem. Soc., Chem. Commun., 1988, 1200.
- 645. Burke, S. D.; Saunders, J. O.; Murtiashaw, C. W. J. Org. Chem., 1981, 46, 2425.
- 646. Maerkl, G. Chem. Ber., 1963, 96, 1441.
- 647. Christl, M.; Freund, S. Chem. Ber., 1985, 118, 979.
- 648. Leon, E. U. S. Pat. 3,092,641 (1963); Chem. Abstr., 1964, 60, P2902b.
- 649. du Pont, D. *Neth. Pat. Appl.* 6,404,759 (1964); Chem. Abstr., 1965, **62**, 14529c.
- 650. Raasch, M. S. J. Org. Chem., 1980, 45, 856.
- 651. Shusherina, N. P.; Luk'yanets, E. A.; Levina, R. Y. J. Gen. Chem. USSR (Engl. Transl.), 1964, 34, 2527.
- 652. Kobayashi, G.; Furukawa, S.; Matsuda, Y.; Natsuki, R. Yakugaku Zasshi, 1968, **88**, 767; Chem. Abstr., 1969, **70**, 3728.
- 653. Kobayashi, G.; Matsuda, Y. *Jpn. Patent* 39,539; Chem. Abstr., 1971, **75**, 35738.
- 654. Jackson, P. M.; Moody, C. T.; Shah, P. J. Chem. Soc., Perkin Trans. 1,

1990, 2909.

- 655. Jackson, P. M.; Moody, C. J. J. Chem. Soc., Perkin Trans. 1, 1990, 681.
- 656. Shusherina, N. P.; Levina, R. Y.; Dmitrieva, N. D. Proc. Acad. Sci., USSR (Engl. Transl.), 1959, **126**, 385.
- 657. Baydar, A. E.; Boyd, G. V.; Lindley, P. F.; Watson, F. J. Chem. Soc., Chem. Commun., 1979, 178.
- 658. Bowen, R. D.; Davies, D. E.; Fishwick, C. W. G.; Glasbey, T. O.; Noyce, S. J.; Storr, R. C. Tetrahedron Lett., 1982, 23, 4501.
- 659. Ganesan, A.; Heathcock, C. H. J. Org. Chem., 1993, 58, 6155.
- 660. Schulz, G.; Steglich, W. Chem. Ber., 1977, 110, 3615.
- 661. Meerpoel, L.; Hoornaert, G. Tetrahedron Lett., 1989, 30, 3183.
- 662. Meerpoel, L.; Deroover, G.; van Aken, K.; Lux, G.; Hoornaert, G. Synthesis, 1991, 765.
- 663. Maier, G. Angew. Chem., Int. Ed. Engl., 1974, 13, 425.
- 664. Steglich, W.; Jeschke, R.; Buschmann, E. Gazz. Chim. Ital., 1986, **116**, 361.
- 665. Buschmann, E.; Steglich, W. Angew. Chem., Int. Ed. Engl., 1974, **13**, 484.
- 666. Boger, D. L.; Wysocki R. J. Jr. J. Org. Chem., 1989, 54, 714.
- 667. Hofle, G.; Hollitzer, O.; Steglich, W. Angew. Chem., Int. Ed. Engl., 1972, **11**, 720.
- 668. Huisgen, R.; Gotthardt, H.; Bayer, H. O. Angew. Chem., Int. Ed. Engl., 1964, **3**, 135.
- 669. Huisgen, R.; Gotthardt, H.; Bayer, H. O.; Schaefer, F. C. Angew. Chem., Int. Ed. Engl., 1964, 3, 136.
- 670. Huisgen, R.; Gotthardt, H.; Bayer, H. O.; Schaefer, F. C. Chem. Ber., 1970, **103**, 2611.
- 671. Hershenson, F. M. J. Heterocycl. Chem., 1979, 16, 1093.
- 672. Baum, J. S.; Viehe, H. G. J. Org. Chem., 1976, 41, 183.
- 673. Potts, K. T.; Datta, S. K.; Marshall, J. L. J. Org. Chem., 1979, 44, 622.
- 674. Potts, K. T.; Singh, U. P. J. Chem. Soc., Chem. Commun., 1969, 66.
- 675. Hershenson, F. M. J. Org. Chem., 1975, 40, 1260.
- 676. Padwa, A.; Burgess, E. M.; Gingrich, H. L.; Roush, D. M. J. Org. Chem., 1982, **47**, 786.
- 677. Potts, K. T.; McKeough, D. J. Am. Chem. Soc., 1973, 95, 2749.
- 678. Pizzorno, M. T.; Albonico, S. M. Chem. & Ind. (London), 1978, 349.
- 679. Pizzorno, M. T.; Albonico, S. M. J. Org. Chem., 1974, 39, 731.
- 680. Robins, D. J.; Sakdarat, S. J. Chem. Soc., Chem. Commun., 1979, 1181.

- 681. Robins, D. J.; Sakdarat, S. J. Chem. Soc., Perkin Trans. 1, 1981, 909.
- 682. Anderson, W. K.; Corey, P. F. J. Med. Chem., 1977, 20, 812.
- 683. Rebek, J.; Gehret, J. E. Tetrahedron Lett., 1977, 3027.
- 684. Kane, J. M. J. Org. Chem., 1980, 45, 5396.
- 685. Pizzorno, M. T.; Albonico, S. M. J. Org. Chem., 1977, 42, 909.
- 686. Myers, J. A.; Moore, L. D.; Whitter, W. L.; Council, S. L.; Waldo, R. M.; Lanier, J. L.; Omoji, B. U. J. Org. Chem., 1980, 45, 1202.
- 687. Anderson, W. K.; Corey, P. F. J. Org. Chem., 1977, 42, 559.
- 688. Hershenson, F. M. J. Org. Chem., 1975, 40, 740.
- 689. Potts, K. T.; Yao, S. J. Org. Chem., 1979, 44, 977.
- 690. Hershenson, F. M. J. Org. Chem., 1972, **37**, 3111.
- 691. Gotthardt, H.; Reiter, F. Justus Liebigs Ann. Chem., 1979, 650.
- 692. Huisgen, R.; Grashey, R.; Gotthardt, H.; Schmidt, R. Angew. Chem., Int. Ed. Engl., 1962, 1, 48.
- 693. Kishimoto, S.; Noguchi, S.; Masuda, K. Chem. Pharm. Bull., 1976, **24**, 3001.
- 694. Legrand, J. J.; Renault, C. *Belg. Pat.* 843959; Chem. Abstr., 1977, **87**, 152, 198.
- 695. Gotthardt, H.; Reiter, F. Chem. Ber., 1979, 112, 1193.
- 696. Alemagna, A.; Barbetta, M. Chimica e Industria (Milan), 1964, 46, 1189.
- 697. Angadiyavar, C. S.; George, M. V. J. Org. Chem., 1971, 36, 1589.
- 698. Gotthardt, H.; Reiter, F. Tetrahedron Lett., 1971, 2749.
- 699. Marky, M.; Hansen, H.; Schmid, H. Helv. Chim. Acta, 1971, 54, 1275.
- 700. Dickopp, H. Chem. Ber., 1974, 107, 3036.
- 701. Badami, B. V.; Puranik, G. S. Rev. Roum. Chim., 1975, 20, 981; Chem. Abstr., 1976, 84, 4864.
- 702. Lazaris, A. Y. J. Org. Chem. USSR, (Engl. transl.), 1966, 2, 1322.
- 703. Gotthardt, H.; Huisgen, R.; Knorr, R. Chem. Ber., 1968, **101**, 1056.
- 704. Nakazawa, S.; Kiyosawa, T.; Hirakawa, K.; Kato, H. J. Chem. Soc., Chem. Commun., 1974, 621.
- 705. Sasaki, T.; Kanematsu, K.; Uchide, M. Bull. Chem. Soc. Jpn., 1971, 44, 858.
- 706. Ranganathan, D.; Bamezai, S. Tetrahedron Lett., 1983, 24, 1067.
- 707. McCarthy, A. R.; Ollis, W. D.; Ramsden, C. A. J. Chem. Soc., Perkin Trans. 1, 1974, 624.
- 708. Berk, H. C.; Zwikelmaier, K. E.; Franz, J. E. Synth. Commun., 1980, **10**, 707.
- 709. Masuda, K.; Adachi, J.; Nomura, K. Chem. Pharm. Bull., 1977, 25, 1471.

- 710. Gotthardt, H. Tetrahedron Lett., 1971, 1281.
- 711. Gotthardt, H. Chem. Ber., 1972, 105, 196.
- 712. Potts, K. T.; Baum, J. J. Chem. Soc., Chem. Commun., 1973, 833.
- 713. Eicher, T.; Schaefer, V. Tetrahedron, 1974, 30, 4025.
- 714. Matsukubo, H.; Kato, H. J. Chem. Soc., Chem. Commun., 1974, 412.
- 715. Matsukubo, H.; Kato, H. J. Chem. Soc., Perkin Trans. 1, 1975, 632.
- 716. Matsukubo, H.; Kojima, M.; Kato, H. Chem. Lett., 1975, 1153.
- 717. Turchi, I. J.; Maryanoff, C. A.; Mastracola, A. M. J. Heterocycl. Chem., 1980, **17**, 1593.
- 718. Potts, K. T.; Roy, D. N. J. Chem. Soc., Chem. Commun., 1968, 1061.
- 719. Potts, K. T.; Baum, J.; Houghton, E.; Roy, D. N.; Singh, U. P. J. Org. Chem., 1974, **39**, 3619.
- 720. Barrett, G. C.; Walker, R. Tetrahedron, 1976, **32**, 571.
- 721. Potts, K. T.; Choudhury, D. R.; Elliott, A. J.; Singh, U. P. J. Org. Chem., 1976, **41**, 1724.
- 722. Potts, K. T.; Singh, U. P. J. Chem. Soc., Chem. Commun., 1969, 569.
- 723. Gotthardt, H.; Weisshuhn, M. C.; Dorhofer, K. Angew. Chem., Int. Ed. Engl., 1975, **14**, 422.
- 724. Gotthardt, H.; Weisshuhn, M. C.; Dorhofer, K. Chem. Ber., 1978, **111**, 3336.
- 725. Gotthardt, H.; Weisshuhn, C. M. Chem. Ber., 1978, 111, 2028.
- 726. Gotthardt, H.; Weisshuhn, M. C.; Christl, B. Chem. Ber., 1976, 109, 753.
- 727. Gotthardt, H.; Weisshuhn, C. M. Chem. Ber., 1978, 111, 2021.
- 728. Gotthardt, H.; Christl, B. Tetrahedron Lett., 1968, 4747.
- 729. Gotthardt, H.; Weisshuhn, M. C.; Huss, O. M.; Bauer, D. J. Tetrahedron Lett., 1978, 671.
- 730. Gotthardt, H.; Christl, B. Tetrahedron Lett., 1968, 4751.
- 731. Potts, K. T.; Rochanapruk, T.; Coats, S. J.; Hadjiarapoglou, L.; Padwa, A. J. Org. Chem., 1993, **58**, 5040.
- 732. Dewar, M. J. S.; Chantranupong, L. J. Am. Chem. Soc., 1983, **105**, 7152.
- 733. Gillis, B. T.; Beck, P. E. J. Org. Chem., 1963, 28, 3177.
- 734. Carboni, R. A. U. S. Patent 3,022,305; Chem. Abstr., 1963, 58, 9102.
- 735. Durst, T.; Tetreault-Ryan, L. Tetrahedron Lett., 1978, 2353.
- 736. Masamune, S.; Nakamura, N.; Sapadaro, J. J. Am. Chem. Soc., 1975, **97**, 918.
- 737. Lay, W. P.; Mackenzie, K.; Telford, J. R. J. Chem. Soc. (C), 1971, 3199.
- 738. Hudlicky, T.; Seoane, G.; Pettus, T. J. Org. Chem., 1989, 54, 4239.

- 739. Askani, R. Chem. Ber., 1965, 98, 2551.
- 740. Allred, E. L.; Hinshaw, J. C.; Johnson, A. L. J. Am. Chem. Soc., 1969, 91, 3382.
- 741. Paquette, L. A. J. Am. Chem. Soc., 1970, 92, 5765.
- 742. Askani, R.; Wieduwilt, M. Justus Liebigs Ann. Chem., 1986, 1098.
- 743. Dittmar, W.; Heinrichs, G.; Steigel, A.; Troll, T.; Sauer, J. Tetrahedron Lett., 1970, 1623.
- 744. Horwell, D. C.; Deyrup, J. A. J. Chem. Soc., Chem. Comm., 1972, 485.
- 745. Adam, W.; Berkessel, A. Chem. Ber., 1985, **118**, 5018.
- 746. Askani, R. Chem. Ber., 1969, 102, 3304.
- 747. Snyder, J. P.; Olsen, H. J. Am. Chem. Soc., 1978, 100, 2566.
- 748. Moriarty, R. M. J. Org. Chem., 1963, 28, 2385.
- 749. LeBlanc, B. F.; Sheridan, R. S. J. Am. Chem. Soc., 1985, 107, 4554.
- 750. King, J. F.; Hawson, A.; Deaken, D. M.; Komery, J. J. Chem. Soc., Chem. Commun., 1969, 33.
- 751. Neunhoeffer, H.; Werner, G. Tetrahedron Lett., 1972, 1517.
- 752. Neunhoeffer, H.; Werner, G. Justus Liebigs Ann. Chem., 1973, 1955.
- 753. Neunhoeffer, H.; Frey, G. Justus Liebigs Ann. Chem., 1973, 1963.
- 754. Benson, S. C.; Gress, J. L.; Snyder, J. K. J. Org. Chem., 1990, 55, 3257.
- 755. Jojima, T.; Takeshiba, H.; Konotsune, T. Chem. Pharm. Bull., 1972, **20**, 2191.
- 756. Jojima, T.; Takeshiba, H.; Kinoto, T. Chem. Pharm. Bull., 1980, 28, 198.
- 757. Jojima, T.; Takeshiba, H.; Kinoto, T. Chem. Pharm. Bull., 1976, **24**, 1588.
- 758. Boger, D. L.; Coleman, R. S. J. Org. Chem., 1984, 49, 2240.
- 759. Boger, D. L.; Coleman, R. S. J. Org. Chem., 1986, 51, 3250.
- 760. Boger, D. L.; Coleman, R. S. J. Am. Chem. Soc., 1987, 109, 2717.
- 761. Boger, D. L.; Sakya, S. M. J. Org. Chem., 1988, 53, 1415.
- 762. Boger, D. L.; Zhang, M. J. Am. Chem. Soc., 1991, 113, 4230.
- 763. Oishi, E.; Iwamoto, K.; Okada, T.; Suzuki, S.; Tanji, K.; Miyashita, A.; Higashino, T. Chem. Pharm. Bull., 1994, 42, 2219.
- 764. Oishi, E.; Taido, N.; Iwamoto, K.; Miyashita, A.; Higashino, T. Chem. Pharm. Bull., 1990, **38**, 3268.
- 765. Oishi, E.; Taido, N.; Miyashita, A.; Sato, S.; Ohta, S.; Ishida, H.; Tanji,
   K.; Higashino, T. Chem. Pharm. Bull., 1991, **39**, 1713.
- 766. Oishi, E.; Yamada, A.; Hayashi, E.; Tanji, K.; Miyashita, A.; Higashino, T. Chem. Pharm. Bull., 1989, **37**, 13.
- 767. Oishi, E.; Yamada, A.; Hayashi, E.; Higashino, T. Chem. Pharm. Bull., 1987, **35**, 2686.

- 768. Steigel, A.; Sauer, J. Tetrahedron Lett., 1973, 1213.
- 769. Paquette, L. A.; Epstein, M. J. J. Am. Chem. Soc., 1971, 93, 5936.
- 770. Wilson, W. S.; Warrener, R. N. Tetrahedron Lett., 1970, 4787.
- 771. Christl, M.; Lanzendorfer, U.; Freund, S. Angew. Chem., Int. Ed. Engl., 1981, **20**, 674.
- 772. Padwa, A.; Eisenbarth, P. Tetrahedron, 1985, 41, 283.
- 773. Neunhoeffer, H.; Clausen, M.; Votter, H.; Ohl, H.; Kruger, C.; Angermund, K. Justus Liebigs Ann. Chem., 1985, 1732.
- 774. Sugita, T.; Koyama, J.; Tagahara, K.; Suzuta, Y. Heterocycles, 1985, **23**, 2789.
- 775. Okatani, T.; Koyama, J.; Tagahara, K.; Suzuta, Y. Heterocycles, 1987, **26**, 595.
- 776. Boger, D. L.; Panek, J. S. J. Org. Chem., 1981, 46, 2179.
- 777. Neunhoeffer, H.; Freuhauf, H. Justus Liebigs Ann. Chem., 1972, **758**, 120.
- 778. Burg, B.; Dittmar, W.; Reim, H.; Steigel, A.; Sauer, J. Tetrahedron Lett., 1975, 2897.
- 779. Reim, H.; Steigel, A.; Sauer, J. Tetrahedron Lett., 1975, 2901.
- 780. Li, J.; Snyder, J. K. J. Org. Chem., 1993, 58, 516.
- 781. Boger, D. L.; Panek, J. S. J. Am. Chem. Soc., 1985, 107, 5745.
- 782. Gockel, U.; Hartmannsgruber, U.; Steigel, A.; Sauer, J. Tetrahedron Lett., 1980, 21, 595.
- 783. Dittmar, W.; Sauer, J.; Steigel, A. Tetrahedron Lett., 1969, 5171.
- 784. Martin, J. C.; Muchowski, J. M. J. Org. Chem., 1984, 49, 1040.
- 785. Maddox, M. L.; Martin, J. C.; Muchowski, J. M. Tetrahedron Lett., 1980, **21**, 7.
- 786. Taylor, E. C.; Macor, J. E. Tetrahedron Lett., 1986, 27, 2107.
- 787. Taylor, E. C.; Macor, J. E.; French, L. G. J. Org. Chem., 1991, 56, 1807.
- 788. Rocha Gonsalves, A. M.; Pinho e Melo, T. M. V. D.; Gilchrist, T. L. Tetrahedron, 1992, **48**, 6821.
- 789. Seitz, G.; Dietrich, S. Arch. Pharm. (Weinheim, Ger.), 1984, 317, 379.
- 790. Steigel, A.; Sauer, J.; Kleier, D. A.; Binsch, G. J. Am. Chem. Soc., 1972, **94**, 2770.
- 791. Taylor, E. C.; French, L. G. J. Org. Chem., 1989, 54, 1245.
- 792. Elix, J. A.; Wilson, W. S.; Warrener, R. N.; Calder, I. C. Aust. J. Chem., 1972, **25**, 865.
- 793. Elix, J. A.; Wilson, W. S.; Warrener, R. N. Tetrahedron Lett., 1970, 1837.
- 794. Sagi, M.; Sato, O.; Konno, S.; Yamanaka, H. Heterocycles, 1989, **29**, 2253.

- 795. Boger, D. L.; Panek, J. S. J. Org. Chem., 1983, 48, 621.
- 796. Seitz, G.; Dhar, R.; Kampchen, T. Arch. Pharm. (Weinheim, Ger.), 1982, **315**, 697.
- 797. Dhar, R.; Huhnermann, W.; Kampchen, T.; Overheu, W.; Seitz, G. Chem. Ber., 1983, **116**, 97.
- 798. Seitz, G.; Dhar, R.; Huhnermann, W. Chem.-Ztg., 1982, 106, 100.
- 799. Martin, J. C. J. Org. Chem., 1982, 47, 3761.
- 800. Boger, D. L.; Panek, J. S.; Yasuda, M. Org. Synth., 1988, 66, 142.
- 801. Boger, D. L.; Panek, J. S. J. Org. Chem., 1982, 47, 3763.
- 802. Boger, D. L.; Duff, S. R.; Panek, J. S.; Yasuda, M. J. Org. Chem., 1985, 50, 5782.
- 803. Boger, D. L.; Duff, S. R.; Panek, J. S.; Yasuda, M. J. Org. Chem., 1985, 50, 5790.
- 804. Boger, D. L.; Panek, J. S. Tetrahedron Lett., 1984, 25, 3175.
- 805. Mohrle, H.; Dwuletzki, H. Chem. Ber., 1986, 119, 3600.
- 806. Maggiora, L.; Mertes, M. P. J. Org. Chem., 1986, 51, 950.
- 807. Taylor, E. C.; Pont, J. L. Tetrahedron Lett., 1987, 28, 379.
- 808. John, R.; Seitz, G. Archiv. Pharm. (Weinheim, Ger.), 1989, 322, 561.
- 809. Taylor, E. C.; Macor, J. E.; Pont, J. L. Tetrahedron, 1987, 43, 5145.
- 810. Seitz, G.; Dietrich, S.; Gorge, L.; Richter, J. Tetrahedron Lett., 1986, **27**, 2747.
- 811. Shorshnev, S. V.; Esipov, S. E.; Chernyshev, A. I.; Pozharskii, A. F.; Kuz'menko, V. V.; Gulevskaya, A. V. Chem. Heterocycl. Compd. (Engl. Transl.), 1990, 26, 191.
- 812. Neunhoeffer, H.; Lehmann, B. Justus Liebigs Ann. Chem., 1977, 1413.
- 813. Taylor, E. C.; Macor, J. E. J. Org. Chem., 1989, 54, 1249.
- 814. Taylor, E. C.; Macor, J. E. Tetrahedron Lett., 1986, 27, 431.
- 815. Seitz, G.; George, L.; Dietrich, S. Tetrahedron Lett., 1985, 26, 4355.
- 816. Taylor, E. C.; Pont, J. L.; Warner, J. C. Tetrahedron, 1987, 43, 5159.
- 817. Seitz, G.; Dietrich, S. Arch. Pharm. (Weinheim, Ger.), 1985, 318, 1051.
- 818. Seitz, G.; Dietrich, S. Arch. Pharm. (Weinheim, Ger.), 1985, 318, 1048.
- 819. Taylor, E. C.; Macor, J. E. Tetrahedron Lett., 1985, 26, 2419.
- 820. Taylor, E. C.; Macor, J. E. Tetrahedron Lett., 1985, 26, 2415.
- 821. Seitz, G.; John, R. Chem.-Ztg., 1988, 112, 243.
- 822. Konno, S.; Matsuya, Y.; Kumazawa, M.; Amano, M.; Kokubo, T.; Sagi,
  M.; Yamanaka, H. Yakugaku Zasshi, 1993, **113**, 40; Chem. Abstr., 1993, **118**, 234009s.
- 823. Taylor, E. C.; Macor, J. E. J. Org. Chem., 1987, **52**, 4280.

- 824. Charushin, V. N.; van Veldhuizen, B.; van der Plas, H. C.; Stam, C. H. Tetrahedron, 1989, 45, 6499.
- 825. Taylor, E. C.; Pont, J. L.; van Engen, D.; Warner, J. C. J. Org. Chem., 1988, **53**, 5093.
- 826. Taylor, E. C.; Pont, J. L.; Warner, J. C. J. Heterocycl. Chem., 1988, 25, 1733.
- 827. Taylor, E. C.; Warner, J. C.; Pont, J. L. J. Org. Chem., 1988, 53, 800.
- 828. Taylor, E. C.; Pont, J. L.; Warner, J. C. J. Org. Chem., 1988, 53, 3568.
- 829. Taylor, E. C.; McDaniel, K. F.; Warner, J. C. Tetrahedron Lett., 1987, **28**, 1977.
- 830. Taylor, E. C.; Harrington, P. M.; Warner, J. C. Heterocycles, 1988, **27**, 1925.
- 831. Taylor, E. C.; Warner, J. C. Heterocycles, 1987, 26, 2673.
- 832. Seitz, G.; Richter, J. Chem. Ber., 1989, 122, 2177.
- 833. Barlow, M. G.; Haszeldine, R. N.; Simpkin, D. J. J. Chem. Soc., Chem. Commun., 1979, 658.
- 834. Barlow, M. G.; Haszeldine, R. N.; Simpkin, D. J. J. Chem. Soc., Perkin Trans. 1, 1982, 1245.
- 835. Beynon, G.; Figeys, H. P.; Lloyd, D.; Mackie, R. K. Bull. Soc. Chim. Belg., 1979, 88, 905.
- 836. Kolbinger, H.; Reissenweber, G.; Sauer, J. Tetrahedron Lett., 1976, 4321.
- 837. Battiste, M. A.; Barton, T. J. Tetrahedron Lett., 1967, 1227.
- 838. Birkofer, L.; Hansel, E.; Steigel, A. Chem. Ber., 1982, 115, 2574.
- 839. Marcelis, A. T. M.; van der Plas, H. C. Heterocycles, 1985, 23, 683.
- 840. Meresz, O.; Foster-Verner, P. A. J. Chem. Soc., Chem. Commun., 1972, 950.
- 841. Paske, D.; Ringshandl, R.; Sellner, I.; Sichert, H.; Sauer, J. Angew. Chem., Int. Ed. Engl., 1980, **19**, 456.
- 842. Heinrichs, G.; Krapf, H.; Schroder, B.; Steigel, A.; Troll, T.; Sauer, J. Tetrahedron Lett., 1970, 1617.
- 843. Carpino, L. A. J. Am. Chem. Soc., 1963, 85, 2144.
- 844. Seitz, G.; Dhar, R.; Mohr, R.; Overheu, W. Arch. Pharm. (Weinheim, Ger.), 1984, **317**, 237.
- 845. Overhue, W.; Seitz, G.; Wassmuth, H. Chem.-Ztg., 1989, 113, 188.
- 846. Seitz, G.; Wassmuth, H. Arch. Pharm. (Weinheim, Ger.), 1990, 323, 89.
- 847. Seitz, G.; Mohr, R. Arch. Pharm. (Weinheim, Ger.), 1986, 319, 690.
- 848. Neumann, W. P.; Kleiner, F. G. Justus Liebigs Ann. Chem., 1968, 716, 29.

- 849. Molz, T.; Konig, P.; Goes, R.; Gauglitz, G.; Meier, H. Chem. Ber., 1984, 117, 833.
- 850. Sauer, J.; Mielert, A.; Lang, D.; Peter, D. Chem. Ber., 1965, 98, 1435.
- 851. Bachmann, M.; Neunhoeffer, H. Justus Liebigs Ann. Chem., 1979, 675.
- 852. Figeys, H. P.; Mathy, A.; Dralants, A. Synth. Commun., 1981, 11, 655.
- 853. Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. J. Am. Chem. Soc., 1978, **100**, 1597.
- 854. Takahashi, M.; Hikita, Y.; Fukui, M. Heterocycles, 1989, 29, 1379.
- 855. Steigel, A.; Sauer, J.; Kleier, D. A.; Binsch, G. J. Am. Chem. Soc., 1970, 92, 3787.
- 856. Fuhlhuber, H. D.; Sauer, J. Tetrahedron Lett., 1977, 4393.
- 857. Schuster, H.; Sichert, H.; Sauer, J. Tetrahedron Lett., 1983, 24, 1485.
- 858. Takahashi, M.; Suzuki, N.; Igari, Y. Bull. Chem. Soc. Jpn., 1975, **48**, 2605.
- 859. Anderson, D. J.; Hassner, A. Synthesis, 1975, 483.
- 860. Anderson, D. J.; Hassner, A. J. Chem. Soc., Chem. Commun., 1974, 45.
- 861. Moerck, R. E.; Battiste, M. A. J. Chem. Soc., Chem. Commun., 1974, 782.
- 862. Nair, V. J. Heterocycl. Chem., 1975, 12, 183.
- 863. Elix, J. A.; Wilson, W. S.; Warrener, R. N. Synth. Commun., 1972, 2, 73.
- 864. Paquette, L. A.; Kelley, J. F. Tetrahedron Lett., 1969, 4509.
- 865. Sasaki, T.; Kanamatsu, K.; Iizuka, K.; Ando, I. J. Org. Chem., 1976, 41, 1425.
- 866. Sasaki, T.; Kanematsu, K.; Kataoka, T. J. Org. Chem., 1975, 40, 1201.
- 867. Christl, M.; Luddeke, H.; Nagyrevi-Neppel, A.; Freitag, G. Chem. Ber., 1977, **110**, 3745.
- 868. Reinhoudt, D. N.; Kouwenhoven, C. G. Rec. Trav. Chim. Pays-Bas, 1974, 93, 321.
- 869. Berger, U.; Dannhardt, G.; Obergrusberger, R. Arch. Pharm. (Weinheim), 1982, **315**, 428.
- 870. Scharf, H. D.; Mattay, J. Tetrahedron Lett., 1976, 3509.
- 871. Roffey, R.; Verge, J. P. J. Heterocycl. Chem., 1969, 6, 497.
- 872. Satish, S.; Mitra, A.; George, M. V. Tetrahedron, 1979, 35, 277.
- 873. Anastassiou, A. G. Acc. Chem. Res., 1976, 9, 453.
- 874. Anastassiou, A. G.; Reichmanis, E. J. Chem. Soc., Chem. Commun., 1976, 313.
- 875. Anastassiou, A. G.; Girgenti, S. J. Angew. Chem., Int. Ed. Engl., 1975, **14**, 814.
- 876. Butte, W. A.; Case, F. H. J. Org. Chem., 1961, 26, 4690.

- 877. Warrener, R. N.; Elix, J. A.; Wilson, W. S. Aust. J. Chem., 1973, 26, 389.
- 878. McCay, I. W.; Warrener, R. N. Tetrahedron Lett., 1970, 4779.
- 879. McCay, I. W.; Paddon-Row, M. N.; Warrener, R. N. Tetrahedron Lett., 1972, 1401.
- 880. Paddon-Row, M. N.; Warrener, R. N. Tetrahedron Lett., 1972, 1405.
- 881. Paddon-Row, M. N. Tetrahedron Lett., 1972, 1409.
- 882. Warrener, R. N.; Kretschmer, G.; Paddon-Row, M. N. J. Chem. Soc., Chem. Commun., 1977, 806.
- 883. Giles, R. G. F.; Green, I. R. J. Chem. Soc., Perkin Trans. 1, 1974, 228.
- 884. Sasaki, T.; Hayakawa, K.; Manabe, T.; Nishida, S.; Wakabayashi, E. J. Org. Chem., 1981, 46, 2021.
- 885. Warrener, R. N.; Collin, G. J.; Hutchison, G. I.; Paddon-Row, M. N. J. Chem. Soc., Chem. Commun., 1976, 373.
- 886. Warrener, R. N.; Paddon-Row, M. N.; Russell, R. A.; Watson, P. L. Aust. J. Chem., 1981, 34, 397.
- 887. Sasaki, T.; Manabe, T.; Hayakawa, K. Tetrahedron Lett., 1981, **22**, 2579.
- 888. Harrison, P. A.; Russell, R. A.; Warrener, R. N.; Paddon-Row, M. N. Tetrahedron Lett., 1977, 3291.
- 889. Katada, T.; Eguchi, S.; Sasaki, T. J. Org. Chem., 1986, 51, 314.
- 890. Cragg, G. M. L.; Giles, R. G. F.; Roos, G. H. P. J. Chem. Soc., Perkin Trans. 1, 1975, 1339.
- 891. Giles, R. G. F.; Roos, G. H. P. J. Chem. Soc., Chem. Commun., 1975, 260.
- 892. Moursounidis, J.; Wege, D. Tetrahedron Lett., 1986, 27, 3045.
- 893. Warrener, R. N.; Pitt, I. G.; Russell, R. A. Aust. J. Chem., 1991, **44**, 1275.
- 894. Russell, R. A.; Evans, D. A. C.; Warrener, R. N. Aust. J. Chem., 1984, 37, 1699.
- 895. Deyrup, J. A.; Gingrich, H. L. Tetrahedron Lett., 1977, 3115.
- 896. Takahashi, M.; Ishida, H.; Kohmato, M. Bull. Chem. Soc. Jpn., 1976, **49**, 1725.
- 897. Rusinov, G. L.; Postovskii, I. Y.; Kovalev, E. G. Proc. Acad. Sci., USSR, Ser. Chem. (Engl. Transl), 1980, 253, 407.
- 898. Ashe, A. J. III; Bellville, D. J.; Friedman, H. S. J. Chem. Soc., Chem. Commun., 1979, 880.
- 899. Greatbanks, D.; Landquist, J. K. Tetrahedron Lett., 1972, 1659.
- 900. Boger, D. L.; Patel, M. J. Org. Chem., 1988, 53, 1405.
- 901. Boger, D. L.; Coleman, R. S.; Panek, J. S.; Yohannes, D. J. Org. Chem.,

1984, **49**, 4405.

- 902. Boger, D. L.; Panek, J. S.; Patel, M. Org. Synth., 1992, 70, 79.
- 903. Birkofer, L.; Stilke, R. J. Organomet. Chem., 1974, 74, C1-C3.
- 904. Birkofer, L.; Hansel, E. Chem. Ber., 1981, **114**, 3154.
- 905. Avram, M.; Dinulescu, I. G.; Marica, E.; Nenitzescu, C. D. Chem. Ber., 1962, **95**, 2248.
- 906. Seitz, G.; Kampchen, T. Arch. Pharm. (Weinheim, Ger.), 1975, 308, 237.
- 907. Seitz, G.; Overheu, W. Arch. Pharm. (Weinheim, Ger.), 1981, 314, 376.
- 908. Seitz, G.; Overheu, W. Arch. Pharm. (Weinheim, Ger.), 1979, 312, 452.
- 909. Seitz, G.; Overheu, W. Arch. Pharm. (Weinheim, Ger.), 1977, 310, 936.
- 910. Boger, D. L.; Patel, M. Tetrahedron Lett., 1987, 28, 2499.
- 911. Boger, D. L.; Baldino, C. M. J. Am. Chem. Soc., 1993, 115, 11418.
- 912. Hoffmann, R. W. Angew. Chem., Int. Ed. Engl., 1968, **7**, 754 (referenced as a personal communication to RWH from Juergen Sauer).
- 913. Seitz, G.; Overheu, W. Chem.-Ztg., 1979, 103, 230.
- 914. Seitz, G.; Wassmuth, H. Chem.-Ztg., 1988, 112, 281.
- 915. Seitz, G.; Dhar, R.; Dietrich, S. Arch. Pharm. (Weinheim, Ger.), 1983, **316**, 472.
- 916. Boger, D. L.; Panek, J. S. Tetrahedron Lett., 1983, 24, 4511.
- 917. Seitz, G.; Kampchen, T. Arch. Pharm. (Weinheim, Ger.), 1977, 310, 269.
- 918. Huber, F.; Sauer, J.; McDonald, W. S.; Noth, H. Chem. Ber., 1982, **115**, 444.
- 919. Sellner, I.; Schuster, H.; Sichert, H.; Sauer, J.; Noth, H. Chem. Ber., 1983, **116**, 3751.
- 920. Neidlein, R.; Tadesse, L. Helv. Chim. Acta, 1988, 71, 249.
- 921. Johnson, G. C.; Levin, R. H. Tetrahedron Lett., 1974, 2303.
- 922. Martin, H. D.; Hekman, M. Angew. Chem., Int. Ed. Engl., 1976, 15, 431.
- 923. Neuberg, R.; Schroder, G.; Oth, J. F. M. Justus Liebigs Ann. Chem., 1978, 1368.
- 924. Christl, M. Angew. Chem., Int. Ed. Engl., 1973, 12, 660.
- 925. Friedrichsen, W.; von Wallis, H. Tetrahedron, 1978, 34, 2509.
- 926. Semmelhack, M. F.; Weller, H. N.; Clardy, J. J. Org. Chem., 1978, **43**, 3791.
- 927. Benson, S. C.; Palabrica, C. A.; Snyder, J. K. J. Org. Chem., 1987, **52**, 4610.
- 928. Seitz, G.; Kampchen, T. Arch. Pharm. (Weinheim, Ger.), 1976, **309**, 679.
- 929. Pindur, U.; Kim, M. Tetrahedron Lett., 1988, **29**, 3927.
- 930. Inoue, H.; Origuchi, T.; Umano, K. Bull. Chem. Soc. Jpn., 1984, 57, 806.

- 931. Bach, N. J.; Kornfeld, E. C.; Jones, N. D.; Chaney, M. O.; Dorman, D. E.; Paschal, J. W.; Clemens, J. A.; Smalstig, E. B. J. Med. Chem., 1980, 23, 481.
- 932. Gnichtel, H.; Gumprecht, C. Justus Liebigs Ann. Chem., 1985, 628.
- 933. Ban, T.; Nagai, K.; Miyamota, Y.; Harano, K.; Yasuda, M.; Kanematsu, K. J. Org. Chem., 1982, 47, 110.
- 934. Seitz, G.; Kampchen, T. Chem.-Ztg., 1975, 99, 503.
- 935. Seitz, G.; Kampchen, T.; Overheu, W. Arch. Pharm. (Weinheim, Ger.), 1978, **311**, 786.
- 936. Seitz, G.; Kampchen, T.; Overheu, W.; Martin, U. Arch. Pharm. (Weinheim, Ger.), 1981, **314**, 892.
- 937. Takimoto, H. H.; Denault, G. C. Tetrahedron Lett., 1966, 5369.
- 938. Seitz, G.; Gorge, L. Chem.-Ztg., 1987, 111, 16.
- 939. Seitz, G.; Gorge, L. Chem.-Ztg., 1984, 108, 331.
- 940. Clough, S. C.; Kang, J. C.; Johnson, W. R.; Osdene, T. S. Chem. Ind. (London), 1973, 324.
- 941. Rees, C. W.; Yelland, M. J. Chem. Soc., Perkin Trans. 1, 1973, 221.
- 942. McOmie, J. F. W.; Perry, D. H. J. Chem. Soc., Chem. Commun., 1973, 248.
- 943. Jung, M. E.; Lowe, J. A. J. Org. Chem., 1977, 42, 2371.
- 944. Vanmaele, L. J.; De Clerq, P. J.; Vandewalle, M. Tetrahedron Lett., 1982, 23, 995.
- 945. Vanmaele, L. J.; De Clerq, P. J.; Vandewalle, M. Tetrahedron, 1985, **41**, 141.
- 946. Solo, A. J.; Sachdev, H. S.; Gilani, S. S. H. J. Org. Chem., 1965, **30**, 769.
- 947. Tokitoh, N.; Okazaki, R. J. Am. Chem. Soc., 1987, **109**, 1856.
- 948. Liebe, J.; Wolff, C.; Krieger, C.; Weiss, J.; Tochtermann, W. Chem. Ber., 1985, **118**, 4144.
- 949. Barton, D. H. R.; Shioiri, T.; Widdowson, D. A. J. Chem. Soc., Chem. Commun., 1970, 939.
- 950. Barton, D. H. R.; Shioiri, T.; Widdowson, D. A. J. Chem. Soc. (C), 1971, 1968.
- 951. Garry, A. B.; Midgley, J. M.; Whalley, W. B.; Wilkins, B. J. J. Chem. Soc., Perkin Trans. 1, 1977, 809.
- 952. Garry, A. B.; Midgley, J. M.; Whalley, W. B.; Wilkins, B. J. J. Chem. Soc., Chem. Commun., 1972, 167.
- 953. Anastasia, M.; Derossi, M. J. Chem. Soc., Chem. Commun., 1979, 164.
- 954. Yamada, S.; Nakayama, K.; Takayama, H. Tetrahedron Lett., 1981, 22, 2591.

- 955. Morris, D. S.; Williams, D. H.; Norris, A. F. J. Chem. Soc., Chem. Commun., 1981, 424.
- 956. Barton, D. H. R.; Lusinchi, X.; Ramirez, J. S. Tetrahedron Lett., 1983, 24, 2995.
- 957. de Costa, B. R.; Makk, N.; Midgley, J. M.; Modi, N. T.; Watt, R. A.; Walley, W. B. J. Chem. Soc., Perkin Trans. 1, 1985, 1331.
- 958. Kubodera, N.; Miyamoto, K.; Watanabe, H.; Kato, M.; Sasahara, K.; Ochi, K. J. Org. Chem., 1992, **57**, 5019.
- 959. Snyder, J. P.; Lee, L.; Banduroo, V. T.; Yu, C. Y.; Boyd, R. J. J. Am. Chem. Soc., 1972, 94, 3260.
- 960. Olsen, H.; Snyder, J. P. J. Am. Chem. Soc., 1974, 96, 7839.
- 961. Sket, B.; Zupan, M.; Pollak, A. J. Heterocycl. Chem., 1976, 13, 671.
- 962. Corrie, J. E. T.; Kirby, G. W.; Laird, A. E.; Mackinnon, L. W.; Tyler, J. K. J. Chem. Soc., Chem. Commun., 1978, 275.
- 963. Defoin, A.; Augelmann, G.; Fritz, H.; Geffroy, G.; Schmidlin, C.; Streith, J. Helv. Chim. Acta, 1985, 68, 1998.
- 964. Kirby, G. W.; Bentley, K. W.; Horsewood, P.; Singh, S. J. Chem. Soc., Perkin Trans. 1, 1979, 3064.
- 965. Bentley, K. W.; Horsewood, P.; Kirby, G. W.; Singh, S. J. Chem. Soc., Chem. Commun., 1969, 1411.
- 966. Horsewood, P.; Kirby, G. W.; Sharma, R. P.; Sweeny, J. G. J. Chem. Soc., Perkin Trans. 1, 1981, 1802.
- 967. Corrie, J. E. T.; Kirby, G. W.; Sharma, R. P. J. Chem. Soc., Chem. Commun., 1975, 915.
- 968. O'Bannon, P. E.; Dailey, W. P. Tetrahedron Lett., 1988, 29, 5719.
- 969. Corrie, J. E. T.; Kirby, G. W.; Mackinnon, J. W. M. J. Chem. Soc., Perkin Trans. 1, 1985, 883.
- 970. Kirby, G. W.; McGuigan, H.; McLean, D. J. Chem. Soc., Perkin Trans. 1, 1985, 1961.
- 971. Keck, G. E.; Yates, J. B. Tetrahedron Lett., 1979, 4627.
- 972. Freer, A. A.; Islam, M. A.; Kirby, G. W.; Mahajan, M. P. J. Chem. Soc., Perkin Trans. 1, 1991, 1001.
- 973. Keck, G. E.; Webb, R. R.; Yates, J. B. Tetrahedron, 1981, 37, 4007.
- 974. Kirby, G. W. Chem. Soc. Rev., 1977, 6, 1.
- 975. Ranganathan, D.; Ranganathan, S.; Rao, C. B. Tetrahedron, 1981, **37**, 637.
- 976. Kirby, G. W.; Mackinnon, J. W. M. J. Chem. Soc., Chem. Commun., 1977, 23.
- 977. Corrie, J. E. T.; Kirby, G. W.; Sharma, R. P. J. Chem. Soc., Perkin Trans. 1, 1982, 1571.

- 978. Keck, G. E.; Yates, J. B. J. Org. Chem., 1982, 47, 3590.
- 979. Keck, G. E.; Nickell, D. G. J. Am. Chem. Soc., 1980, 102, 3632.
- 980. Keck, G. E.; Webb, R. R. II J. Am. Chem. Soc., 1981, 103, 3173.
- 981. Christie, C. C.; Kirby, G. W.; McGuigan, H.; Mackinnon, J. W. M. J. Chem. Soc., Perkin Trans. 1, 1985, 2469.
- 982. Kirby, G. W.; McGuigan, H.; Mackinnon, J. W. M.; McLean, D.; Sharma, R. P. J. Chem. Soc., Perkin Trans. 1, 1985, 1437.
- 983. Kirby, G. W.; Mackinnon, J. W. M.; Sharma, R. P. Tetrahedron Lett., 1977, 215.
- 984. Kirsch, G.; Golde, R.; Neef, G. Tetrahedron Lett., 1989, 30, 4497.
- 985. Gilchrist, T. L.; Peck, M. E.; Rees, C. W. J. Chem. Soc., Chem. Commun., 1975, 913.
- 986. Carpanelli, C.; Gaiani, G. Gazz. Chim. Ital., 1982, **112**, 191.
- 987. Mock, W. L.; Nugent, R. M. J. Am. Chem. Soc., 1975, 97, 6521.
- 988. Macaluso, A.; Hamer, J. J. Org. Chem., 1966, 31, 3049.
- 989. Hamer, J.; Ahmad, M. Acta Cient. Venezolano, 1965, 15, 247.
- 990. Srinivasan, R.; Brown, K. H.; Ors, J. A.; White, L. S.; Adam, W. J. Am. Chem. Soc., 1979, **101**, 7424.
- 991. Takahashi, Y.; Morishima, S.; Miyashi, T. J. Photochem. Photobiol. (A), 1992, **65**, 157.
- 992. Wasserman, H. H.; Scheffer, J. R.; Cooper, J. L. J. Am. Chem. Soc., 1972, 94, 4991.
- 993. Wasserman, H. H.; Vinick, F. J.; Chang, Y. C. J. Am. Chem. Soc., 1972, 94, 7180.
- 994. Rigaudy, J.; Perlat, M.; Simon, D.; Cuong, N. K. Bull. Soc. Chim. Fr., 1976, 493.
- 995. Dufraisse, C.; Rigaudy, J.; Bassetier, I. I.; Cuong, N. K. C. R. Hebd. Seances. Acad. Sci., 1965, **260**, 5031.
- 996. Barton, T. J.; Kilgour, J. A. J. Am. Chem. Soc., 1976, 98, 7746.
- 997. Barton, T. J.; Kilgour, J. A. J. Am. Chem. Soc., 1974, 96, 2278.
- 998. Peddle, G. J. D.; Roark, D. N.; Good, A. M.; McGeachin, S. G. J. Am. Chem. Soc., 1969, **91**, 2807.
- 999. Matsumoto, H.; Arai, T.; Watanabe, H.; Nagai, Y. J. Chem. Soc., Chem. Commun., 1984, 724.
- 1000 Smith, C. L.; Pounds, J. J. Chem. Soc., Chem. Commun., 1975, 910.
- 1001 Quin, L. D.; Kisalus, J. C.; Mesch, K. A. J. Org. Chem., 1983, 48, 4466.

1002 Kashman, Y.; Awerbouch, O. Tetrahedron, 1975, 31, 53.

- 1003 Quin, L. D.; Szewczyk, J.; Szewczyk, K. M.; McPhail, A. T. J. Org. . Chem., 1986, **51**, 3341.
- 1004 Quin, L. D.; Pete, B.; Szewczyk, J.; Hughes, A. N. Tetrahedron Lett., . 1988, **29**, 2627.

1005 Quin, L. D.; Bourdieu, C.; Quin, G. S. Tetrahedron Lett., 1990, 31, 6473.

1006 Bodalski, R.; Quin, L. D. J. Org. Chem., 1991, 56, 2666.

- 1007 Clapp, C. H.; Satterthwait, A.; Westheimer, F. H. J. Am. Chem. Soc., . 1975, **97**, 6873.
- 1008 Clapp, C. H.; Westheimer, F. H. J. Am. Chem. Soc., 1974, 96, 6710.

1009 Quin, L. D.; Marsi, B. G. J. Am. Chem. Soc., 1985, 107, 3389.

- 1010 Niecke, E.; Ruger, R. Angew. Chem., Int. Ed. Engl., 1983, 22, 155.
- 1011 Jung, F.; Molin, M.; Van der Elzen, R.; Durst, T. J. Am. Chem. Soc., . 1974, **96**, 935.

1012 Ogata, M.; Matsumoto, H.; Kida, S. Heterocycles, 1979, 12, 1285.

- 1013 Kametani, T.; Higa, T.; Fukumoto, K.; Koizumi, M. Heterocycles, 1976, . **4**, 23.
- 1014 Kametani, T.; Higa, T.; Loc, C. V.; Ihara, M.; Kaizumi, M.; Fukumoto, K. J. Am. Chem. Soc., 1976, **98**, 6186.
- 1015 Weidinger, H.; Kranz, J. Chem. Ber., 1963, 96, 2070.
- 1016 Urove, G. A.; Welker, M. A.; Eaton, B. E. J. Organomet. Chem., 1990, . **384**, 105.
- 1017 Urove, G. A.; Welker, M. E. Organometallics, 1988, 7, 1013.