CHEMICAL REVIEWS

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CHEMISTRY OF CYCLOPENTADIENONES

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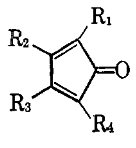
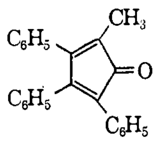
CONTENTS

I. Introduction

This article covers the synthesis, reactions, and physical properties of the class of compounds known as cyclopentadienones (I). The carbonyl carbon atom is numbered as 1 and the remainder of the atoms in the ring follow in order. Thus, II is 2-methyltriphenylcyclopentadienone, and III is tetraphenylcyclopentadienone. This name is rather cumbersome for continual citation and therefore the trivial name will be used. Thus, III will be referred to as tetracyclone, the ending cyclone generally being accepted in the literature for cyclopentadienone, and tetracyclone being used almost exclusively for tetraphenylcyclopentadienone.



I



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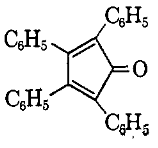
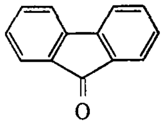
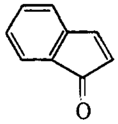


III

The consideration of cyclopentadienones containing fused rings on the cyclopentadienone moiety has been restricted in the aromatic series to those compounds in which the rings are fused on the *c*-face of the five-membered ring. Thus the class of compounds comprising fluorenone (IV) and indenone (V) and derivatives of them have not been included. This omission was made since one or both double bonds of the five-membered ring may properly be considered as part of the aromatic system and therefore the chemistry of these compounds would not be characteristic of cyclopentadienones.

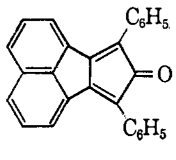


IV

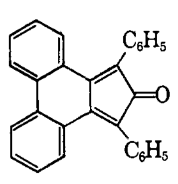


V

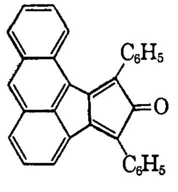
Among the cyclopentadienones having fused rings on the *c*-face which are discussed are 7,9-diphenyl-8H-cyclopent[*a*]acenaphthylen-8-one (VI), 1,3-diphenyl-2H-cyclopenta[*l*]phenanthren-2-one (VII), and 1,3-diphenyl-2H-cyclopent[*a*]aceanthrylen-2-one (VIII). The trivial names for these compounds are acecyclone (VI), phencyclone (VII), and aceanthrenecyclone (VIII) and they will be used exclusively in this paper.



VI

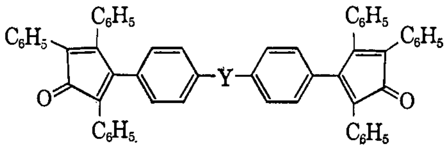


VII

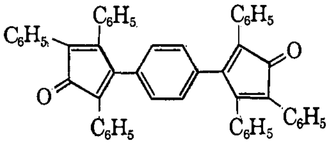


VIII

The class of compounds referred to by the trivial name "bistetracyclones" has the formulas IXa–h and the formal names listed below.



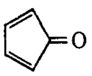
IXa,b,c,d,e,f, and g



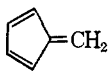
IXh

a, Y = nil	3,3′-(4,4′-biphenylene)bis[2,4,5-triphenylcyclopentadienone]
b, Y = CH_2	4,4′-methylenedi-*p*-phenylenebis-[2,4,5-triphenylcyclopentadienone]
c, Y = O	3,3′-(oxydi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone]
d, Y = S	3,3′-(thiodi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone]
e, Y = $(CH_2)_2$	3,3′-(4,4′-ethylenedi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone]
f, Y = $(CH_2)_3$	3,3′-(4,4′-propylenedi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone]
g, Y = $(CH_2)_4$	3,3′-(4,4′-butylenedi-*p*-phenylene)bis[2,4,5-triphenylcyclopentadienone]
h	3,3′-(1,4-phenylene)bis[2,4,5-triphenylcyclopentadienone]

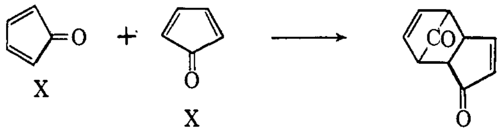
The molecular orbital calculations of the parent compound cyclopentadienone (X) (82, 106, 107) predict that this compound will be extremely reactive. The details are given in the discussion of the physical properties. The 2,3-bond would be particularly reactive and the compound would show a stronger dienic ability than fulvene (XI) in a Diels–Alder reaction (82). In view of these conclusions, it may be expected that cyclopentadienone and simple cyclopentadienones would dimerize to yield compounds such as XII.



X

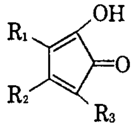


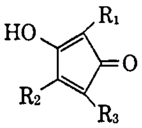
XI

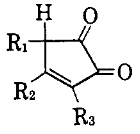


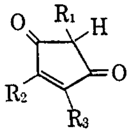
This observation is borne out by the experimental facts in that almost all of the simple cyclopentadienones that have been prepared are dimeric.

Also included in this article are hydroxycyclopentadienones such as XIII and XIV. These cyclopentadienones are actually enols and as such should participate in a keto–enol equilibrium. Experimentally it is found that this equilibrium favors the ketonic forms XV and XVI.


XIII


XIV


XV


XVI

The compounds represent an unusual system of crossed conjugated double bonds in a five-membered ring. The elusive parent compound has been sought assiduously for theoretical reasons with little success. The stable tetraaryl derivatives are powerful dienophiles and have been used, not only for the synthesis of highly aromatic, highly arylated compounds, but also for the examination of the mechanism of the Diels–Alder reaction itself. All of the cyclones are colored and many have been studied for the effect of substituents and fused rings on the ultraviolet and visible absorption of tetracyclone. The cyclones have frequently been studied by means of molecular orbital methods in attempts to understand their unusual reactivity, color, and dipole moments. It is to summarize in one place the references to this many-purposed class of compounds that this article was written.

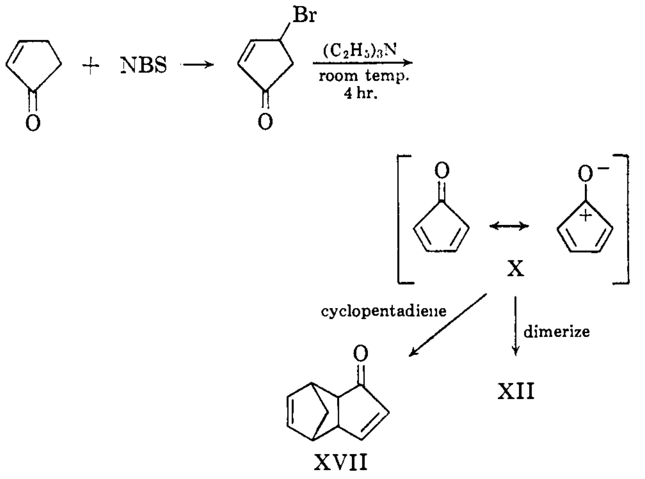
II. SYNTHESIS

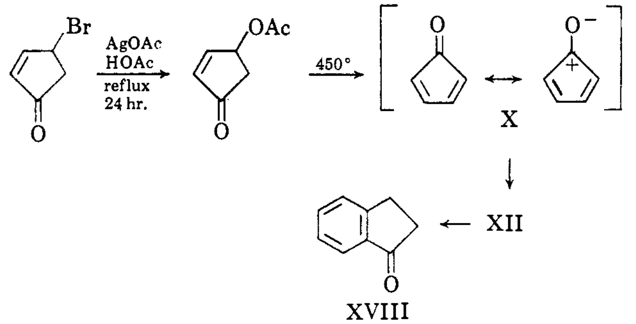
A. CYCLOPENTADIENONES CONTAINING NO ARYL GROUPS

1. *Cyclopentadienone*

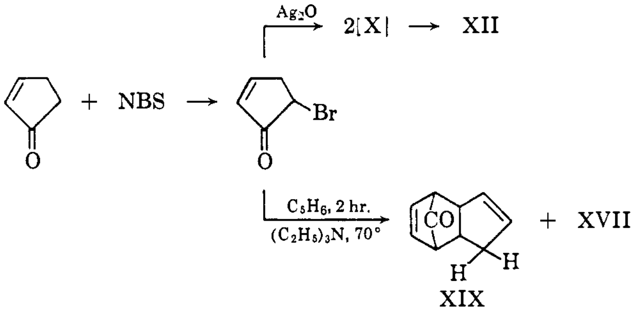
The parent compound cyclopentadienone has escaped synthesis and isolation; reactions which lead to it produce its dimer, as expected, or a product formed sequentially from it.

One method of preparation of cyclopentadienone consists of the dehydrobromination of 4-bromo-2-cyclopentenone by treatment with triethylamine (96, 97). The transient existence of this compound was demonstrated by trapping it with cyclopentadiene which yielded the expected product 3-oxotricyclo-[5.2.1.0^{2,6}]deca-4,8-diene (XVII) as well as the dimer XII of cyclopentadienone. Along with this preparation was also reported the pyrolysis of 4-acetoxy-2-cyclopentenone. The reaction yielded indanone (XVIII), suggesting prior formation and dimerization of cyclopentadienone and its subsequent aromatization (96, 97).

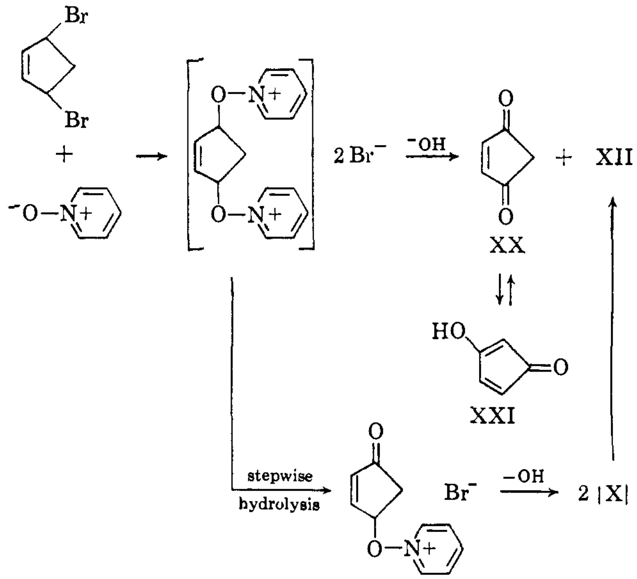




Dicyclopentadienone (XII) has also resulted from the treatment of 4-bromo-2-cyclopentenone, incorrectly characterized (96) in these references as the 5-bromo form shown below, with silver oxide (167, 168). When the dehydrobromination of the same intermediate was carried out using triethylamine in the presence of cyclopentadiene as the trapping agent, not only was XVII formed as previously mentioned but also the isomeric form XIX (166–168). This isomer XIX, not previously observed, occurs from a Diels–Alder reaction between cyclopentadienone and cyclopentadiene in which the cyclopentadiene functions as the dienophile.

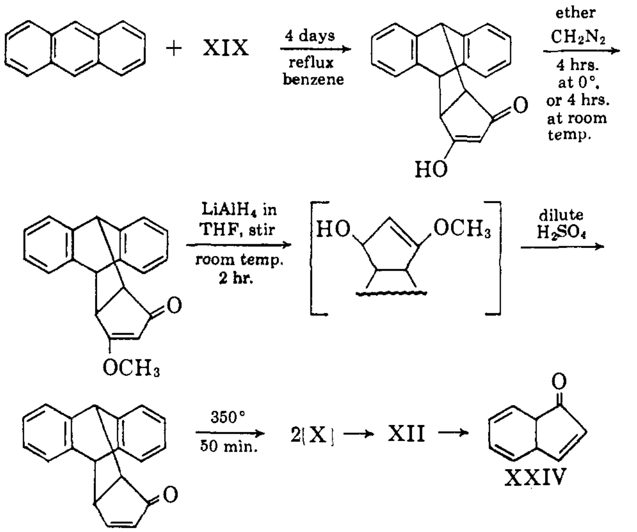


Treatment of 3,5-dibromocyclopentene with pyridine N-oxide and then base afforded 3,5-diketocyclopentene (XX) and the dimer XII (105). Compound XII was postulated as being formed from the nonisolable cyclopentadienone (X), which in turn may have been formed from the reaction of XXII with base. Compound XX may be viewed as the ketonic form of 3-hydroxycyclopentadienone (XXI).



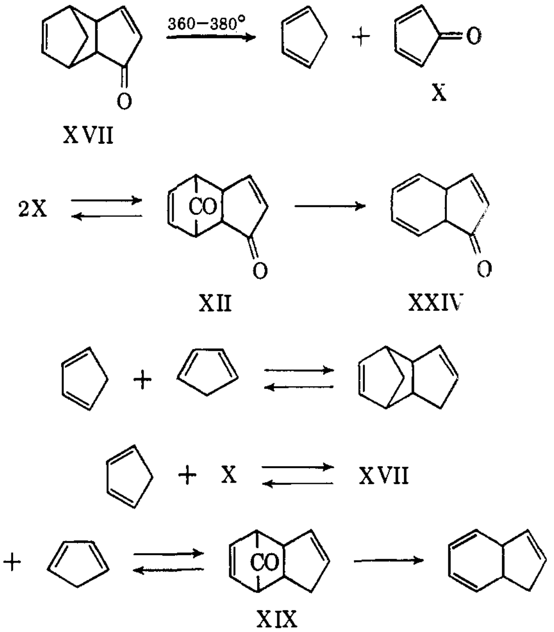
XX XII XXI XXII

By the use of a novel retro-Diels–Alder reaction of compound XXIII, cyclopentadienone (X) has been formed (98). However, under the conditions of the reaction, not only did dimerization occur but also aromatization to yield the dihydroindenone XXIV.



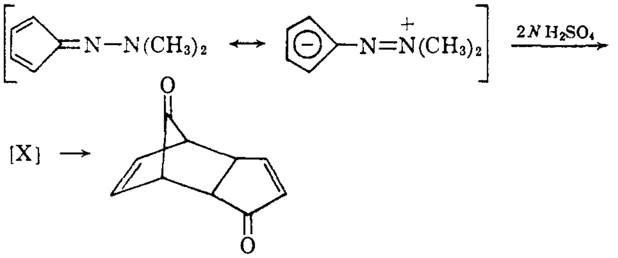
XXIII XXIV

Another retro-Diels–Alder reaction which has been used to attempt to prepare cyclopentadienone has been the pyrolysis of XVII (13). From the structures of the products it has been postulated that the cyclopentadienone and the cyclopentadiene formed are capable of undergoing dimerization or reaction with each other.



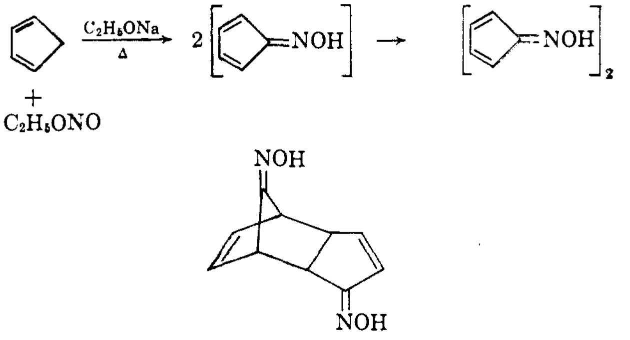
XVII X XII XXIV XVII XIX

Another reaction which produces the cyclopentadienone dimer XII is the sulfuric acid hydrolysis of cyclopentadienone N,N-dimethylhydrazone (169).



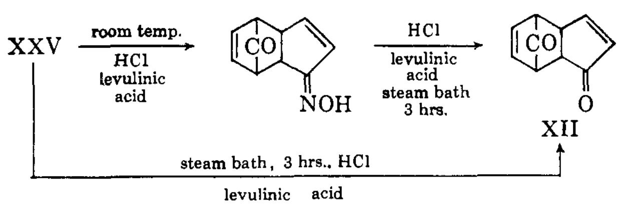
XII

It is interesting to note that the oxime of cyclopentadienone also dimerizes in a similar fashion. This oxime when prepared from cyclopentadiene afforded a dimer (270) to which the structure XXV was later assigned (14). This work has been confirmed more recently (139).



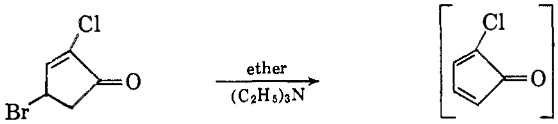
XXV

Hydrolysis of this dimeric oxime gave by *trans*-oximation the dimer XII of cyclopentadienone (100).



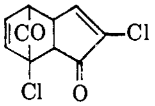
2. Chlorocyclopentadienones

Like the parent compound, cyclopentadienone (X), simple chloro-substituted cyclopentadienones are also dimeric and have not been isolated in the monomeric state. The least halogenated member of this class of compounds to have been prepared is 2-chlorocyclopentadienone (XXVI). Its synthesis is quite similar to that for cyclopentadienone (X) in that it consists of the dehydrobromination of 4-bromo-2-chloro-2-cyclopentenone with triethylamine in ether solution (97).

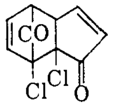


XXVI

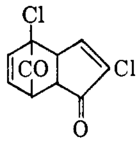
With the exclusion of *endo* and *exo* isomers there are four possible structures of the dimer of XXVI which one must consider, namely XXVII, XXVIIa, XXVIII, and XXVIIIa. An ultraviolet spectrum of the dimer eliminates both XXVIIa and XXVIIIa as possibilities (94).



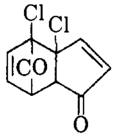
XXVII



XXVIIa

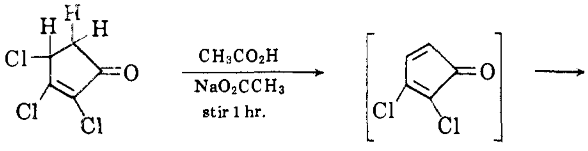


XXVIII

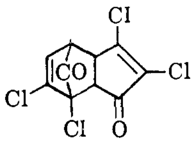


XXVIIIa

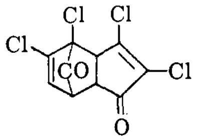
The transient 2,3-dichlorocyclopentadienone (XXIX) has been prepared by dehydrochlorination of 2,3,4-trichloro-2-cyclopentenone, and in this case also the structure of the dimer is not known but proposed as either XXX or XXXI (213). In a similar manner, 2,3-dichloro-5-bromocyclopentadienone (XXXII) was synthesized, the resulting dimer being either XXXIII or XXXIV (213).



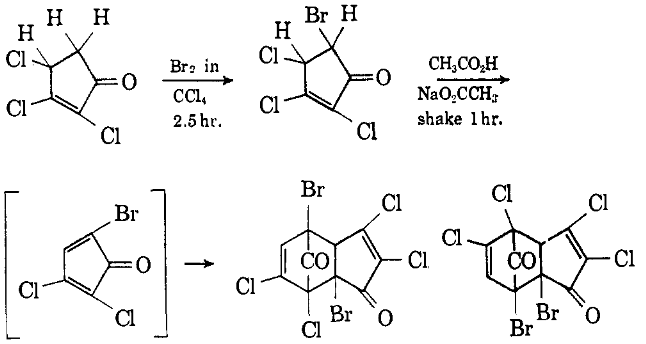
XXIX



XXX

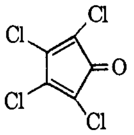


XXXI

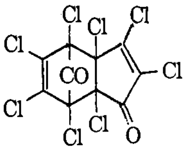


XXXII XXXIII XXXIV

In the case of tetrachlorocyclopentadienone (XXXV), the dimer has an unambiguous structure (XXXVI) without the consideration of *endo* or *exo* forms.

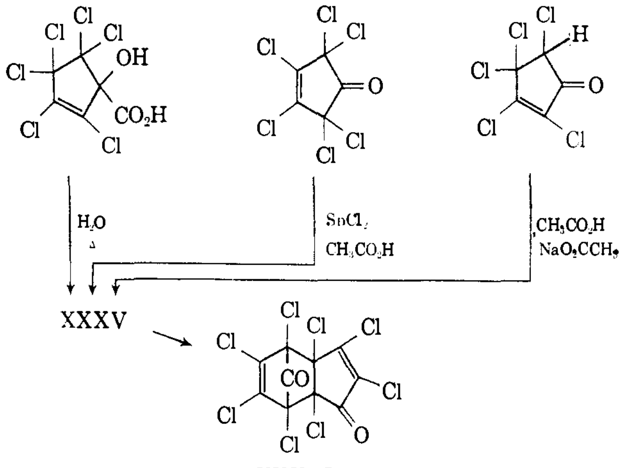


XXXV



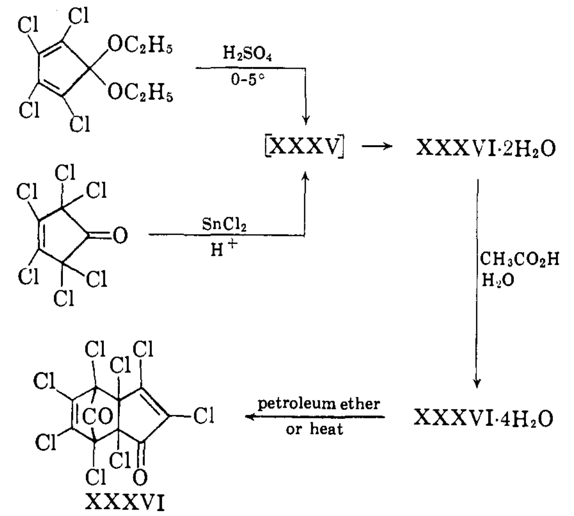
XXXVI

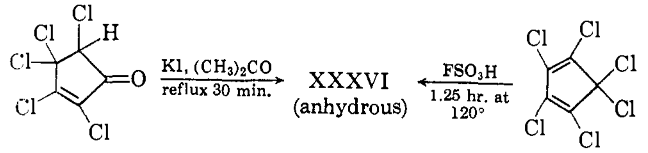
Several reaction paths are known for the synthesis of XXXV. Heating hexachloro-1-hydroxy-2-cyclopentene-1-carboxylic acid in water, removal of two chlorines from hexachloro-3-cyclopentenone with stannous chloride, and dehydrochlorination of 2,3,4,4,5-pentachloro-2-cyclopentenone with sodium acetate all yield the same product (290).



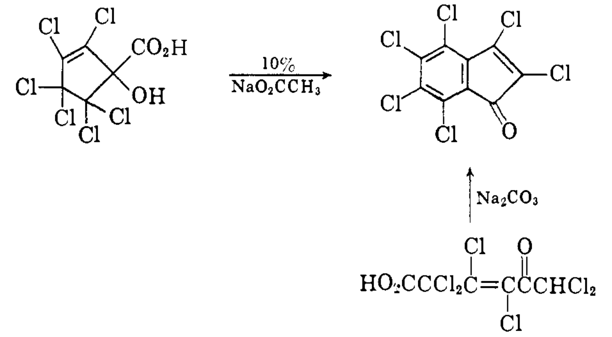
XXXVI

Actually, it was demonstrated that XXXVI was a dihydrate which could be dehydrated; it could also be prepared directly in anhydrous form (220).

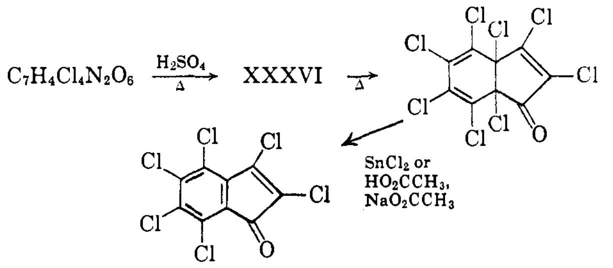




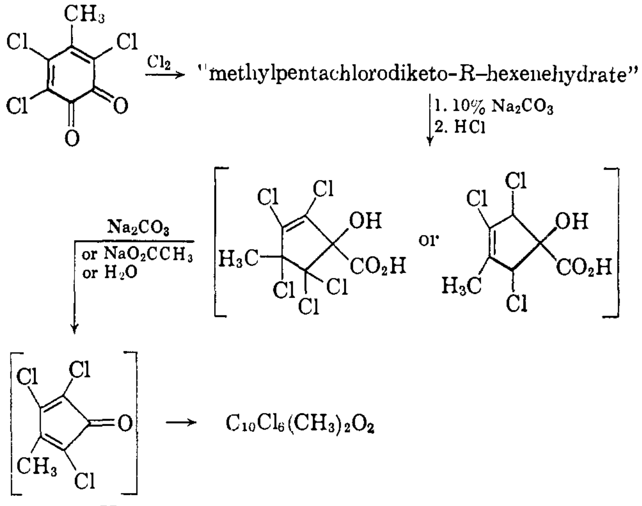
If the previously cited precursor, hexachloro-1-hydroxy-2-cyclopentene-1-carboxylic acid, is heated in 10% sodium acetate solution, then hexachloroindenone is the product (289). This is also produced when 2,2,3,4,-6,6-hexachloro-5-oxo-3-hexenoic acid is treated with sodium carbonate (288).



This reaction proceeds through tetrachlorocyclopentadienone (41), which then dimerizes and aromatizes. The intermediate in the aromatization, octachloro-3a,7a-dihydroindenone, has been isolated and converted to hexachloroindenone (291).

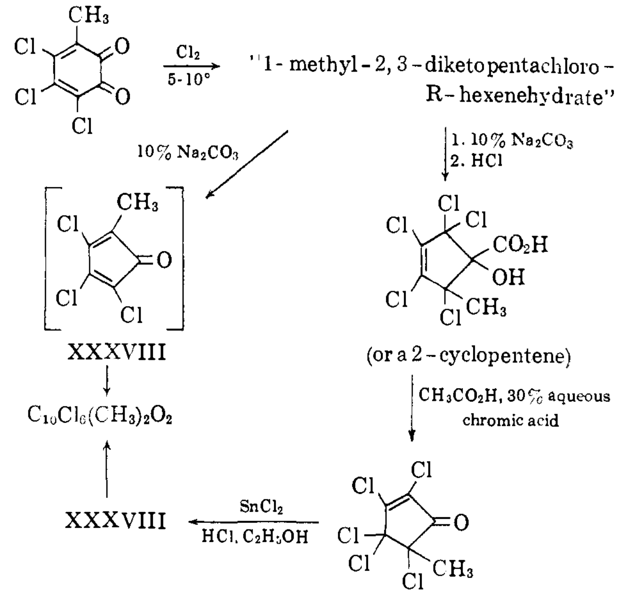


The treatment of pentachloro-4-methyl-1-hydroxy-2-cyclopentene-1-carboxylic acid, which may have been the 3-cyclopentene isomer, with either sodium carbonate, sodium acetate solution, or just water yielded a dimeric product: $C_{10}Cl_6(CH_3)_2O_2$ (68). This dimer had been proposed to be the same as that from the nonisolable 3-methyltrichlorocyclopentadienone (XXXVII) (41). The dimer of 2-methyltrichlorocyclopentadienone (XXXVIII) is also known. It has been synthesized from the same reaction sequence that was used for the 3-methyl isomer (237) utilizing an



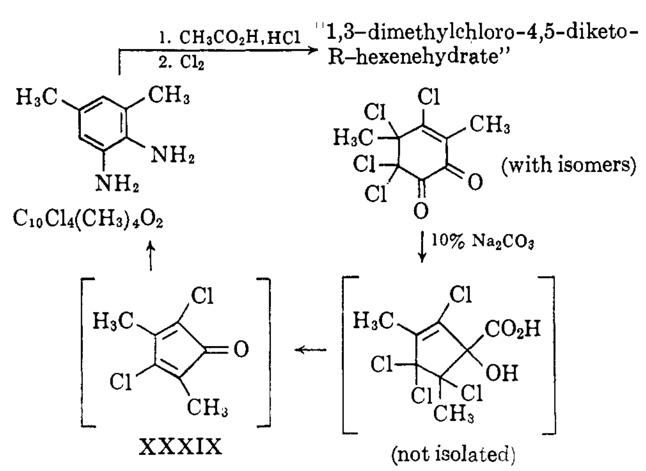
XXXVII

isomeric starting material. The dimer was subsequently proposed as that which would result from XXXVIII (41).



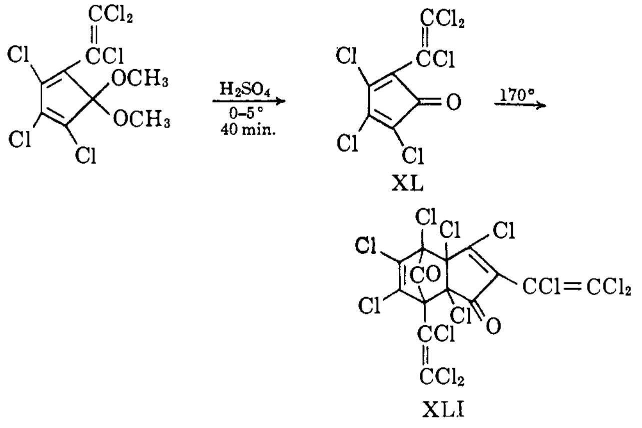
This same reaction scheme has also been applied to 1,2-diamino-3,5-dimethylbenzene (155) to prepare the dimer of the nonisolable 2,4-dimethyl-3,5-dichlorocyclopentadienone (XXXIX) (41).

An exceptionally stable compound in this class of



XXXIX

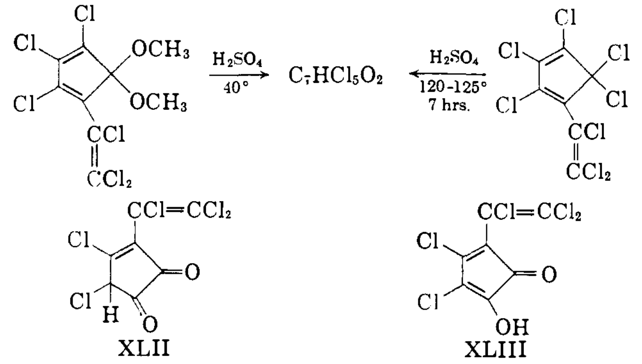
compounds is the highly chlorinated 1-(trichlorovinyl)-2,3,4-trichlorocyclopentadienone (XL) (214, 221). It is unusual since it is reported that the monomer can be isolated and dimerizes to XLI only upon heating.



XL

XLI

If the initial reaction with sulfuric acid is run at a higher temperature, a diketone with the empirical formula $C_7HCl_5O_2$ is obtained (221). Although no structure is given, one possibility might be XLII, the ketonic form of XLIII. This same diketone may also be prepared from 2-(trichlorovinyl)pentachlorocyclopentadiene (221).

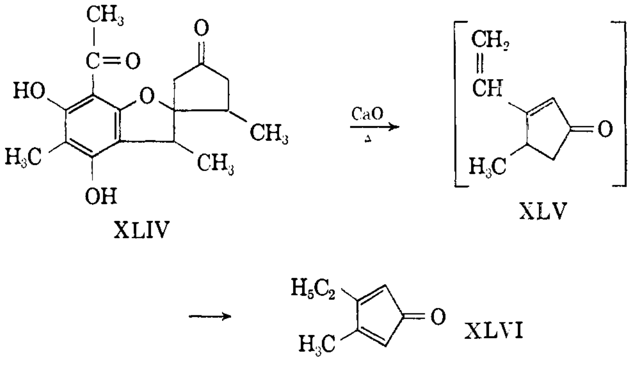


XLII

XLIII

3. *Other Alkylcyclopentadienones*

The dry distillation over lime of the naturally occurring compound tetrahydrodecarbousnol (XLIV) is reported to yield the peppermint flavored 3-methyl-4-ethylcyclopentadienone (XLVI), with XLV being postulated as an intermediate (56, 226). It is rather unusual that this compound is reported as a monomer in view of its high boiling point, 115° (30 mm.); it is more likely a dimer.

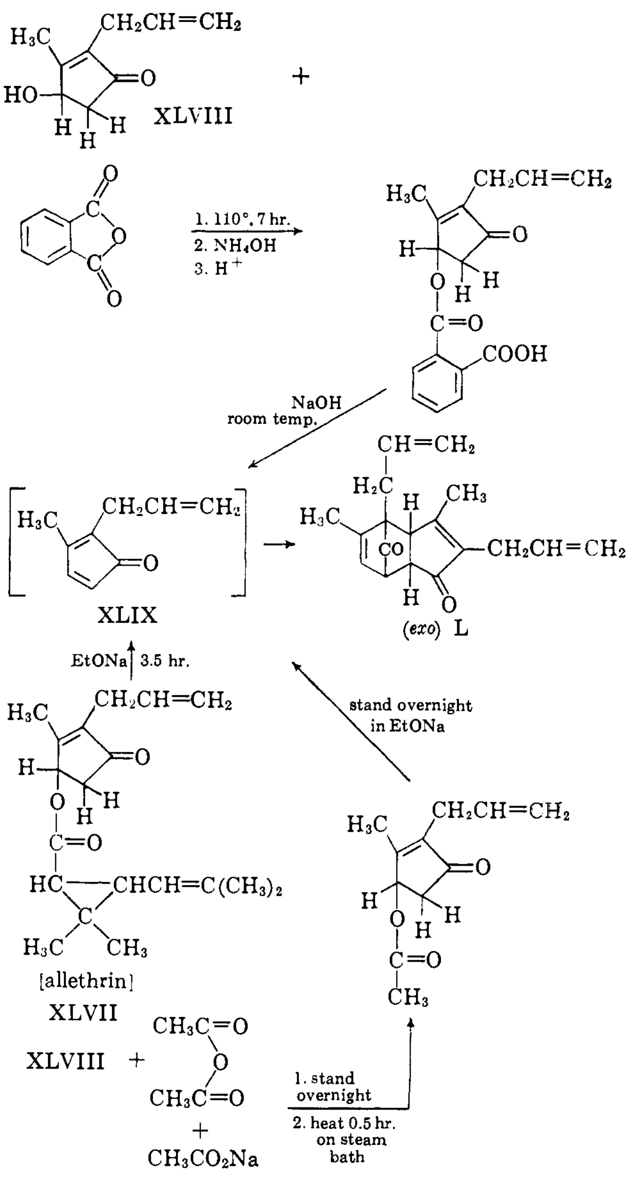


XLIV

XLV

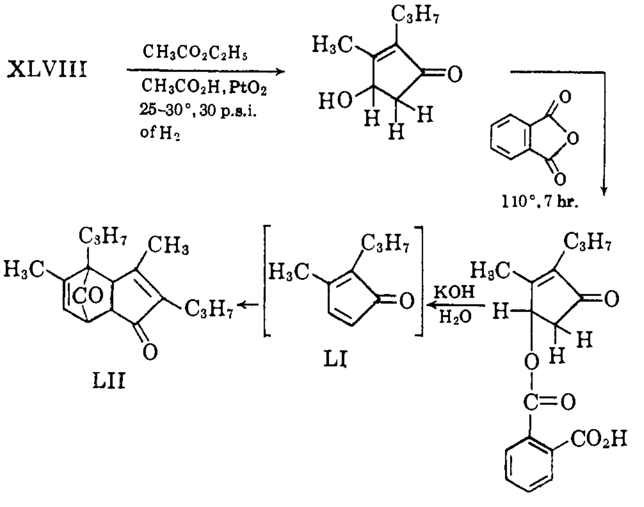
XLVI

SCHEME I

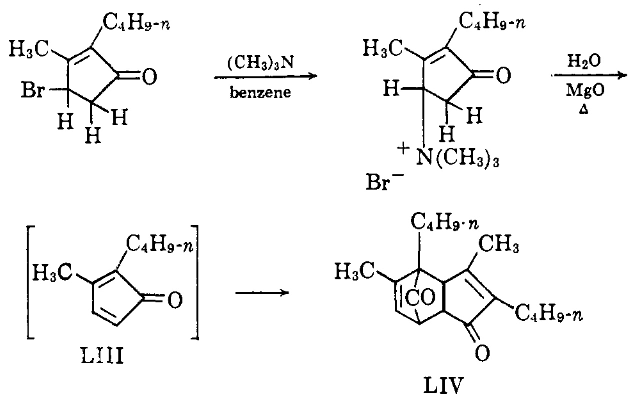


Another naturally occurring compound which has been used for the synthesis of a cyclopentadienone is allethrin (XLVII). Both allethrin and its saponified product alletrolone (XLVIII) have been used to prepare 2-allyl-3-methylcyclopentadienone (XLIX), which is stable as the *exo* dimer L (47, 202) (Scheme I).

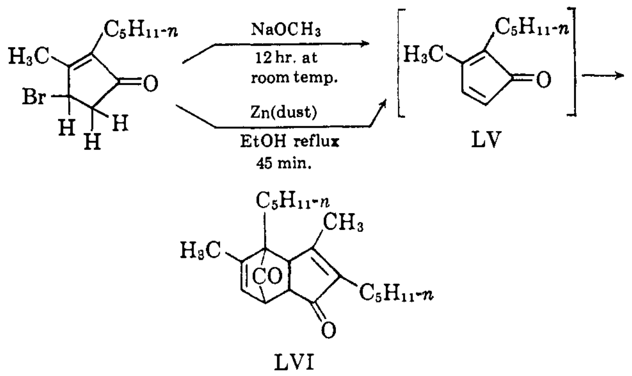
The allyl group of XLVIII has been reduced, and the resulting 2-propyl-3-methyl-4-hydroxy-2-cyclopentenone has been converted to the dimer (LII) of 2-propyl-2-methylcyclopentadienone (LI) (47).

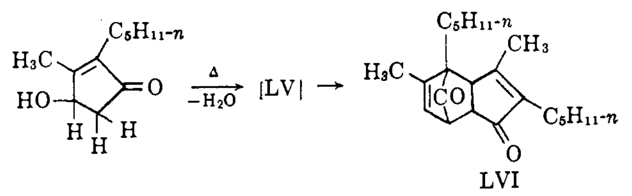


Although it was not completely characterized, the dimer LIV of 2-*n*-butyl-3-methylcyclopentadienone (LIII) is known. It was synthesized by the dehydrobromination of 2-*n*-butyl-3-methyl-4-bromo-2-cyclopentenone (90).

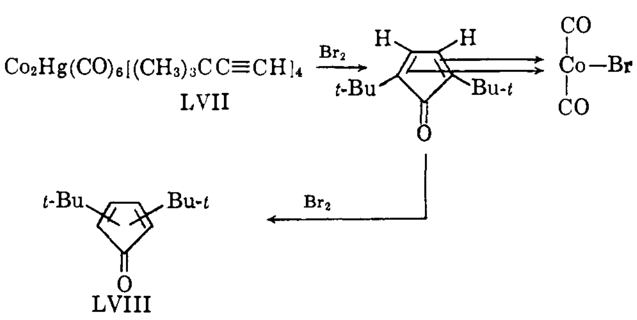


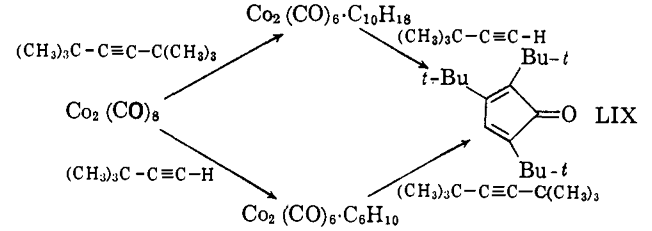
Dehydrobromination of 2-*n*-pentyl-3-methyl-4-bromo-2-cyclopentenone with either sodium methoxide or zinc in ethanol affords 2-*n*-pentyl-3-methylcyclopentadienone (LV) which also exists as a dimer LVI (90). This particular dimer has also been prepared by the dehydration of 2-*n*-pentyl-3-methyl-4-hydroxy-2-cyclopentenone (264).





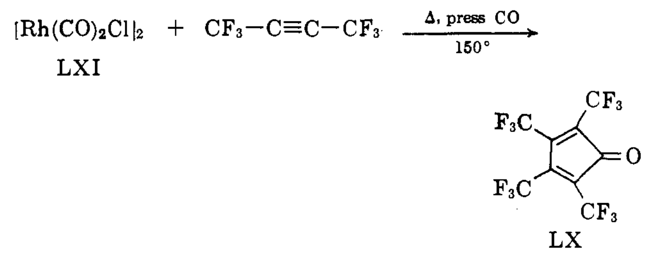
A cyclopentadienone containing *t*-butyl groups has been prepared, utilizing the novel dicobaltmercurohexacarbonyltetrakis(*t*-butylacetylene) (LVII) as the starting material (200). The product, which is a bis(*t*-butyl)cyclopentadienone (LVIII), was isolated but was not completely characterized. Dicobaltoctacarbonyl itself has been utilized in the synthesis of 2,3,5-tris(*t*-butyl)cyclopentadienone (LIX) (174). Like LVIII, this cyclopentadienone is also monomeric, probably owing to a steric inhibition toward dimerization.



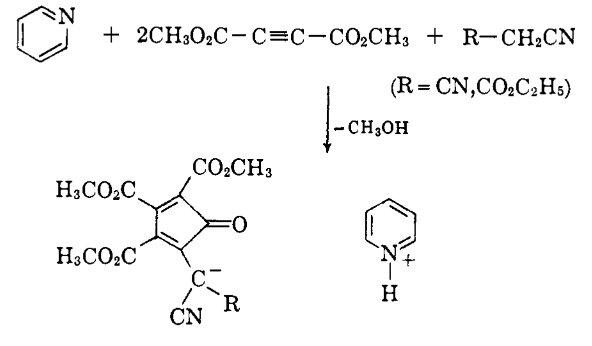


Another known monomeric cyclopentadienone is the tetrakis(trifluoromethyl)cyclopentadienone (LX), which was obtained as a by-product of the thermal reaction of excess bis(trifluoromethyl)-2-butyne with the metal carbonyl LXI (76, 108). The evidence for LX includes the F^{19} resonance spectrum (76), and a mass spectrometric measurement which showed the presence of a parent ion of mass 352 (108). That LX is monomeric may be due to the electron-withdrawing effect of the trifluoromethyl groups.

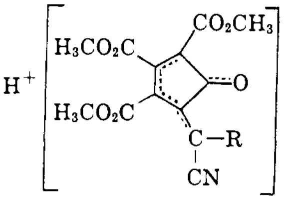
A novel set of salts containing a cyclopentadienone ring in the anion portion was recently prepared by the



reaction of pyridine, dimethylbutynedioic acid, and substituted acetonitriles (204). The solution of the acid forms are colorless and very strongly acidic (204).

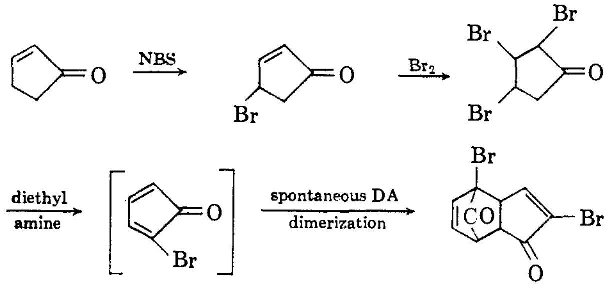


deep blue (R = CN,CO2C2H5)



R	p*K*a
CN	1.98
$CO_2C_2H_5$	2.4

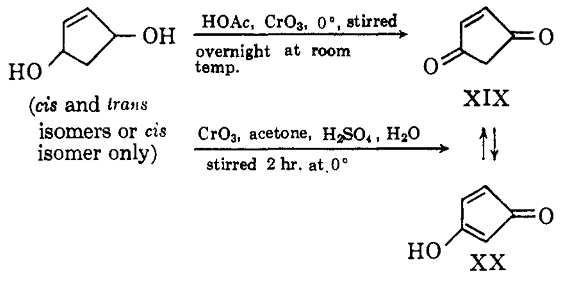
Treatment of 2,3,4-tribromocyclopentanone with diethylamine produces 2-bromocyclopentadienone which undergoes a spontaneous Diels-Alder dimerization to give the dimer XXVIIIb (145).



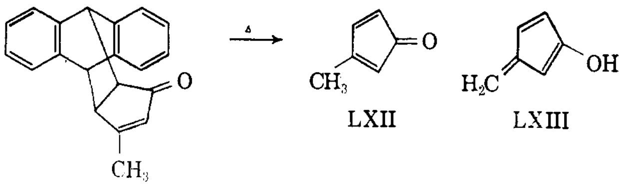
XXVIIIb

Several hydroxycyclopentadienones devoid of aryl groups are known. The simplest member of this group is the 3-hydroxycyclopentadienone (XX) which appears exclusively in the ketonic form XIX (103, 105). Its synthesis involves oxidation of 3,5-cyclopentenediol with chromic acid (103, 104, 150). As with most hydroxycyclopentadienones, this stability of the ketonic form seems to account for the lack of dimerization.

3-Methylcyclopentadienone (LXII) has been synthesized by a retro-Diels-Alder reaction (230) similar to that used for the synthesis of cyclopentadienone (98).



The structure was given as monomeric but is not conclusively proved. In view of the fact that it is reported to be yellow, easily polymerizable, and to have a boiling point of 218-220° (230), it could possibly be LXIII, the tautomer of LXII.



The condensation of 2 moles of ethyl orthoformate with 1 mole of diacetylacetone in the presence of acetic anhydride yields 2-ethyl-3-acetoxy-5-acetylcyclopentadienone (LXIV) (192). This was subsequently converted into 2-ethyl-3-hydroxycyclopentadienone (LXV) and 2-ethyl-3-acetoxycyclopentadienone (LXVI) (192).

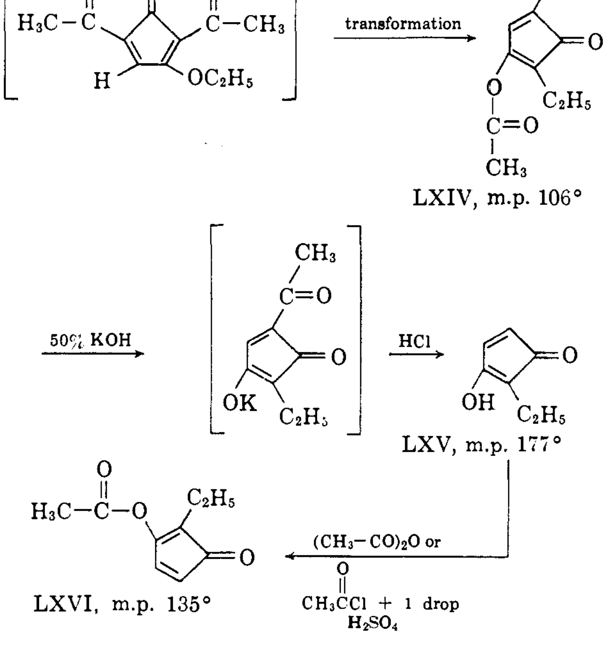


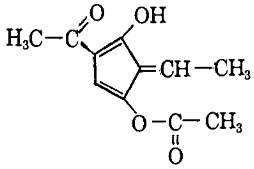
TABLE I

CYCLOPENTADIENONES CONTAINING NO ARYL GROUPS

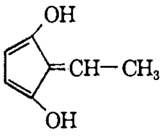
Compound 1				
R_1	R_2	R_3	R_4	Ref.
H	H	H	H	13,[a] 14,[b] 96,[a] 98,[a] 100,[a] 105,[a] 139,[a] 167,[a] 168,[a] 169,[a] 270[b]
Br	H	H	H	145[a]
H	CH_3	H	H	230
t-C_4H_9	t-C_4H_9	H	t-C_4H_9	174
		(Di-t-C_4H_9)		200[c]
Cl	Cl	Cl	Cl	220,[a] 288,[a] 289,[a] 290,[a] 291[a]
$CO_2C_2H_5$	$CO_2C_2H_5$	$CO_2C_2H_5$	OH	248[d]
Cl	CH_3	Cl	Cl	68[a]
CH_3	Cl	Cl	Cl	237[a]
CH_3	Cl	CH_3	Cl	155[a]
H	H	CH_3	n-C_4H_9	90[a]
H	H	CH_3	n-C_5H_{11}	90,[a] 264[a]
H	H	CH_3	$CH_2{=}CHCH_2$	202,[a] 47[a]
H	H	CH_3CO_2	C_2H_5	192
H	H	OH	C_2H_5	192
CH_3CO	H	CH_3CO_2	C_2H_5	192
Cl	Cl	Cl	$Cl_2C{=}CCl$	214, 221[c]
CH_3	H	H	OH	95[d]
H	CH_3	C_2H_5	H	56, 226
CF_3	CF_3	CF_3	CF_3	76, 108
OH	Cl	Cl	$Cl_2C{=}CCl$	221[c,d]
Cl	Cl	H	H	213[a]
Cl	Cl	H	Br	213[a]
Cl	H	H	H	97[a]
H	OH	H	H	104,[d] 105[d]
CH_3CO_2	CH_3CO_2	CH_3CO_2	$\bar{C}(CN)_2$	204[e]
CH_3CO_2	CH_3CO_2	CH_3CO_2	$NC\bar{C}CO_2C_2H_5$	204[e]

[a] Bimolecular compound. [b] Dioxime dimer. [c] Incompletely characterized. [d] Cyclopentenedione. [e] Salts.

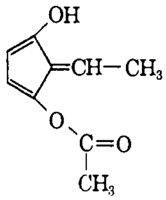
The structures for compounds LXIV, LXV, and LXVI were not completely proved and their color and high melting points seem to indicate that they could possibly have the tautomeric structures LXVII, LXVIII, and LXIX.



LXVII



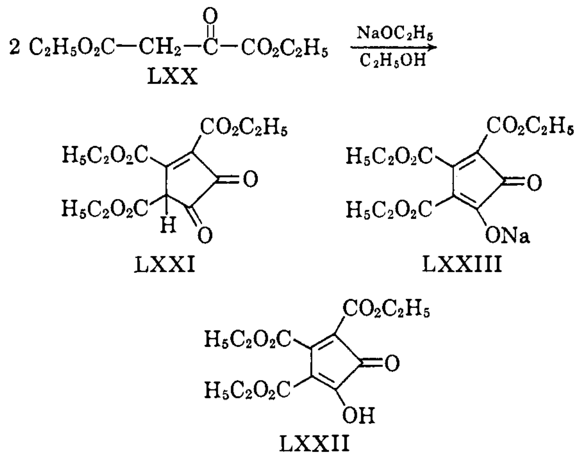
LXVIII



LXIX

A condensation of diethyl oxosuccinate (LXX) yields a red diketone LXXI (248) which is actually the ketonic form of 2-hydroxy-3,4,5-tris(carboethoxy)cyclopentadienone (LXXII) (158, 248). Upon dissolution of this red ketone in base, the solution acquires a blue color that is attributed to LXXIII (158, 248), the sodium salt of LXXII. The question as to whether LXXI or LXXII is the true structure or as to where the equilibrium lies has not been settled.

Table I summarizes the cyclopentadienones containing no aryl groups that have been prepared.



B. CYCLOPENTADIENONES CONTAINING ONE ARYL GROUP

Only two cyclopentadienones containing one aryl group have been synthesized and both contain hydroxy groups (see Table II).

The reaction of the sodium salt of acetylacetone with phenylpropiolyl chloride affords LXXIV which can be converted to the red 2-acetyl-3-methyl-4-phenyl-5-hydroxycyclopentadienone (LXXV) (249). In basic

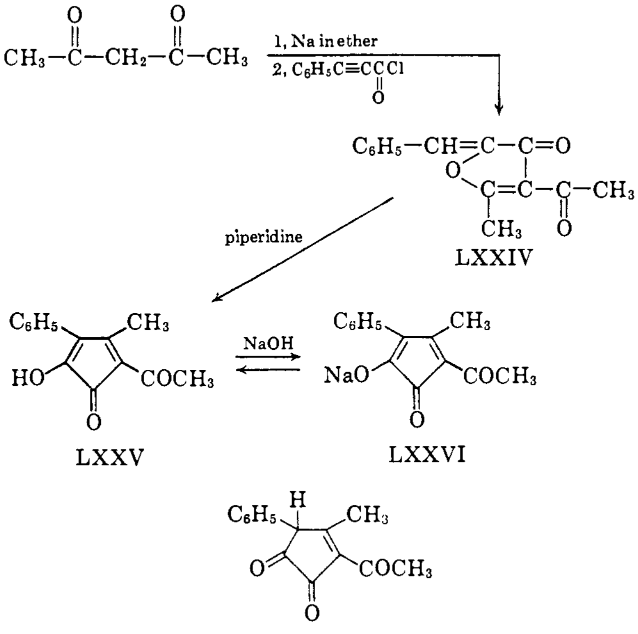
TABLE II

CYCLOPENTADIENONES CONTAINING ONE ARYL GROUP

Compound 1				
R_1	R_2	R_3	R_4	Ref.
OH	C_6H_5	H	$N(CH_3)C_6H_5$	109[a]
C_6H_5	CH_3	$COCH_3$	OH	249[a]

[a] Cyclopentenedione.

solution it gives a blue coloration which was attributed (158, 249) to the sodium salt LXXVI of the enol form. In contrast to the previously described hydroxycyclopentadienones, the authors seem to prefer the enolic form LXXV to the ketonic form LXXVII, based solely upon its acidic properties (249).



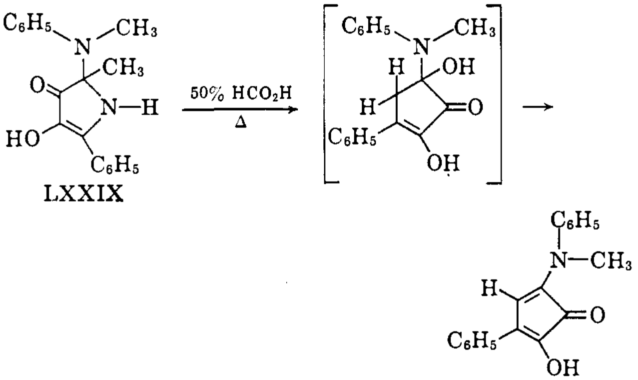
LXXIV

LXXV

LXXVI

LXXVII

The other cyclopentadienone, 2-hydroxy-3-phenyl-5-(phenylmethylamino)cyclopentadienone (LXXVIII), was prepared by treatment of LXXIX with formic acid (109). In this case also the authors seem to prefer the enolic form LXXVIII, although the compound does yield a quinoxaline derivative (109).



LXXIX

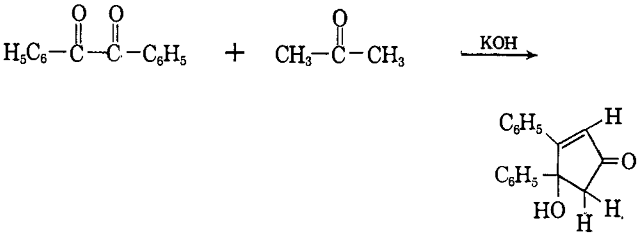
LXXVIII

C. CYCLOPENTADIENONES CONTAINING TWO ARYL GROUPS

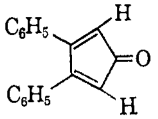
1. *Diarylcyclopentadienones*

In the presence of base, benzil and acetone condense to yield 3,4-diphenyl-4-hydroxy-2-cyclopenten-1-one (179, 181, 182, 184). After an incorrect assignment (179), the correct structure (LXXX) was later given (182). Dehydration of LXXX would be expected to give 3,4-diphenylcyclopentadienone (LXXXI). The dehydration was carried out using various methods (32, 33, 42, 161, 179, 182). The product, however, was bimolecular (32–34, 161, 179, 182) conforming to the analysis $(C_{17}H_{12}O)_2$. On heating this bimolecular compound, it evolved carbon monoxide (33, 34, 179, 182) according to the equation

$$C_{34}H_{24}O_2 \xrightarrow[\Delta]{} C_{33}H_{24}O + CO$$

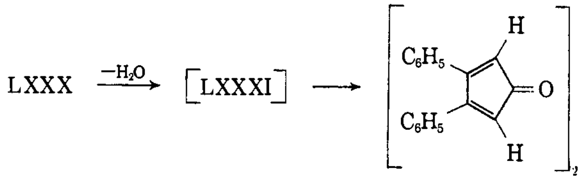


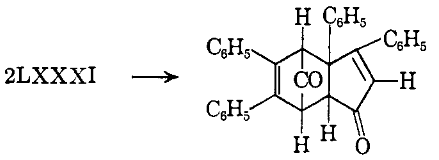
LXXX



LXXXI

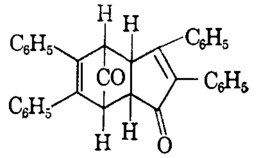
The dehydration was subsequently interpreted as yielding LXXXI which then dimerized (24, 25, 33–35, 38, 41). The dimerization was interpreted as a Diels-Alder reaction of LXXXI (24, 25, 33, 34, 41) which afforded 3a,4,7,7a-tetrahydro-3,3a,5,6-tetraphenyl-4,7-methanoindene-1,8-dione (LXXXII). Structure LXXXIII was also assigned to LXXXII (24, 25). This compound was thought to have occurred by phenyl migration in the dimer LXXXII.



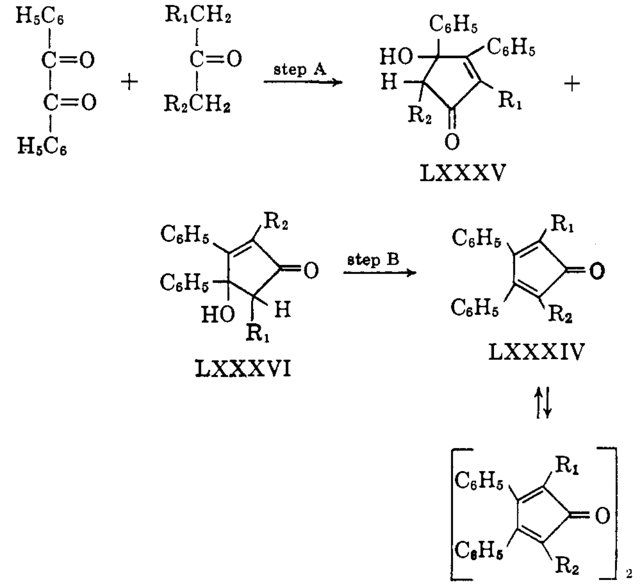


LXXXII

A series of 3,4-diphenylcyclopentadienones LXXXIV isolated as the dimers has been prepared by the de-


LXXXIII

hydration of the corresponding 3,4-diphenyl-4-hydroxy-2-cyclopenten-1-ones LXXXV and/or LXXXVI (24, 25, 32, 33, 38, 41, 161, 179, 182, 183, 185, 258). The condensation of benzil and the appropriately substituted 2-propanone utilized aqueous and/or alcoholic potassium hydroxide (41, 161, 180–185, 258). Although a variety of conditions has been used to carry out the dehydration, step B, acetic anhydride containing a few drops of sulfuric acid appears to be preferred (38, 41, 161, 258). The position of the equilibrium for the dimerization of LXXXIV to LXXXVII depends upon the R groups (41), and accounts for the fact that for some 3,4-diphenylcyclopentadienones only the dimer could be isolated (24, 25, 32, 33, 38, 41, 161, 179, 182), while for others a dissociating dimer was isolated (35, 41, 258). When both R groups are either C_2H_5 or C_6H_{13}, then the monomer is isolated (41), suggesting that this dimerization is governed by steric factors. Generally the monomer is red, the dimer colorless; thus, a dissociating dimer is a colorless compound that gives a red solution (41). When both R groups are identical, the dimerization can be represented as (29, 33–35, 38, 41)



LXXXV
LXXXVI
LXXXIV
LXXXVII

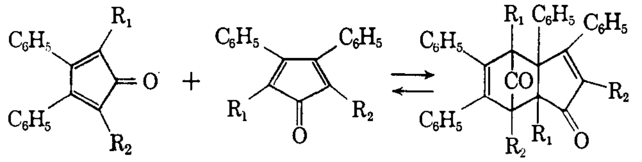
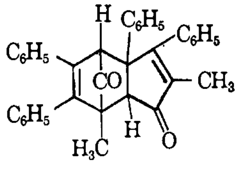

XC

TABLE III

FORMATION OF 3,4-DIPHENYL-4-HYDROXY-2-CYCLOPENTENONES (STEP A)

			Product	
R_1	R_2	Ref.	LXXXV Ref.	LXXXVI Ref.
H	H	181–184		
H	CH_3	41, 180, 181, 183	181–183	183
H	n-C_5H_{11}	41, 180, 183, 247	182, 183, 247	183
H	n-$C_{10}H_{21}$	41		
H	CH_2CO_2H	41, 185	185	185
CH_3	CH_3	41, 161, 180, 183		
CH_3	n-C_3H_7	41		
CH_3	C_2H_5	258		
C_2H_5	C_2H_5	41, 183		
C_6H_{13}	C_6H_{13}	41		
H	OC_6H_5	41		

For the cases where $R_1 = H$, $R_2 = CH_3$ and $R_1 = H$, $R_2 = n\text{-}C_5H_{11}$, the structures LXXXVIII and LXXXIX were proposed (38, 247) for the respective dimers.


LXXXVIII

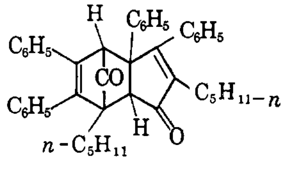
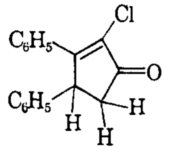

LXXXIX

Table III summarizes the formation of 3,4-diphenyl-4-hydroxy-2-cyclopentenones, step A, which were later transformed into cyclopentadienones, step B, Table IV.

The dimer of 3,4-diphenylcyclopentadienone (LXXXVII, $R_1 = R_2 = H$) has also been prepared by the dehydrohalogenation of certain halocyclopentenones (29, 32, 179) according to Chart I. There has been some question concerning the structure of XCI (83), for which structure XCII (83) has also been put forward. Compound XCII was reported to be unaffected by boiling with alcoholic silver nitrate, methyl alcoholic silver nitrate, or pyridine (83). However, upon warming with piperidine it gave a nearly quantitative yield of LXXXVII ($R_1 = R_2 = H$) (83).


XCII

Although it was not isolated, the dimer XCIII of 2,3-diphenylcyclopentadienone (XCIV) has been proposed as an intermediate in the dehydrochlorination of 2,3-diphenyl-5-chloro-2-cyclopentenone (29, 45). The orientation of phenyls in XCIII has not been rigorously established.

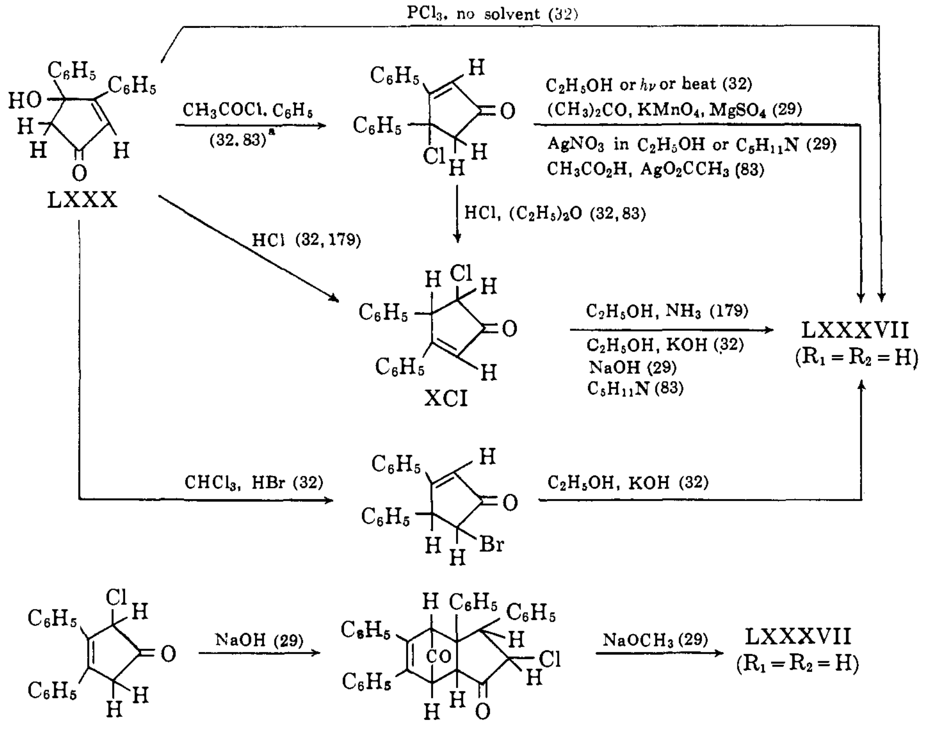
TABLE IV

3,4-DIPHENYLCYCLOPENTADIENONES (STEP B)

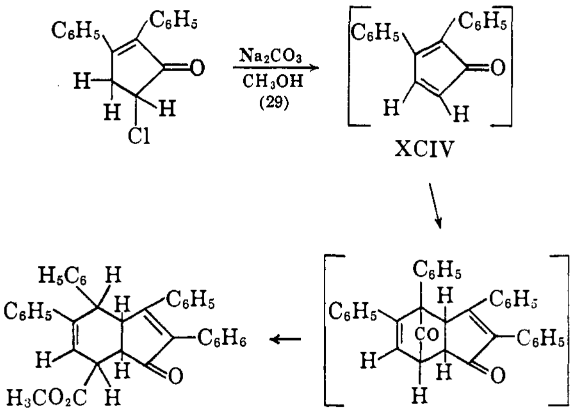
R_1	R_2	Reactant	Conditions	Product	Ref.
H	H		Hot dilute H_2SO_4	LXXXVII	179
			$(CH_3CO)_2O$, NaO_2CCH_3	LXXXVII	182
			C_2H_5OH, H_2SO_4	LXXXVII	161
			PCl_3	LXXXVII	32
			CH_3CO_2H, H_2SO_4	LXXXII	25, 33
			Maleic anhydride	[a]	33
			$(CH_3CO)_2O$, H_2SO_4	LXXXII	41,[b] 161
H	CH_3	LXXXV	HCO_2H	LXXXVII	183
		LXXXV	CH_3CO_2H, H_2SO_4	LXXXVII	161
		LXXXVI	H_2SO_4 or CH_3CO_2H	LXXXVII	183
		LXXXVI	$(CH_3CO)_2O$, H_2SO_4	LXXXVII	161
		[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVII	41[b]
		[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVIII	38
H	n-C_5H_{11}	[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVII	41[b]
		[d]	$CHCl_3$, $(CH_3CO)_2O$, H_2SO_4	LXXXIX	38,[c] 247[c]
H	n-$C_{10}H_{21}$	[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVII	41[b]
H	CH_2CO_2H	LXXXVI	NH_2OH	LXXXVII	41,[c,e] 185
CH_3	CH_3		CH_3CO_2H	XC	161
			$(CH_3CO)_2O$, H_2SO_4	XC	35,[f] 41,[f] 161
CH_3	n-C_3H_7	[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVII	41[f]
CH_3	C_2H_5	[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVII	258[f]
C_2H_5	C_2H_5		$(CH_3CO)_2O$, H_2SO_4	LXXXIV	41
C_6H_{13}	C_6H_{13}		$(CH_3CO)_2O$, H_2SO_4	LXXXIV	41
H	OC_6H_5	[d]	$(CH_3CO)_2O$, H_2SO_4	LXXXVII[g]	41

[a] Maleic anhydride addition product isolated. [b] Product is nondissociating dimer. [c] LXXXIII proposed as the structure of product. [d] Not stated whether LXXXV, LXXXVI, or a mixture of both is used. [e] Reference 185 does not list the product as LXXXVII; ref. 41 lists the product as the dihydroxylamine salt of the dimer LXXXVII. [f] Product is a dissociating dimer. [g] LXXXVII was not isolated but converted by heating directly into 7-phenoxy-2,3,5,6-tetraphenyl-1-indenone.

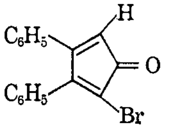
CHART I



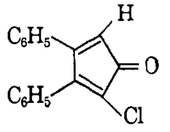
[a] $SOCl_2$, PCl_3, or $AlCl_3$ has been used in place of CH_3COCl.



The bimolecular compounds $C_{34}H_{22}Br_2O_2$ and $C_{34}H_{22}Cl_2O_2$ which are presumably the dimers of 3,4-diphenyl-2-bromocyclopentadienone (XCV) and 3,4-diphenyl-2-chlorocyclopentadienone (XCVI), respectively, have been synthesized according to Chart II (32).

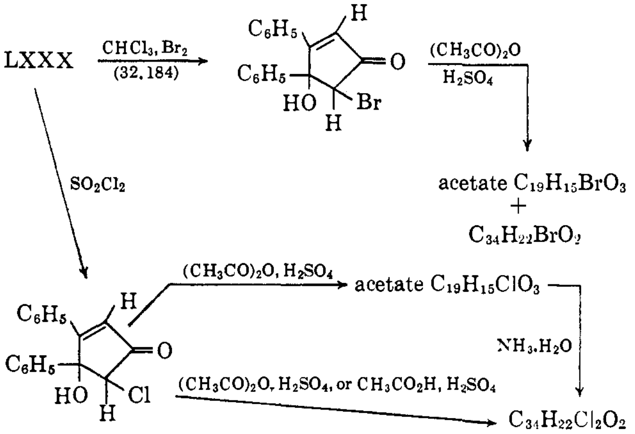


XCV



XCVI

CHART II

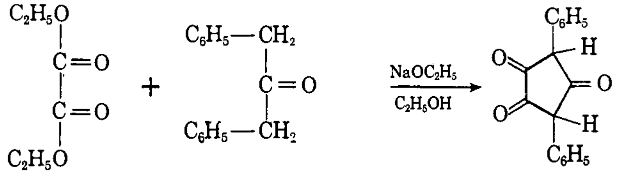


Finally, cyclopentadienones containing two aryl groups have been synthesized by the cyclization of acetylenes using dicobalt hexacarbonyldiphenylacetylene (XCVII) and dicobalt hexacarbonyltrimethylsilylphenylacetylene (XCVIII) according to Chart III (200).

2. *Diarylhydroxycyclopentadienones*

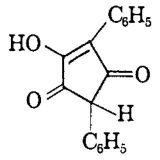
As previously mentioned, these enols are capable of keto-enol tautomerization and those hydroxycyclopentadienones which contain two aryl groups also appear to exist mainly in the keto form (86, 158).

One approach to the synthesis of these compounds is the sodium ethoxide catalyzed condensation of diethyl oxalate with benzyl ketone to yield 2,5-diphenylcyclopenta-1,3,4-trione (XCIX) (86). On the basis of



XCIX

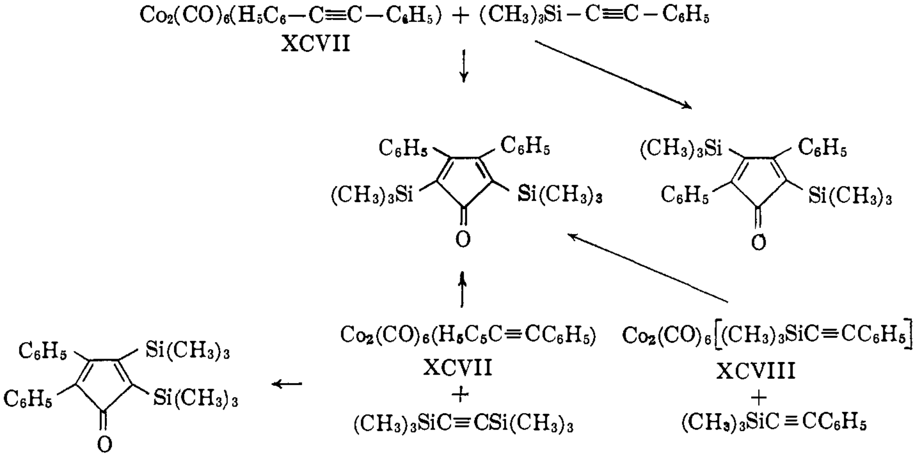
acidity and alkylation reactions of XCIX the structure 2,5-diphenyl-3-hydroxy-2-cyclopentene-1,4-dione (C), was assigned to it (86). Compound C can in turn be

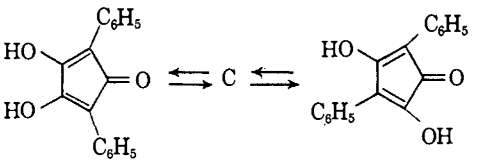


C

viewed as the ketonic tautomer of the cyclopentadienones, 2,5-diphenyl-3,4-dihydroxycyclopentadienone (CI) and 2,4-diphenyl-3,5-dihydroxycyclopentadienone (CII). The equilibrium is in favor of C. When placed in a solution containing one equivalent of base, C dissolves with the formation of a yellow color, while

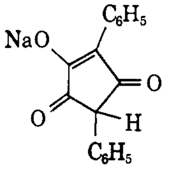
CHART III



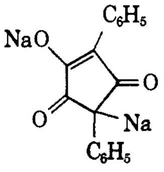


CI CII

if two equivalents of base are used, a purple solution results (86). The structures of these salts have been given as CIII and CIV, respectively. In view of the

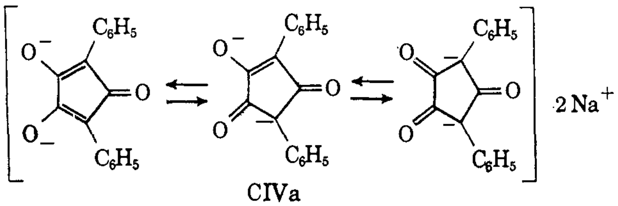


CIII



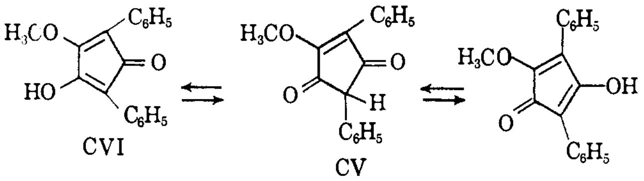
CIV

color of CIV and what is now known about resonance, CIV can perhaps be better represented by CIVa.



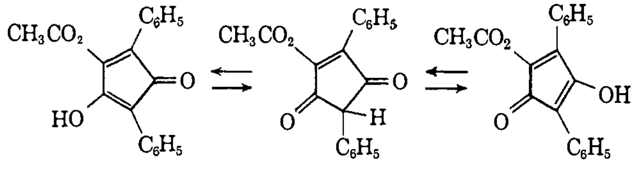
CIVa

The structures CIII and CIV were assigned on the basis of the reactions in Chart IV (86). The reaction product, 2,5-diphenyl-3-methoxy-2-cyclopentene-1,4-dione (CV), may be viewed as the ketonic tautomer of the cyclopentadienones, 2,5-diphenyl-3-methoxy-4-hydroxycyclopentadienone (CVI) and 2,4-diphenyl-5-methoxy-3-hydroxycyclopentadienone (CVII).



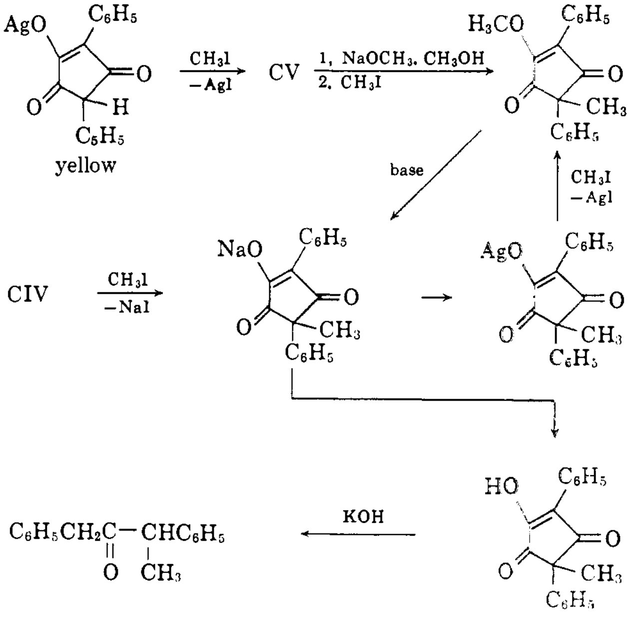
CVI CV CVII

Acetylation of C gave 2,5-diphenyl-3-acetoxy-2-cyclopentene-1,4-dione (CVIII) (86), which is the ketonic form of the cyclopentadienones 2,5-diphenyl-3-acetoxy-4-hydroxycyclopentadienone (CIX) and 2,4-diphenyl-3-hydroxy-5-acetoxycyclopentadienone (CX). In all of these cases it appears that cyclopentenedione–hydroxycyclopentadienone tautomerization is in favor of the dione.



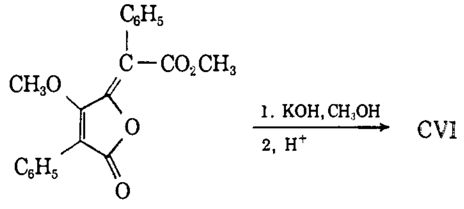
CIX CVIII CX

CHART IV



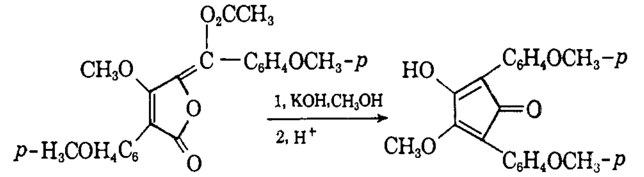
$$\mathrm{CIII} \xrightarrow{CH_3I} \text{no reacn.}$$

Compound CVI was also prepared from CXI, 2-oxo-3-phenyl-4-methoxy-5-(α-carbomethoxybenzal)-2H,5H-furan, "methyl vulpinate," by solution in methanolic potassium hydroxide followed by dilution and acidification (196). Although the structure is written as CVI, it is reported (196) to be identical with



CXI

the product from a different preparation (86) whose structure was given as CV. A similar reaction using CXII, 2-oxo-3-(*p*-methoxyphenyl)-4-methoxy-5-(α-carbomethoxy-*p*-methoxybenzal)-2H,5H-furan, "methyl *p,p*′-dimethoxyvulpinate," yielded CXIII, 2,5-bis(*p*-methoxyphenyl)-3-hydroxy-4-methoxycyclopentadienone (196).



CXII CXIII

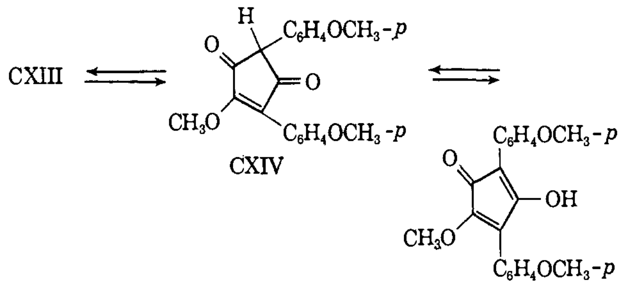
Compound CXIII can be viewed as the enolic tautomer of CXIV, 2,5-bis(*p*-methoxyphenyl)-3-methoxy-2-cyclopentene-1,4-dione, which in turn is the ketonic tautomer of the cyclopentadienone CXV, 2,4-bis-(*p*-methoxyphenyl)-3-hydroxy-5-methoxycyclopenta-

Table V

Cyclopentadienones Containing Two Aryl Groups

Compound 1				
R_1	R_2	R_3	R_4	Ref.
H	H	C_6H_5	C_6H_5	45[a]
H	C_6H_5	C_6H_5	H	29,[a,b] 32,[a] 33,[a] 34,[a] 158,[a] 161,[a] 179,[a] 182[a]
H	C_6H_5	C_6H_5	CH_3	38,[c] 161,[a] 183[a]
H	C_6H_5	C_6H_5	Cl	32[a]
H	C_6H_5	C_6H_5	Br	32[a]
CH_3	C_6H_5	C_6H_5	CH_3	35, 161, 258
CH_3	C_6H_5	C_6H_5	C_2H_5	258
CH_3	C_6H_5	C_6H_5	n-C_3H_7	41
C_2H_5	C_6H_5	C_6H_5	C_2H_5	41, 258
n-C_3H_7	C_6H_5	C_6H_5	n-C_3H_7	41
C_6H_{13}	C_6H_5	C_6H_5	C_6H_{13}	41
C_6H_5	Br	Br	C_6H_5	200
C_6H_5	OH	CH_3O	C_6H_5	86,[d] 196
p-$CH_3OC_6H_5$	OH	CH_3O	p-$CH_3OC_6H_5$	196
H	C_6H_5	C_6H_5	n-$C_{10}H_{21}$	41
H	C_6H_5	C_6H_5	n-C_5H_{11}	38
C_6H_6	C_6H_5	Br	OH	158[d]
H	C_6H_5	C_6H_5	OC_6H_5	41
C_6H_5	C_6H_5	$Si(CH_3)_3$	$Si(CH_3)_3$	200
C_6H_5	$Si(CH_3)_3$	C_6H_5	$Si(CH_3)_3$	200
$Si(CH_3)_3$	C_6H_5	C_6H_5	$Si(CH_3)_3$	200
C_6H_5	C_6H_5	H	OH	158[d]
C_6H_5	OH	C_6H_5	OH	86[d]
H	C_6H_5	C_6H_5	CH_2CO_2H	185[e]
C_6H_5	CH_3CO_2	OH	C_6H_5	86[d]

[a] Bimolecular compound. [b] As dinitrophenylhydrazone. [c] Trapped as intermediate. [d] Cyclopentenedione. [e] Dihydroxylamine salt of dimer by Allen and VanAllan (41).

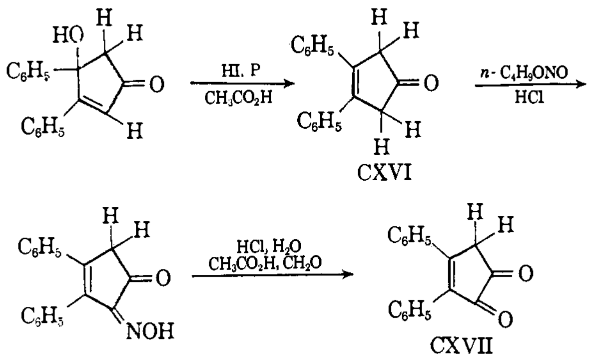


CXIV

CXV

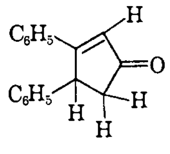
dienone. Since CXIII is reported to be a yellow compound that gives violet solutions in methanolic potassium hydroxide (196), it seems reasonable that it is in equilibrium with CXIV and CXV, with CXIV being favored as the prevalent form.

The following reaction sequence has been employed for the preparation of CXVII, 3,4-diphenyl-3-cyclopentene-1,2-dione (158). It should be noted that CXVI was later assigned the structure CXVIII (45). Although CXVII is the ketonic tautomer of CXIX, 2,3-diphenyl-5-hydroxycyclopentadienone, the properties of the compound are consistent with structure CXVII which is reported to show no tendency to enolize and to have one very reactive carbonyl group (158). Table V summarizes the known cyclopentadienones with two aryl groups.

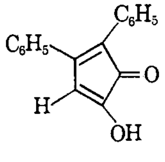


CXVI

CXVII



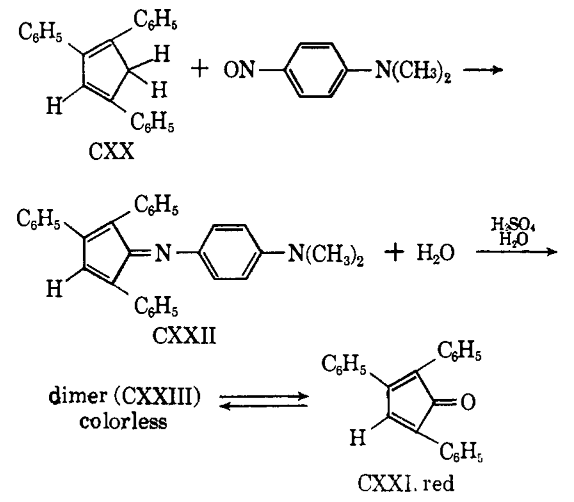
CXVIII



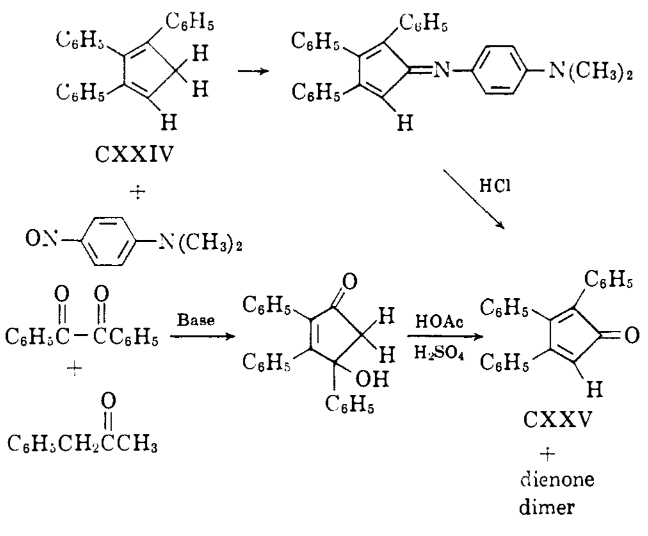
CXIX

D. CYCLOPENTADIENONES CONTAINING THREE ARYL GROUPS

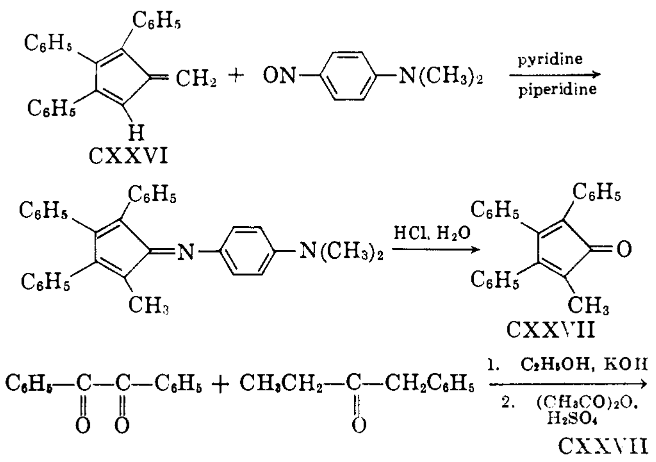
The hydrocarbon 2,3,5-triphenylcyclopentadiene (CXX) can be oxidized to 2,3,5-triphenylcyclopentadienone (CXXXI) *via* reaction with p-nitrosodimethylaniline (134). The p-nitrosodimethylaniline first forms the anil CXXII which is then hydrolyzed under acidic conditions. This cyclopentadienone, CXXI, is in equilibrium with its dimer CXXIII. Like the diarylcyclopentadienones, the monomer CXXI is red, which accounts for the red color obtained when the colorless dimer is dissolved (134).



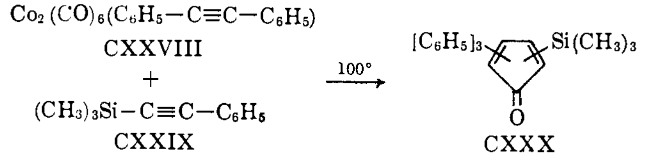
If the isomeric 2,3,4-triphenylcyclopentadiene (CXXIV) is used as the hydrocarbon, then of course the isomeric 2,3,4-triphenylcyclopentadienone (CXXV) is produced. Unlike CXXI, CXXV is an isolable monomer that is blue while its dimer is yellow (229). This particular cyclopentadienone may also be prepared by condensation of phenylacetone with benzil followed by dehydration of the resulting 2,3,4-triphenyl-4-hydroxy-2-cyclopentenone (229). This reaction sequence also leads to the blue monomer and yellow dimer (229).



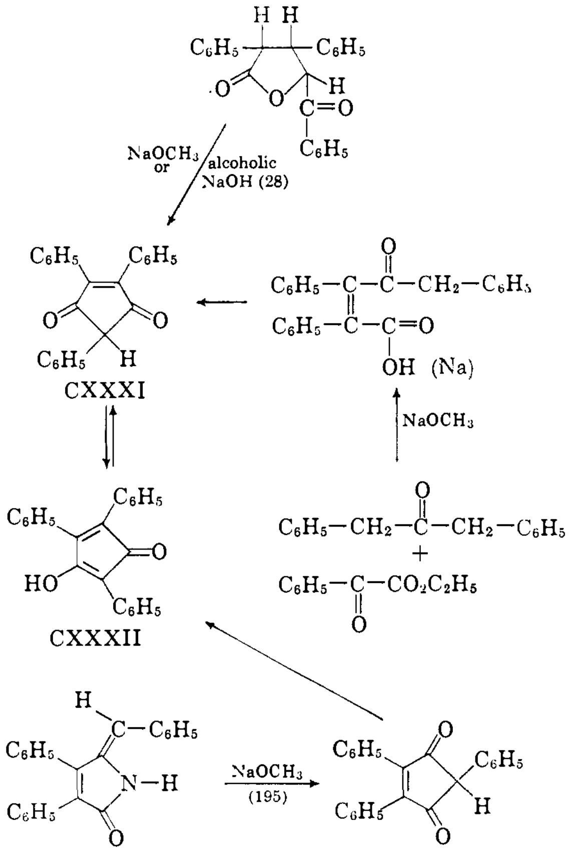
An unusual example of this oxidation is the reaction of 1,2,3-triphenylfulvene (CXXVI) with *p*-nitrosodimethylaniline in a pyridine–piperidine medium. In this reaction the anil of 2-methyl-3,4,5-triphenylcyclopentadienone is obtained, which, upon acid hydrolysis, yields the cyclopentadienone CXXVII (229). This cyclopentadienone is a red-brown monomer (229) which may also be prepared by the condensation of benzil with 1-phenyl-2-butanone (41).



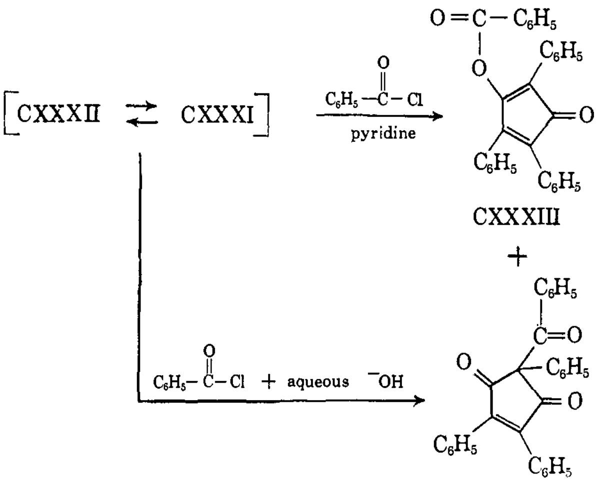
Triphenyltrimethylsilylcyclopentadienone (CXXX), which was incompletely characterized, has been prepared by the treatment of dicobalt hexacarbonyldiphenylacetylene (CXXVIII) with phenyltrimethylsilylacetylene (CXXIX) (200).



As with most of the other hydroxycyclopentadienones, those containing three aryl groups also exist mainly in the keto form. Thus, the condensation of



benzyl ketone and ethyl phenylglyoxylate with sodium methoxide or the rearrangement and dehydration of 2-oxo-3,4-diphenyl-5-benzoyltetrahydrofuran yields 2,3,5-triphenyl-2-cyclopentene-1,4-dione (CXXXI), the ketonic and stable form of the cyclopentadienone, 2,3,5-triphenyl-4-hydroxycyclopentadienone (CXXXII) (28). This compound has also been prepared by the rearrangement and deamination of 2-oxo-3,4-diphenyl-5-benzal-2H,5H-pyrrole (195). Benzoylation of CXXXI in pyridine yielded the products resulting from both O- and C-attack, while benzoylation in aqueous base yielded the C-benzoylated material (195). The O-benzoylated product is 2,3,5-triphenyl-4-benzoyloxycyclopentadienone (CXXXIII), a derivative of CXXXII.



CXXXIII

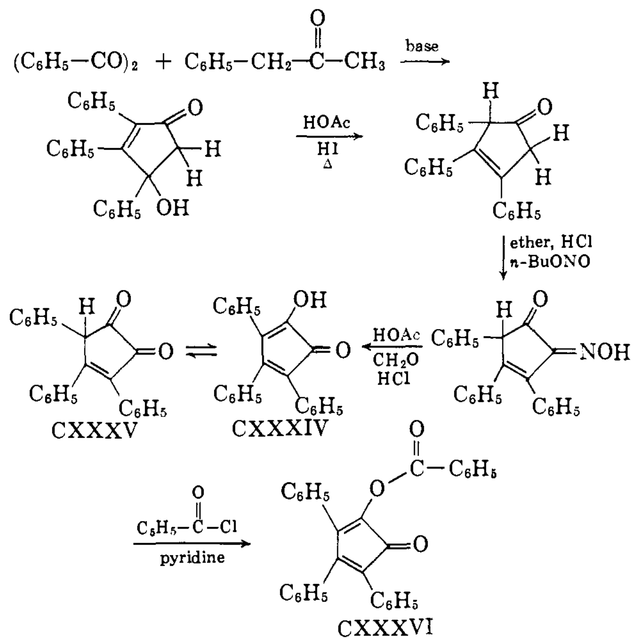
The isomeric 2,3,4-triphenyl-5-hydroxycyclopentadienone (CXXXIV), which exists mainly as the diketone CXXXV, has also been synthesized (194). The synthesis involves condensation of phenylacetone with benzil followed by reduction of the product with hydrogen iodide to yield 2,3,4-triphenyl-3-cyclopentenone. Oxidation of the latter to the monooxime of CXXXV with butyl nitrite was followed by acid hydrolysis to CXXXV. Benzoylation of CXXXV in pyridine afforded 2,3,4-triphenyl-5-benzoyloxycyclopentadienone (CXXXVI), a derivative of CXXXIV (194).

Table VI

Cyclopentadienones Containing Three Aryl Groups

Compound 1				
R₁	R₂	R₃	R₄	Ref.
H	C_6H_5	C_6H_5	C_6H_5	229
CH_3	C_6H_5	C_6H_5	C_6H_5	41, 229
OH	C_6H_5	C_6H_5	C_6H_5	194[a]
C_6H_5	$C_6H_5CO_2$	C_6H_5	C_6H_5	195
$C_6H_5CO_2$	C_6H_5	C_6H_5	C_6H_5	194
(C_6H_5, C_6H_5, C_6H_5, $(CH_3)_3Si$)				200[b]
C_6H_5	H	C_6H_5	C_6H_5	134[c]
C_6H_5	OH	C_6H_5	C_6H_5	28,[a] 195[a]

[a] Cyclopentenedione. [b] Incompletely characterized. [c] In equilibrium with the dimer.



CXXXV CXXXIV

CXXXVI

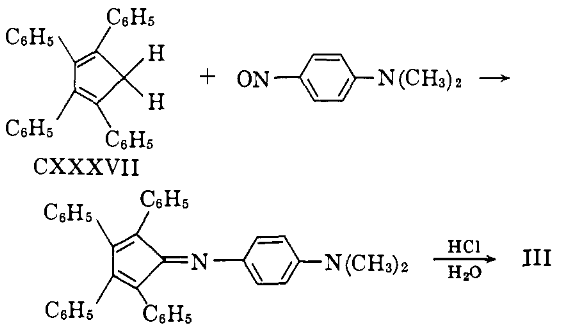
It is interesting to note the colors of these compounds in relation to their proposed structures. Compound CXXXI is bright yellow while its O-benzoylated derivate CXXXIII is red. The isomeric CXXXV is orange while its O-benzoylated derivate is also red. A color shift is also noted for basic solutions of these hydroxycyclopentadienones; that for CXXXI is blue, while that for CXXXV is deep blue-green.

Table VI summarizes those cyclopentadienones containing three aryl groups that have been prepared.

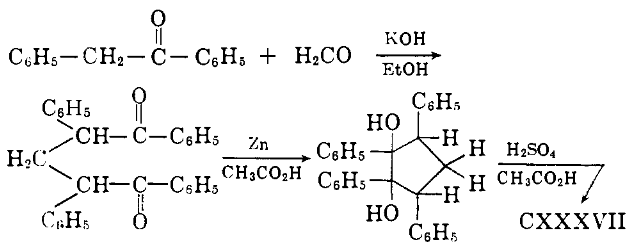
E. CYCLOPENTADIENONES CONTAINING FOUR ARYL GROUPS

1. *Tetraphenylcyclopentadienones*

The oxidation of tetraarylcyclopentadienes *via* *p*-nitrosodimethylaniline has also been used for the fully arylated cyclopentadienones. Condensation of *p*-nitrosodimethylaniline with 2,3,4,5-tetraphenylcyclopentadiene (CXXXVII) afforded a blue anil which upon hydrolysis gave tetracyclone (III) (287). The 2,3,4,5-tetraphenylcyclopentadiene (CXXXVII) was prepared by the base-catalyzed coupling of deoxybenzoin with formaldehyde followed by a pinacol-type ring closure and finally by dehydration (287). This



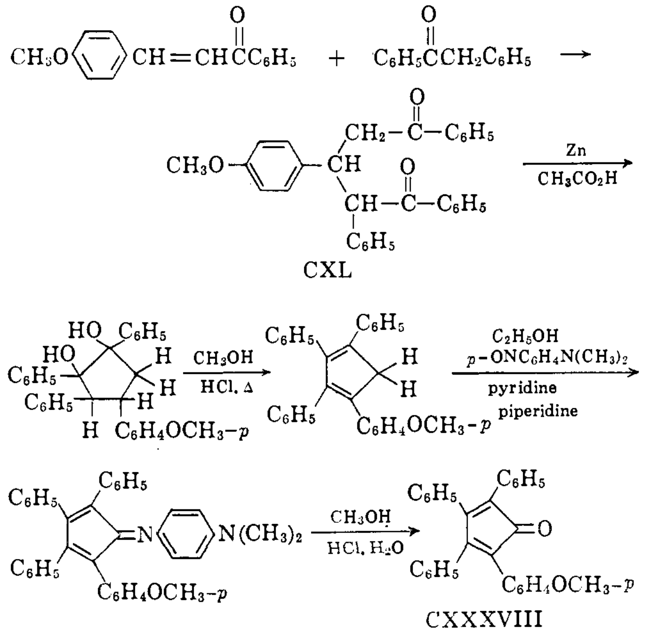
CXXXVII



CXXXVII

general procedure was also used to prepare several substituted 2,3,4,5-tetraphenylcyclopentadienes which could then be converted to the corresponding substituted tetracyclones (218).

This sequence was modified (138) for the preparation of 2-*p*-methoxyphenyl-3,4,5-triphenylcyclopentadienone (CXXXVIII). Here the 1,5-diketone was prepared by the Michael addition of deoxybenzoin to anisalacetophenone (CXXXIX). The resulting 1,5-diketone (CXL) was then converted to the cyclopentadienone (CXXXVIII) *via* oxidation with *p*-nitrosodimethylaniline (138).

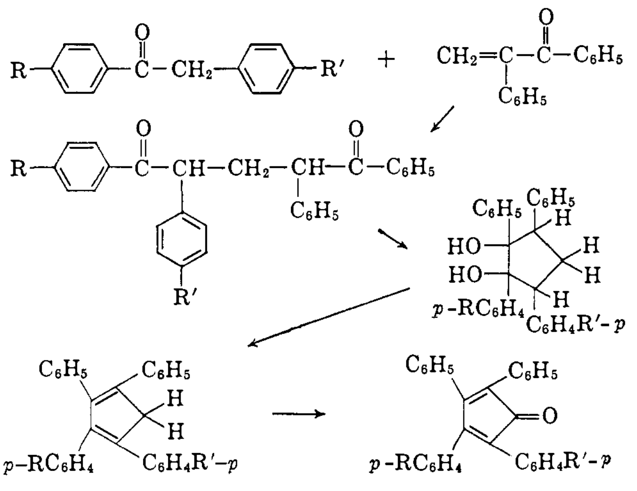


CXL

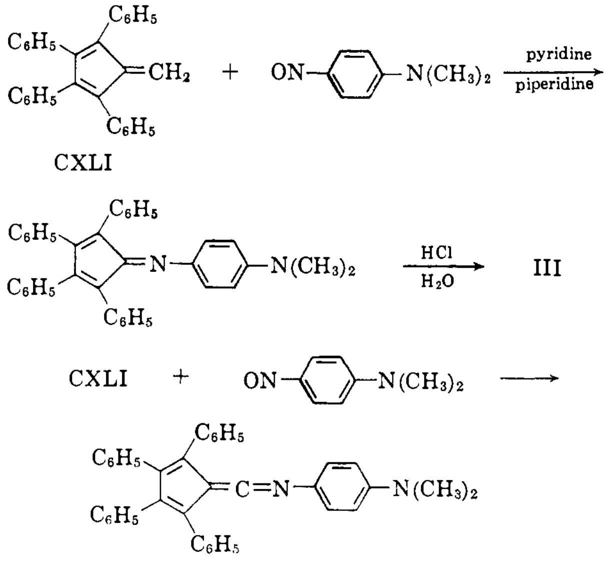
CXXXVIII

The Michael addition of substituted deoxybenzoins to α-phenylacrylophenone resulted in the preparation of several unsymmetrically substituted 1,5-diketones which were converted to the corresponding tetracyclones using the same procedure as previously mentioned (218) (see top of next column).

The reaction of 1,2,3,4-tetraphenylfulvene (CXLI) with *p*-nitrosodimethylaniline followed by hydrolysis gave tetracyclone (III) (148, 267). This conversion parallels the reaction of 1,2,3-triphenylfulvene (CXXVI), except that in this case the methylene group is split out probably as bis(1-piperidyl)methane, while with triphenylfulvene it is retained. This reaction had previously been reported as yielding CXLII (127) which was later disproved (148, 267).



R′ = H	H	H	Cl	CH_3	CH_3O
R = Cl	CH_3	CH_3O	H	H	H



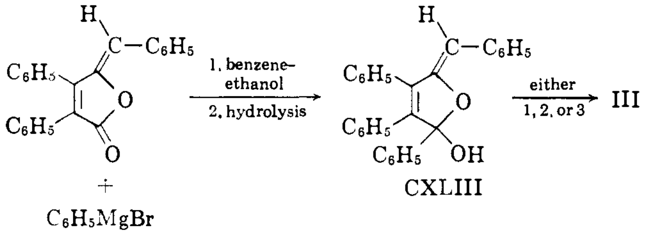
CXLI

III

CXLI + $ON-C_6H_4-N(CH_3)_2$ ⟶

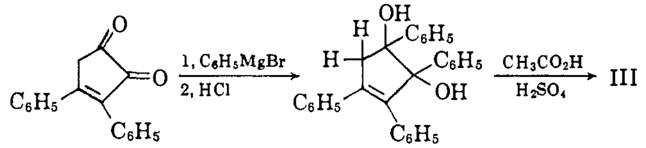
CXLII

Tetracyclone has also been obtained from the rearrangement of 2-benzal-3,4,5-triphenyl-4-hydroxy-2H,-5H-furan (CXLIII) using both acidic and basic conditions (207): (1) hot CH_3CO_2H and a few drops H_2SO_4; (2) refluxing CH_3CO_2H and a few drops of H_2SO_4; (3) aqueous alcoholic NaOH.



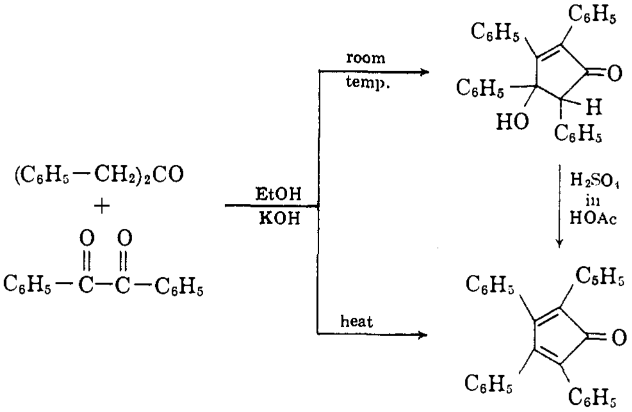
CXLIII

By heating 1,2,3,4-tetraphenyl-3,4-dihydroxy-1-cyclopentene (CXLIV) in acetic acid containing sulfuric acid, a dehydration and oxidation took place in which tetracyclone is formed (158).



CXLIV

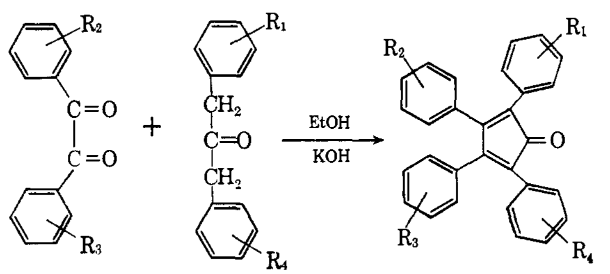
By far the most useful synthesis of tetracyclone has been the base-catalyzed condensation of benzil with benzyl ketone (133).



It is worthy of note that when this condensation was first carried out, tetracyclone was unknown and the authors removed this "coloring matter" from the 2,3,4,5-tetraphenyl-4-hydroxycyclopentenone which they isolated and characterized (171).

Using this condensation, a nearly quantitative yield of tetracyclone has been reported (114) while standardization of the procedure (188) has given reproducible yields of 91–96%. A most recent preparation involves reaction of benzyl ketone and benzil with Triton B in triethylene glycol at 100° (151, 153).

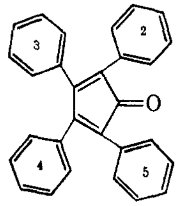
This synthesis lends itself not only to the preparation of tetracyclone but also to substituted tetracyclones, for, if substituents are placed in either the benzil or the dibenzyl ketone or both, they will then appear in the corresponding phenyl rings of the tetracyclone (51, 54, 87, 88, 91, 114, 138, 147, 156, 157, 188, 197, 203, 269).



$R_1 = R_2 = R_3 = R_4 = H$	tetracyclone (Table VII)
$R_2 = R_3 = R_4 = H$	2-aryl-3,4,5-triphenylcyclopentadienones (Table VII)
$R_1 = R_3 = R_4 = H$	3-aryl-2,4,5-triphenylcyclopentadienones (Table VIII)
$R_2 = R_3 = H$	2,5-diaryl-3,4-diphenylcyclopentadienones (Table IX)
$R_1 = R_4 = H$	3,4-diaryl-2,5-diphenylcyclopentadienones (Table X)
$R_2 = H$	2,3,5-triaryl-4-phenylcyclopentadienones (none prepared)
$R_1 = H$	2,3,4-triaryl-5-phenylcyclopentadienones (Table XI)
$R_1 \neq H$, $R_2 \neq H$, $R_3 \neq H$, $R_4 \neq H$	tetraarylcyclopentadienones (Table XII)

Table VII

2-Aryl-3,4,5-triphenylcyclopentadienones

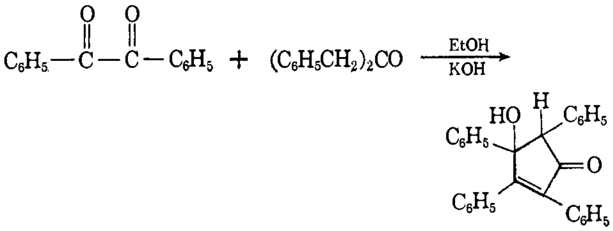


2	3	4	5	Ref.
...	..	..	..	72, 114, 120, 133, 138, 148, 151, 153, 158, 163, 176, 188, 194, 195, 207, 209, 254, 255, 261, 287
p-OCH$_3$	..	..	..	87, 138, 147
p-CH$_3$	..	..	..	87, 147, 218
p-F	..	..	..	87, 147, 218
p-Cl	..	..	..	87, 147, 218
p-Br	..	..	..	87
p-OC$_6$H$_5$	..	..	..	91
p-SC$_6$H$_5$	..	..	..	91
p-SCH$_3$	..	..	..	88, 147, 203
p-SO$_2$CH$_3$	..	..	..	88
p-N(CH$_3$)$_2$	..	..	..	157
o-F	..	..	..	91
o-Cl	..	..	..	260
m-OCH$_3$	..	..	..	147
m-F	..	..	..	147
m-Cl	..	..	..	147

In some cases when substituents were in the *ortho* position, potassium hydroxide was found to be inferior or useless as the base. In these cases, benzyltrimethylammonium hydroxide was used successfully (88, 91, 197, 260).

Also, it was found that 4,4′-bis(dimethylamino)benzil would not condense with benzyl ketone using the modified procedure (188). In this case it was observed that stirring at room temperature over a period of approximately 1 week using a stronger potassium hydroxide solution produced the desired 3,4-bis(4-dimethylaminophenyl)-2,5-diphenylcyclopentadienone (57, 223).

The course of the condensation of benzil with benzyl ketone has never been rigorously proved. However, 2,3,4,5-tetraphenyl-4-hydroxycyclopentenone (CXLV) (tetraphenylcyclopentenolone) was obtained (131, 171)



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + (C_6H_5CH_2)_2CO \xrightarrow[KOH]{EtOH}$$

CXLV

TABLE VIII

3-ARYL-2,4,5-TRIPHENYLCYCLOPENTADIENONES[a]

2	3	4	5	Ref.
..	p-OCH_3	..	..	87, 138, 156, 218
..	p-OC_2H_5	..	..	156
..	p-OC_3H_7-n	..	..	156
..	p-OC_3H_7-i	..	..	156
..	p-OC_4H_9-n	..	..	156
..	p-OC_5H_{11}-n	..	..	156
..	p-OC_6H_{13}-n	..	..	156
..	p·OC_7H_{15}-n	..	..	156
..	p-OC_8H_{17}-n	..	..	156
..	p-OC_9H_{19}-n	..	..	156
..	p-$OC_{10}H_{21}$-n	..	..	156
..	p-$OC_{11}H_{23}$-n	..	..	156
..	p-OC_6H_5	..	..	91
..	p-CH_3	..	..	87, 218
..	p-n-C_4H_9	..	..	156
..	p-i-C_4H_9	..	..	156
..	p-neo-C_5H_{11}	..	..	156
..	p-C_6H_5	..	..	138
..	p-Cl	..	..	87, 218
..	p-Br	..	..	87
..	p-$N(CH_3)_2$	..	..	87, 138
..	p-$N(CH_3)_3{}^+Ts^-$	..	..	88
..	p-SCH_3	..	..	88
..	p-SC_6H_5	..	..	91
..	p-SO_2CH_3	..	..	88
..	o-OCH_3	..	..	197
..	o-OC_2H_5	..	..	197
..	o-CH_3	..	..	197
..	o-F	..	..	197
..	o-Cl	..	..	260
..	o-Br	..	..	197
..	m-OCH_3	..	..	197
..	m-OC_2H_5	..	..	197

[a] See structure in Table VII for ring positions.

TABLE IX

2,5-DIARYL-3,4-DIPHENYLCYCLOPENTADIENONES[a]

2	3	4	5	Ref.
p-OCH_3	..	..	p-OCH_3	88, 218
p-OC_6H_5	..	..	p-OC_6H_5	91
p-CH_3	..	..	p-CH_3	88
p-Cl	..	..	p-Cl	218, 269
p-Br	..	..	p-Br	88
p-SC_6H_5	..	..	p-SC_6H_5	91
p-$N(CH_3)_2$	..	..	p-$N(CH_3)_2$	273
o-F	..	..	o-F	91
o-Cl	..	..	o-Cl	260
m-CH_3	..	..	m-CH_3	54

[a] See structure in Table VII for ring positions.

TABLE X

3,4-DIARYL-2,5-DIPHENYLCYCLOPENTADIENONES[a]

2	3	4	5	Ref.
..	p-OCH_3	p-OCH_3	..	88, 138, 218
..	p-OC_2H_5	p-OC_2H_5	..	138
..	p-OC_6H_5	p-OC_6H_5	..	91, 138
..	3,4-Methylene-dioxy	3,4-Methylene-dioxy	..	51
..	p-CH_3	p-CH_3	..	88, 138, 218
..	p-i-C_3H_7	p-i-C_3H_7	..	138
..	p-C_5H_5	p-C_6H_5	..	138
..	p-2-Naphthyl	p-2-Naphthyl	..	51
..	p-Cl	p-Cl	..	218, 269
..	p-Br	p-Br	..	37, 88, 138
..	p-SC_6H_5	p-SC_6H_5	..	91, 138
..	p-$N(CH_3)_2$	p-Cl	..	138
..	p-$N(CH_3)_2$	p-$N(CH_3)_2$	..	142, 143, 223
..	p-$N(C_2H_5)_2$	p-$N(C_2H_5)_2$	..	223
..	o-F	o-F	..	197
..	o-Cl	o-Cl	..	260
..	m-OCH_3	m-OCH_3	..	197
..	m-OC_2H_5	m-OC_2H_5	..	197
..	m-CH_3	m-CH_3	..	54
..	3,5-Dimethyl	3,5-Dimethyl	..	54

[a] See structure in Table VII for ring positions.

TABLE XI

2,3,4-TRIARYL-5-PHENYLCYCLOPENTADIENONES[a]

2	3	4	5	Ref.
o-F	o-F	o-F	..	91

[a] See structure in Table VII for ring positions.

TABLE XII

TETRAARYLCYCLOPENTADIENONES[a]

2	3	4	5	Ref.
p-OCH_3	p-OCH_3	p-OCH_3	p-OCH_3	88, 189[b]
p-OC_2H_5	p-OC_2H_5	p-OC_2H_5	p-OC_2H_5	189[b,c]
p-OC_4H_9	p-OC_4H_9	p-OC_4H_9	p-OC_4H_9	189[b,c]
p-OC_8H_{17}	p-OC_8H_{17}	p-OC_8H_{17}	p-OC_8H_{17}	189[b,c]
p-$OC_{14}H_{29}$	p-$OC_{14}H_{29}$	p-$OC_{14}H_{29}$	p-$OC_{14}H_{29}$	189[b,c]
p-CH_3	p-CH_3	p-CH_3	p-CH_3	88, 189[b]
p-Cl	p-Cl	p-Cl	p-Cl	189,[b] 269
p-Br	p-Br	p-Br	p-Br	88, 189[b]
p-$N(CH_3)_2$	p-$N(CH_3)_2$	p-$N(CH_3)_2$	p-$N(CH_3)_2$	189[b,c]
o-F	o-F	o-F	o-F	91
m-CH_3	m-CH_3	m-CH_3	m-CH_3	54

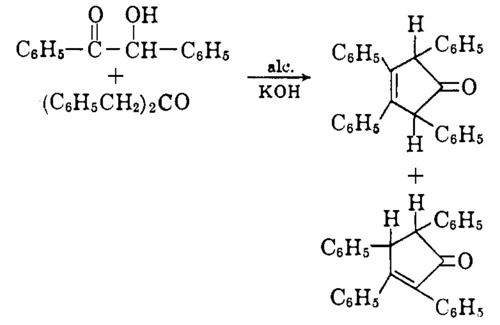
[a] See structure in Table VII for ring positions. [b] No experimental details given. [c] Incorrectly reported; compounds were not actually synthesized.

from the condensation of benzil and dibenzyl ketone at room temperature. Since this compound could be converted to tetracyclone by heating with acetic acid containing a small amount of sulfuric acid (133, 195), it may possibly be an intermediate in this synthesis. [It would be more incisive were CXLV to have been dehydrated under basic conditions.]

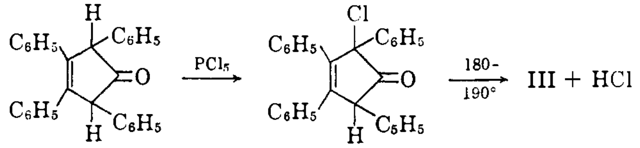
Benzoin, rather than benzil, has been condensed with benzyl ketone under basic conditions (120, 133) yielding 2,3,4,5-tetraphenyl-3-cyclopentenone (CXLVI) (120) and 2,3,4,5-tetraphenyl-2-cyclopentenone (CXLVII). Compound CXLVI was converted to tetracyclone by first treating with phosphorus pentachloride to produce 2,3,4,5-tetraphenyl-2-chloro-3-cyclopentenone (CXLVIII) and then heating to 180–190° (120). Compound CXLVII was also converted to tetracyclone by oxidation with bromine in acetic acid (133).

A previously mentioned diketone (CXXXV) has also been converted to tetracyclone (194).

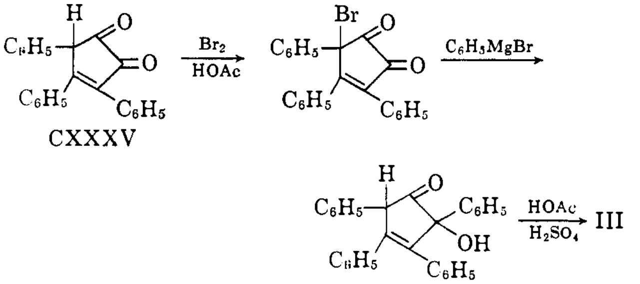
As in the case of the other cyclopentadienones, metal carbonyl compounds have also been used to prepare tetracyclone (72, 176, 255, 261). By irradiating a



CLXVII

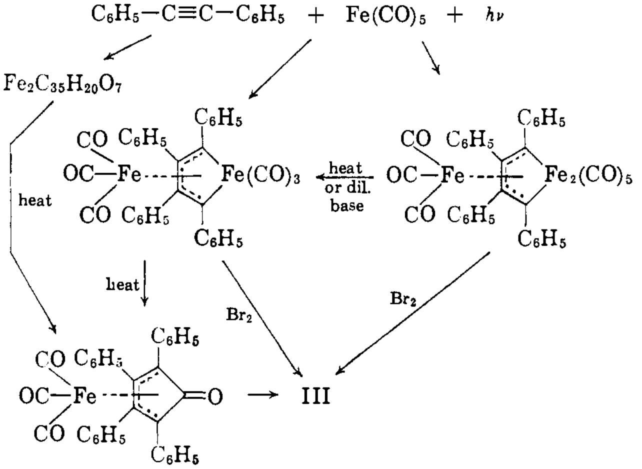


CXLVI CXLVIII



CXXXV

refluxing benzene solution of diphenylacetylene and iron pentacarbonyl with a mercury lamp, a variety of iron carbonyl complexes were obtained which could be decomposed into tetracyclone (254, 255).



The trimer of iron tetracarbonyl was found to react with diphenylacetylene to yield tetracyclone along with other products (176).

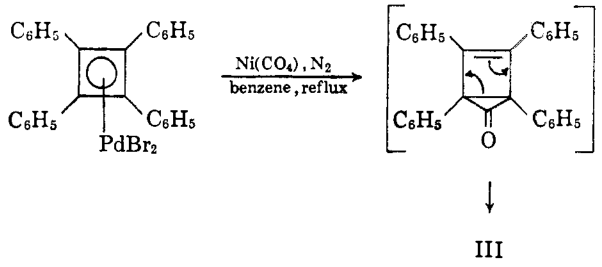
$$[Fe(CO)_4]_3 + C_6H_5C\equiv CC_6H_5 \xrightarrow[80\text{-}90^\circ]{\text{petroleum ether}}$$
$$Fe(CO)_3(C_6H_5-C\equiv C-CH_5)_2 + Fe_3(CO)_8(C_6H_5-C\equiv C-C_6H_5)_2 + \text{other products} + \text{tetracyclone (III)}$$

Diiron heptacarbonylbis(diphenylacetylene) (CXLIX) was found to give tetracyclone when heated in benzene (261).

$$Fe_2(CO)_7(C_6H_5C\equiv CC_6H_5)_2 \xrightarrow[\Delta]{\text{benzene}} \text{III}$$

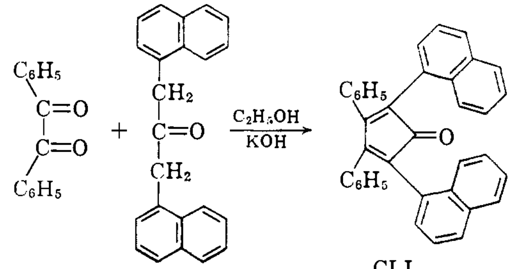
Tetracyclone was also found in the various reactions of other iron carbonyl complexes of diphenylacetylene (176, 177).

Reaction of tetaphenylcyclobutadiene–palladium bromide with nickel tetracarbonyl in benzene under nitrogen produced tetracyclone *via* the suspected intermediate shown (209).



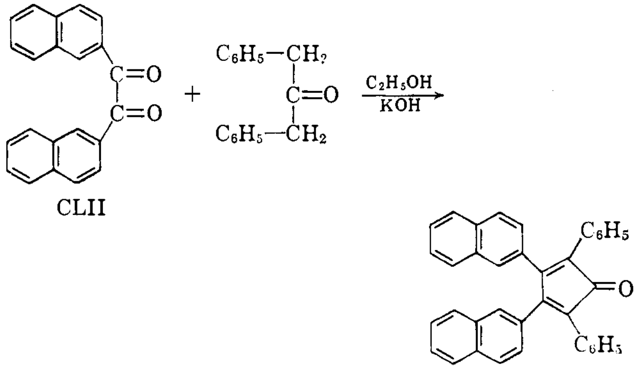
2. *Dinaphthyldiphenylcyclopentadienones*

Similar to the basic condensation of benzil and benzyl ketone which yields tetracyclone, the condensation of 1,3-bis(1-naphthyl)-2-propanone (CL) and benzil results in the formation of 2,5-bis(1-naphthyl)-3,4-diphenylcyclopentadienone (CLI) (178).



CL CLI

An isomeric dinaphthyldiphenylcyclopentadienone has been prepared by the base-catalyzed condensation of β-naphthil (CLII) with benzyl ketone. An almost quantitative yield of 3,4-bis(2-naphthyl)-2,5-diphenylcyclopentadienone (CLIII) was realized (51) (Table XIII).



CLII

CLIII

TABLE XIII

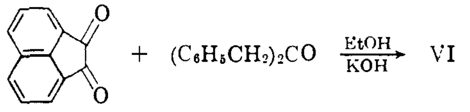
DINAPHTHYLDIPHENYLCYCLOPENTADIENONES

Compound I				
R_1	R_2	R_3	R_4	Ref.
1-Naphthyl	C_6H_5	C_6H_5	1-Naphthyl	178
C_6H_5	2-Naphthyl	2-Naphthyl	C_6H_5	51

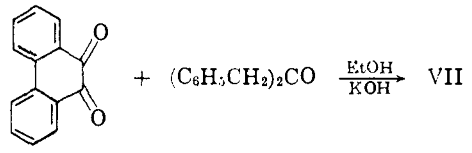
F. MISCELLANEOUS CYCLOPENTADIENONES

1. *Fused Ring Cyclopentadienones*

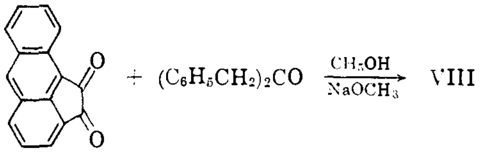
Using the procedure of base-catalyzed condensation of a β-diketone with benzil, the class of cyclopentadienones which have ring systems fused on the *c*-face of the cyclopentadienone were prepared (126). The compounds acecyclone (VI), phencyclone (VII), and aceanthrenecyclone (VIII) were prepared by the respective condensation of acenaphthenequinone (CLIV), phenanthrenequinone (CLV), and aceanthraquinone (CLVI) with benzyl ketone (126). Phencyclone (VII) can be viewed as tetracyclone (III) in which the 3- and 4-phenyls are tied back by an *o,o'*-bond, while acecyclone (VI) can be viewed as tetracyclone in which the 3- and 4-phenyls are fused together. Nearly quantitative yields of acecyclone and phencyclone have been reported using the condensation reactions listed above (114). For both acecyclone and phencyclone the intermediate cyclopentenolones CLVII and CLVIII can be isolated when the reaction is run either at room temperature or with a small quantity of base (114, 126). The acetate (CLIX) of 2,5-diphenyl-3,4-(*o,o'*-biphenylene)-4-hydroxy-2-cyclopentenone (CLVIII) was prepared and converted to phencyclone (VII).



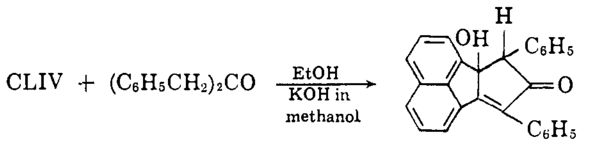
CLIV



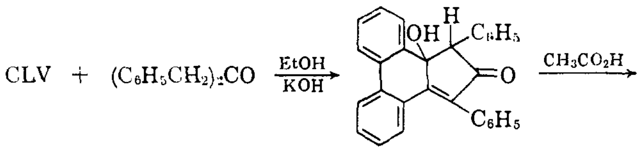
CLV



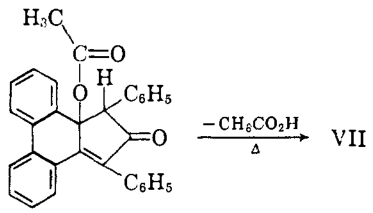
CLVI



CLVII



CLVIII

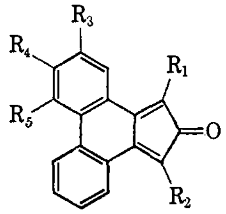


CLIX

By using the appropriately substituted phenanthrenequinones, several substituted phencyclones were prepared (o26) (Table XIV). When either 2- or 4-nitrophenanthrenequinone was used, the intermediate cyclopentenolones were obtained even though the reaction mixture was heated (126).

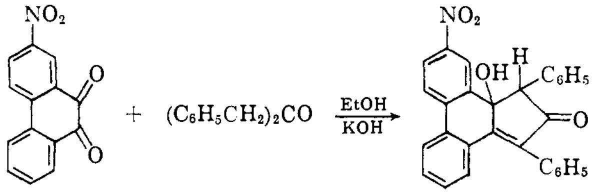
TABLE XIV

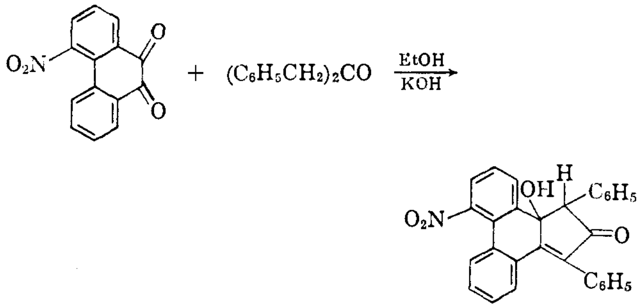
2H-CYCLOPENT[*l*]PHENANTHREN-2-ONES



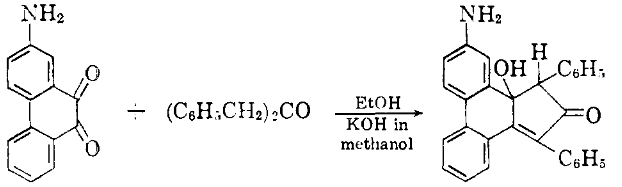
R_1	R_2	R_3	R_4	R_5	Ref.
C_6H_5	C_6H_5	H	H	H	3, 114, 126
C_6H_5	C_6H_5	NH_2	H	H	126
C_6H_5	C_6H_5	H	NH_2	H	126
C_6H_5	C_6H_5	CH_3O	H	H	126
C_6H_5	C_6H_5	Br	H	H	126[a]
H	$CO_2C_2H_5$	H	H	H	89[b]
C_6H_5	C_6H_5	NO_2	H	H	126[c]
C_6H_5	C_6H_5	H	H	NO_2	126[c]
p-ClC_6H_4	p-ClC_6H_4	H	H	H	268

[a] No experimental details given. [b] Polymer. [c] Cyclopentenolone.

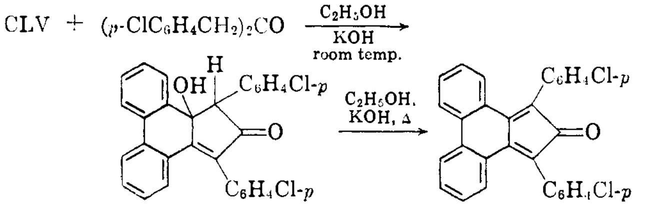




With 2-aminophenanthrenequinone, the cyclopentenolone was also obtained when the reaction was carried out at room temperature (126). These cyclopentenolones give darkly colored solutions in concentrated sulfuric acid, but whether this color is due to the formation of a cyclopentadienone is not stated (126).



The base-catalyzed condensation of 1,3-bis(4-chlorophenyl)-2-propanone with phenanthrenequinone at room temperature yields a cyclopentenolone (CLX). Refluxing this compound in ethanolic potassium hydroxide results in the cyclopentadienone CLXI (268). As is the case with the tetracyclones, all of the phencyclones are monomeric.



CLX CLXI

Several cyclopentadienones of type CLXII have been prepared where neither R_1 or R_2 is an aryl group, nor where just R_1 is an aryl group (43, 89, 259). The synthesis consists of a base-catalyzed condensation of acenaphthenequinone with a substituted 2-propanone. When the condensation is run at room temperature, the product is the cyclopentenolone (43, 89, 146, 259). The latter is then dehydrated by treatment with sulfuric acid in acetic anhydride (43, 259), or by heating in glacial acetic acid (89). If, instead, the condensation is run at the reflux temperature, the cyclopentadienone is formed directly (43).

Heating a 1,3-diaryl-2-propanone with acenaphthenequinone in the presence of alcoholic base yields CLXII where both R groups are aryl (259, 268) (see Table XV). A different type of substituted acecyclone was prepared from the reaction of 3-bromoacenaphthenequinone with benzyl ketone (59).

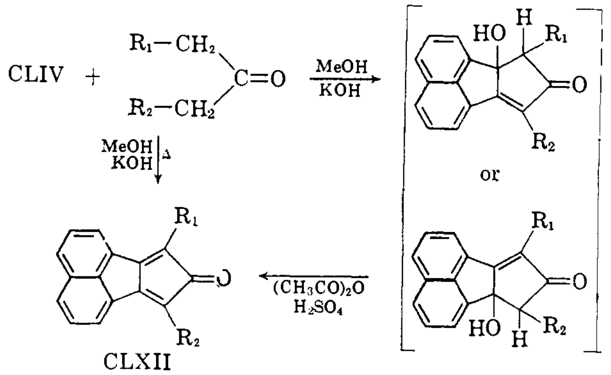
TABLE XV

8H-CYCLOPENT[*a*]ACENAPHTHALEN-8-ONES (CLXII)

R_1	R_2	Ref.
$p\text{-}CH_3C_6H_4$	$p\text{-}CH_3C_6H_4$	259^a
$p\text{-}ClC_6H_4$	$p\text{-}ClC_6H_4$	268^a
C_6H_5	C_6H_5	$114,^a\ 126^a$
$CH(CH_3)_2$	$CH(CH_3)_2$	43^a
$CO_2C_2H_5$	$CO_2C_2H_5$	43^a
C_2H_5	C_2H_5	$43,^{a,c}\ 146,^b\ 259^{a,c}$
$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	$43^{a,c}$
CH_3	C_6H_5	$43^{a,c}$
$n\text{-}C_6H_{13}$	$n\text{-}C_6H_{13}$	$43^{a,c}$
CH_3	C_2H_5	$259^{a,c}$
CH_3	CH_3	$43,^{a,c}\ 259^{a,c}$

[a] Cyclopentadienone prepared. [b] Cyclopentenolone prepared. [c] Exists as a dissociable dimer.

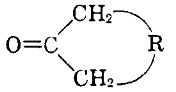
Several of these cyclopentadienones (CLXII) exist as dissociating dimers. The factors which determine whether a monomer or a dissociating dimer is formed again appear to be steric in nature—those cyclopentadienones which are bulky being monomeric.



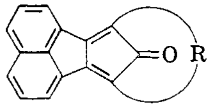
CLXII

In the case where R_1 = H and $R_2 = CO_2C_2H_5$, the cyclopentadienone is reported as a polymer (89).

By using a cyclic ketone of type CLXIII a cyclopentadienone of type CLXIV can be prepared (44).

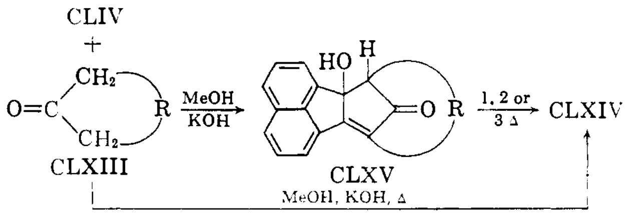


CLXIII



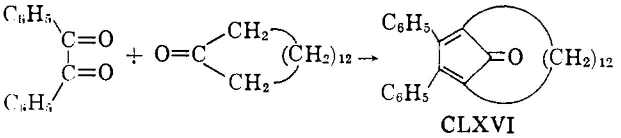
CLXIV

The conditions again were a base condensation using acenaphthenequinone with the ketone. When the reaction was refluxed, the cyclopentadienone was formed directly, while, if it was run at room temperature, the intermediate cyclopentenolone CXLV was formed, which could then be converted to the cyclopentadienone by the following steps: (1) acetic anhydride and sulfuric acid; (2) glacial acetic acid; (3) methanol and sulfuric acid.



$R = -(CH_2)_{11}-, -(CH_2)_{12}-, -(CH_2)_6CH{=}CH(CH_2)_6-$

In addition CLXVI was prepared by the same procedure (44).

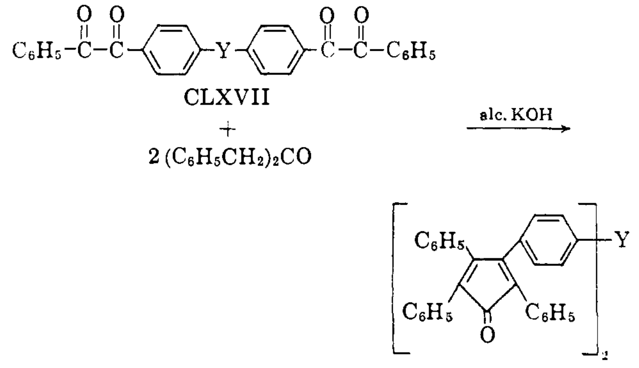


CLXVI

15, 16-diphenylbicyclo[12.2.1]heptadeca-14, 16-dien-17-one

2. "*Bistetracyclones*"

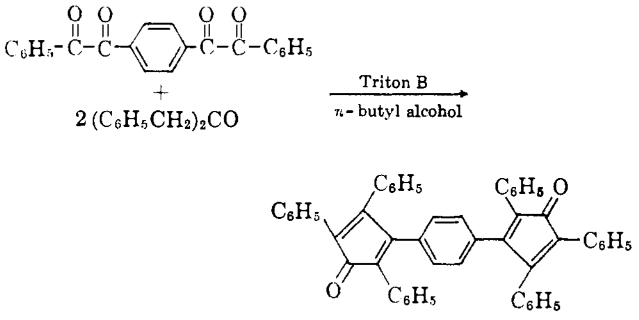
Using the base-catalyzed condensation of benzyl ketone with a bisbenzil, a class of compounds called "bistetracyclones" (IX) linked by a direct bond, O, S, $-CH_2-$, $(CH_2)_2$, $(CH_2)_3$, and $(CH_2)_4$, respectively, was prepared (152, 224, 225). A "bistetracyclone" which has only one phenyl group connecting the two cyclopentadienone rings has also been prepared (224).



CLXVII

IXa–g

$Y = \text{nil}, O, S, CH_2, (CH_2)_2, (CH_2)_3, \text{and } (CH_2)_4$



IXh

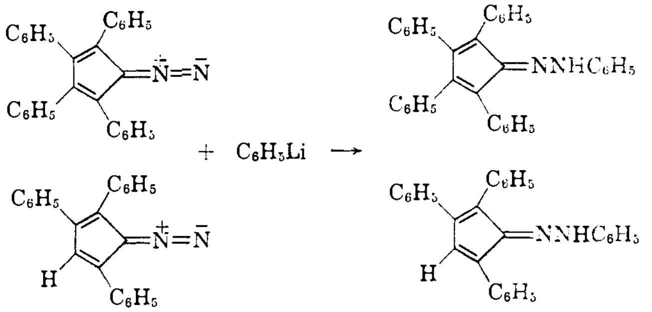
III. REACTIONS

A limited variety of carbonyl derivatives of cyclopentadienones is known. Diels–Alder reaction products are most numerous. Hydrazones may be formed, albeit by less usual methods. Organometallic compounds of lithium and magnesium add, but base- or acid-catalyzed condensations with active methyl or methylene compound are not known. Acetals have not been prepared from the cyclopentadienones. Reductions of the system are interesting in that the hydrogen may reduce the carbon–carbon double bond or the carbonyl group.

The apparent lowered activity of the carbonyl group, particularly toward active methyl and methylene compounds, may be rationalized by electronic considerations. Delocalization of charge from C-1 around the ring and to some extent into the aryl rings would tend to make the carbon of the carbonyl group less electron poor than for the usual carbonyl groups. An additional consideration is that, according to Hückel, the five-membered ring would actually be more stabilized as the anion than as the carbonium ion. Thus, there is less tendency to polarize the carbonyl in the five-membered ring than in the ordinary carbonyl group.

A. CARBONYL DERIVATIVES

A surprisingly limited variety of carbonyl derivatives of cyclopentadienones is known. Many are formed by nonconventional methods. This is particularly true for the hydrazones. Hydrazine and phenylhydrazine reduce tetracyclone to dihydrotetracyclone under usual conditions (191, 263). However, in dioxane–sulfuric acid the *p*-nitrophenyl- and 2,4-dinitrophenylhydrazones are formed readily (191, 205, 263). The phenylhydrazones of triphenyl- and tetraphenylcyclopentadienone have been prepared through the cyclopentadienyldiazo compounds by adding phenyllithium and hydrolyzing (229).



The *p*-dimethylaminophenyl Schiff base of tetracyclone has been prepared in two ways. Conventionally, tetraphenylcyclopentadiene has been condensed in piperidine with *p*-nitrosodimethylaniline (148, 149, 275, 284). The same product was obtained when tetraphenylfulvene was subjected to these reaction conditions (127, 148). Undoubtedly, the methylene group is removed *via* reaction with the piperidine in a reaction similar to reversal of the Mannich reaction and then followed by the expected condensation (267). This condensation had been reported at the 6-position of the same fulvene (127), but the work is probably in

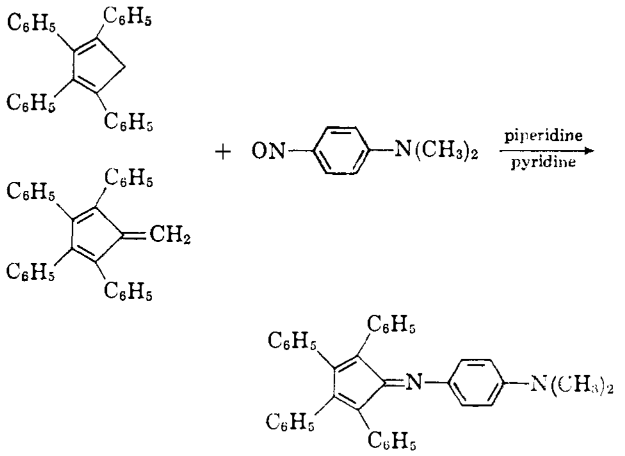


TABLE XVI

DERIVATIVES OF CYCLOPENTADIENONES OBTAINED FROM THE DIENONES

Cyclopentadienone (I)				Derivative	M.p., °C.	Color	Ref.
R_1	R_2	R_3	R_4				
OH	C_6H_5	C_6H_5	H[a]	Oxime[b]	237–239	Yellow	158
C_6H_5	OH	C_6H_5	C_6H_5[a]	Oxime[c,d]	223–226	[e]	195
H	C_6H_5	C_6H_5	H[f]	Oxime[c,d,g]	176	[e]	33
H	C_6H_5	C_6H_5	H[f]	Dioxime[g]	229	[e]	33
H	H	H	H[f]	Dioxime[g,h]	178–180 dec.	[e]	167
H	CH_3	C_2H_5	H	Semicarbazone	224 dec.	Colorless	226
n-C_4H_9	CH_3	H	H[f]	Semicarbazone[b]	227 dec.	[e]	90
n-C_5H_{11}	CH_3	H	H[f]	Semicarbazone[b]	219, 221–223	[e]	90, 264
i-C_3H_7	CH_3	H	H[f]	Semicarbazone[c,d,g]	209–210	[e]	47, 202
i-C_3H_7	CH_3	H	H[f]	Disemicarbazone[g,i]	246–247 dec.	[e]	47, 202
C_6H_5	C_6H_5	C_6H_5	C_6H_5	*p*-Nitrophenylhydrazone	244–245	Red-brown	263
H	H	H	H[f]	2,4-Dinitrophenylhydrazone[b]	147–149 dec.	Deep red	167, 168[h]
H	H	H	H[f]	Di-2,4-dinitrophenylhydrazone[g]	192–193 dec.	Red-orange	167
n-C_4H_9	CH_3	H	H[f]	2,4-Dinitrophenylhydrazone[b]	236	Red	90
n-C_5H_{11}	C_6H_5	C_6H_5	H[f]	2,4-Dinitrophenylhydrazone[b]	199	Red-orange	38
CH_3	C_6H_5	C_6H_5	CH_3[f]	2,4-Dinitrophenylhydrazone[b,j]	242	Red	35, 39
H	C_6H_5	C_6H_5	H	2,4-Dinitrophenylhydrazone[k]	216–217	Carmine	29
C_6H_5	C_6H_5	C_6H_5	C_6H_5	2,4-Dinitrophenylhydrazone	271	Red-brown	191, 205, 263
Phencyclone				2,4-Dinitrophenylhydrazone	318	Red-brown	191
Acecyclone				2,4-Dinitrophenylhydrazone	335–337	Dark brown	191
OH	H	H	CH_3[a]	Quinoxaline[l]	135	Light red	95
OH	C_6H_5	C_6H_5	H[a]	Quinoxaline[l]	236–237	White	158
OH	C_6H_5	C_6H_5	C_6H_5[a]	Quinoxaline[l]	226–227	White	194
OH	C_6H_5	H	$N(CH_3)C_6H_5$[a]	Quinoxaline[c,l]	182	Yellow	109
H	H	H	H[f]	Ethylene ketal[d,g]	94–95	[e]	274
H	H	H	H[f]	Diethylene ketal[g]	92	White	101,[e] 102, 274[e]
Hexachlorocyclopentadiene				Diethyl acetal[m]	[q]	Greenish yellow	201, 227
Hexachlorocyclopentadiene				Dimethyl mercaptal[n]	[o]	[e]	227
Hexachlorocyclopentadiene				Dimethyl acetal[p]	[r]	Colorless	212
OH	H	H	H[a]	Mono- and/or dioxime[c]	[o]	[e]	105
OH	H	H	H[a]	Phenylhydrazone[c]	[o]	[e]	105
OH	H	H	H[a]	*o*-Methyloxime[c]	[o]	[e]	105
OH	H	H	H[a]	*p*-Toluenesulfonhydrazone	185–186 dec.	[e]	105

[a] Dienone exists in diketone form. [b] Derivative formed is of monomer. [c] Structures not given by authors. [d] Mono derivative is formed. [e] Color not reported. [f] Dienone exists in equilibrium with dimer. [g] Derivative formed is of dimer. [h] Product is formed directly from 2-bromocyclopenten-4-one. [i] Product might be a mixture of isomers. [j] Product is also prepared directly from α,β-dimethylanhydroacetonebenzil. [k] Derivative is formed directly from 2-chloro-3,4-diphenylcyclopenten-3-one. [l] Derivative is of diketone. [m] Product is the diethyl acetal of tetrachlorocyclopentadienone. [n] Product is the dimethyl mercaptal of tetrachlorocyclopentadienone. [o] Melting point not reported. [p] Product is the dimethyl acetal of tetrachlorocyclopentadienone. [q] B.p. 80.6° (<1 mm.). [r] B.p. 82–83° (2 mm.)

error (127, 267). A second unusual reaction is that of 1,2,3-triphenylfulvene with *p*-nitrosodimethylaniline which gives the anil of 1,2,3-triphenyl-4-methylcyclopentadiene (229) (see section IID). The mechanism of this interesting reaction is not known.

Recently cyclopentadienone N,N-dimethylhydrazone has been prepared by the reaction of trimethylnitrosimmonium methyl sulfate with cyclopentadienylsodium (169). This hydrazone is unique since it is the first cyclopentadienone derivative prepared which is unsubstituted in the five-membered ring and also stable as the monomer. It also shows no tendency to dimerize or react with dienophiles.

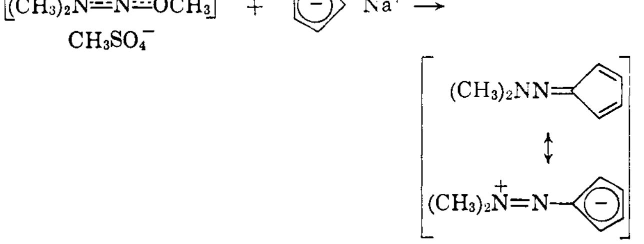


Table XVI contains a summary of the derivatives of cyclopentadienones prepared from the dienones themselves or from their dimers. Included are several quinoxaline derivatives, which are noteworthy in that they are actually derivatives of the isomeric cyclopentenediones. Many of the interesting reactions discussed above are found within the entries of Table XVII which lists the derivatives of the cyclopentadienones which are prepared from compounds other than the dienones. The oxime of cyclopentadienone, which exists as a dimer, has been prepared (139, 270) by nitrosation of cyclopentadiene and is also included in Table XVII.

TABLE XVII

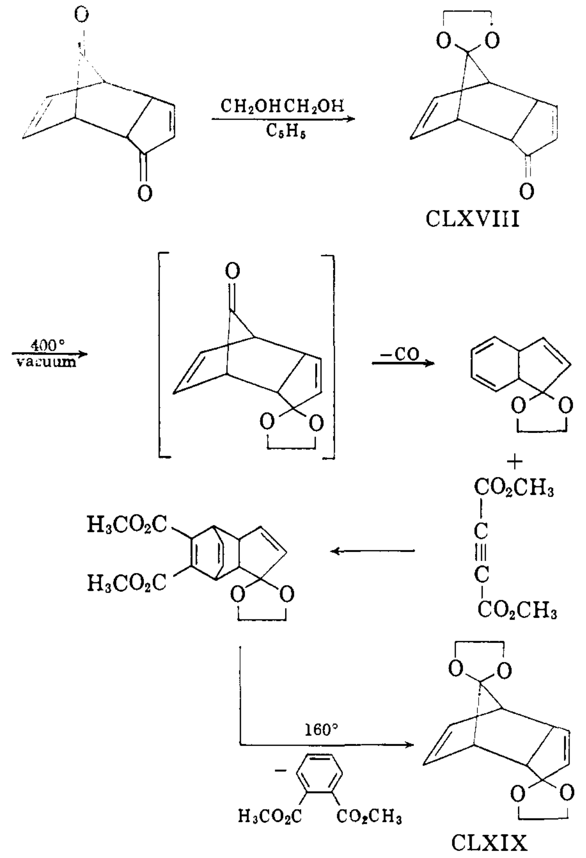
DERIVATIVES OF CYCLOPENTADIENONES PREPARED FROM OTHER COMPOUNDS

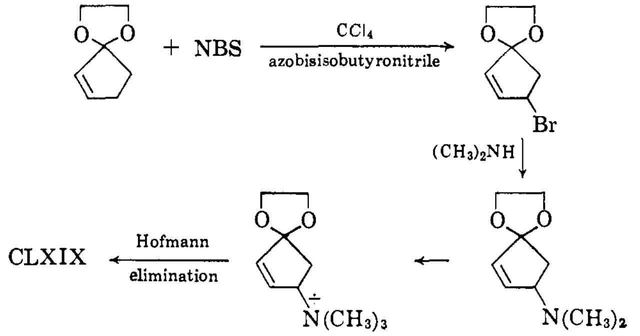
Compound	Derivative	M.p., °C.	Color	Ref.
Cyclopentadiene	Oxime[a]	178–180	Yellow	139, 270
Cyclopentadienylsodium	N,N-Dimethylhydrazone	14	Orange	169
3,4-Diphenylcyclopentenone	Oxime[b]	223–224 dec.	White	158
2,3,4-Triphenylcyclopentadiene	Anil	194	Dark red	229
1,2,3-Triphenylfulvene	Anil[c]	219–221	Purple	229
2,3,5-Triphenylcyclopentadiene	Anil	172–173	Dark blue	134
1,2,3,4-Tetraphenylfulvene	Anil[d]	225–226	Black-violet	127,[e] 148
2,3,4,5-Tetraphenylcyclopentadiene	Anil	224–226	Black	148, 149, 275, 287
2-*p*-Methoxyphenyl-3,4,5-triphenylcyclopentadiene	Anil	204–205	Dark brown	138
1-Diazo-2,3,5-triphenyl cyclopentadiene	Phenylhydrazone[f]	183	Red-brown	229
1-Diazo-2,3,4,5-tetraphenylcyclopentadiene	Phenylhydrazone[g]	226–268	Deep purple	229
7-Phenyl-9-hydro-9a-hydroxy-8-cyclopent[*a*]acenaphthylen-8-one	2,4-Dinitrophenylhydrazone[h]	[i]	[j]	43

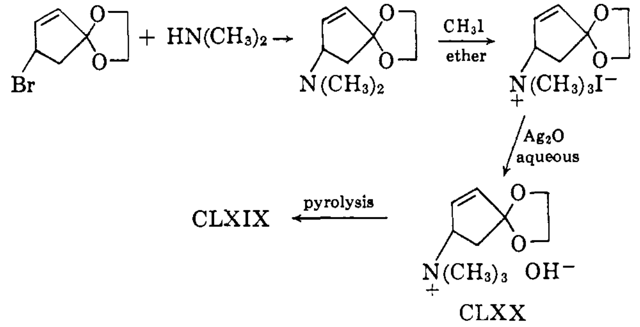
[a] Derivative formed is of dimer. [b] Product is the oxime of 2-hydroxy-4,5-diphenylcyclopentadienone. [c] Derivative formed is the anil of 2-methyl-3,4,5-triphenylcyclopentadienone. [d] Derivative formed is the anil of tetracyclone. [e] These authors incorrectly identified their product (148). [f] Derivative formed is the phenylhydrazone of 2,3,5-triphenylcyclopentadienone. [g] Derivative formed is the phenylhydrazone of tetracyclone. [h] Derivative formed is the 2,4-dinitrophenylhydrazone of 7-phenyl-8-cyclopent[*a*]acenaphthylen-8-one. [i] Melting point not reported. [j] Color not reported.

Three preparations of the ethylene ketal of cyclopentadienone dimer are reported, actually in attempts, at least in one case, to prepare the acetal of the monomer. In one case cyclopentadienone dimer itself was the starting material giving the mono- (CLXVIII) and the diacetal (CLXIX) (274).

In the second case, the synthesis of cyclopentadienone ketal was attempted *via* Hofmann elimination on the ketal of the 4-trimethylammonio salt of cyclopent-2-enone. However, only the dimer of cyclopentadienone ketal (CLXIX) was obtained (101). The final preparation involved pyrolysis of the quaternary ammonium salt of 4-(N,N-dimethylamino)cycopenten-2-ethylene ketal (CLXX) (102).







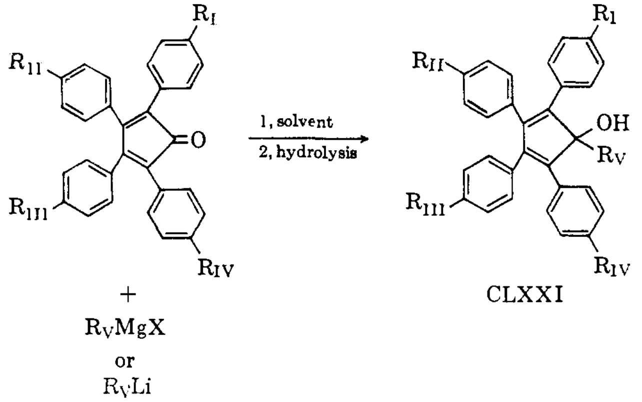
B. GRIGNARD REACTIONS

Since cyclopentadienones contain a carbonyl group, one of the many reactions which they undergo is the Grignard reaction to produce pentasubstituted alcohols such as CLXXI. These alcohols can also be prepared by the reaction of organolithium compounds

TABLE XVIII

ORGANOMETALLIC REACTION WITH TETRACYCLONES

R_I	R_{II}	R_{III}	R_{IV}	R_V	MgX or Li	M.p. of carbinol CLXXI, °C.	Ref.
H	H	H	H	$C_6H_5CH_2$	MgCl	155–156	207, 263
H	H	H	H	$C_6H_5CH_2$	MgBr	156–157	127
H	H	H	H	C_6H_5	MgBr	175–176	36
H	H	H	H	n-C_3H_7	MgI	136–138	265
H	H	H	H	CH_3	MgBr	195	127
H	H	H	H	CH_3	MgI	195–196	75, 263
H	H	H	H	C_2H_5	MgBr	188	127
H	H	H	H	Cyclopentadienyl	MgBr	197.6–198.6	257
H	H	H	H	$(CH_3)_3CCH_2$	MgI	175.5–176.5	75
H	H	H	H	p-$CH_3OC_6H_4$	MgBr	203	36, 73
H	$(CH_3)_2N$	$(CH_3)_2N$	H	C_6H_5	MgBr	270–271	143
CH_3O	H	H	H	C_6H_5	MgBr	164.8–165.8	73
CH_3O	CH_3O	CH_3O	CH_3O	p-$CH_3OC_6H_4$	MgBr	210–211.5	273
CH_3	CH_3	CH_3	CH_3	p-$CH_3C_6H_4$	MgBr	206–208	273
H	Br	Br	H	C_6H_5	MgBr	195	37
Cl	Cl	Cl	Cl	p-ClC_6H_4	MgBr	223.5–224.5	273
H	H	H	H	C_6H_5	Li	176–177	57, 257
H	H	H	H	n-C_3H_7	Li	149.5–153.0	75
H	H	H	H	n-C_4H_9	Li	164.5–169.5	75
H	H	H	H	p-$CH_3C_6H_4$	Li	188–189, 199–200	241
CH_3	H	H	H	C_6H_5	Li	153–154	241
H	CH_3	H	H	C_6H_5	Li	170	241
H	H	H	H	$HC{\equiv}C$	Li	193–194	215
H	H	H	H	p-$(CH_3)_2NC_6H_4$	Li	248–249	57
H	$(CH_3)_2N$	H	H	C_6H_5	Li	203–204	57
H	$(CH_3)_2N$	H	H	p-$(CH_3)_2NC_6H_4$	Li	237	57
H	$(CH_3)_2N$	$(CH_3)_2N$	H	C_6H_5	Li	252	57
H	$(CH_3)_2N$	$(CH_3)_2N$	H	p-$(CH_3)_2NC_6H_4$	Li	251–252	57



CLXXI

with the desired cyclopentadienones. Table XVIII summarizes the various organolithium and organomagnesium halide reagents which have been used on the various tetracyclones.

Very little work has been done in the way of Grignard reactions with other monomeric cyclopentadienones. The only work which does appear in the literature is listed in Table XIX and concerns the reaction of acecyclone (VI) and phencyclone (VII) with respective Grignard reagents.

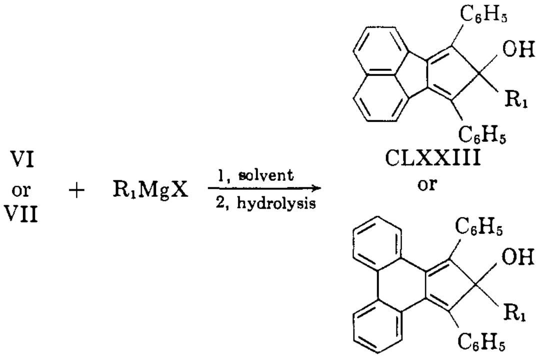
However, by the addition of phenylmagnesium bromide to tetracyclone (III) in isoamyl ether under the conditions shown below, 1,4-addition was observed (36) to yield the product CLXXIV. 1,4-Addition was also observed (64) in the reaction of III with indenyl- and fluorenyllithium under normal conditions.

TABLE XIX

GRIGNARD REACTION WITH OTHER CYCLOPENTADIENONES

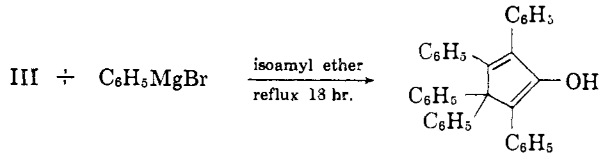
Cyclopentadienones	R_1	Halide	M.p. of carbinol CLXXII or CLXXIII, °C.	Ref.
VI	CH_3	I	197	127
VI	C_2H_5	Br	146	127
VI	$C_6H_5CH_2$	Cl	234–235	127
VII	CH_3	Br	231–232	127
VII	C_2H_5	Br	195, 179–180[a]	3, 127
VII	$C_6H_5CH_2$	Cl	271–272, 264–265[b]	3, 127
VII	C_6H_5	Br	255–257[c]	3
VII	n-C_4H_9	Br	237–239[d]	3

[a] A by-product was also obtained whose m.p. is 84–87°; no structure is given. [b] A yellow by-product was also obtained whose m.p. is 158–159° and which gives the empirical formula $C_{36}H_{28}O_2$ upon analysis; no structure is given. [c] A by-product was also obtained whose m.p. is 110–111°; no structure is given. [d] A by-product was also obtained whose m.p. is 105–110°; no structure is given.

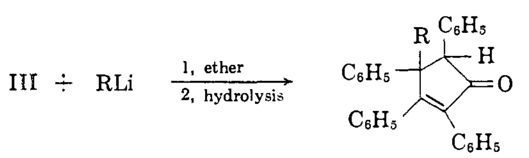


CLXXIII

CLXXII



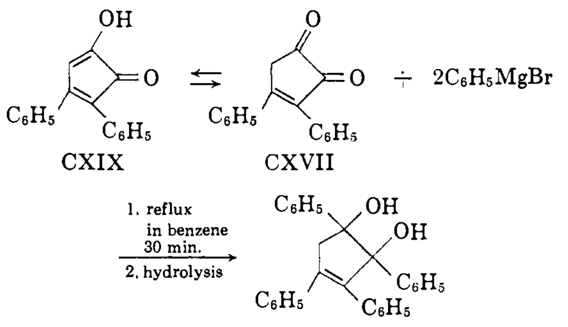
CLXXIV



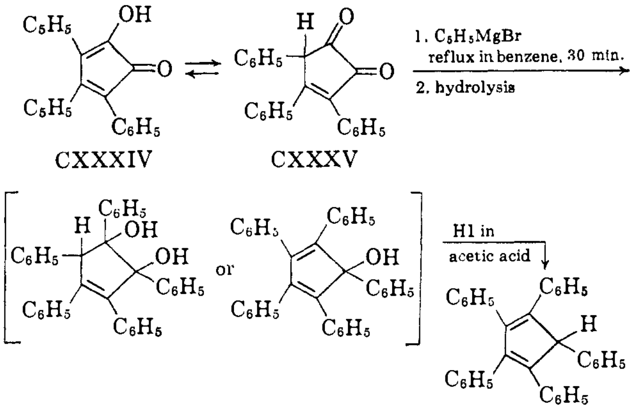
R = 1-indenyl, 9-fluorenyl

Since many of the hydroxycyclopentadienones exist mainly in the diketo form, Grignard reactions with these compounds may require more than 1 mole of Grignard per mole of cyclone. This requirement is also dependent upon the number of aryl groups that the cyclopentadienone contains.

In the case of 2-hydroxy-4,5-diphenylcyclopentadienone (CXIX), which is stable as the diketone CXVII, 2 moles of phenylmagnesium bromide are found to react per mole of cyclone to yield the dialcohol CLXXV (158). However, in the case of 2-hydroxy-3,4,5-triphenylcyclopentadiene (CXXIV) (194), which is also stable as the diketone CXXV, 2.6 moles of phenylmagnesium bromide react to give a nonisolated glycol which, when treated with hydriodic acid in acetic acid, gave 1,2,3,4,5-pentaphenylcyclopentadiene (CLXXVI) (194). The product may be visualized as arising from reduction of the glycol as suggested (194), or from reduction of the corresponding "dienol" which could have arisen by dehydration of the glycol. The latter possibility is similar to the method since reported for other dienols (75).

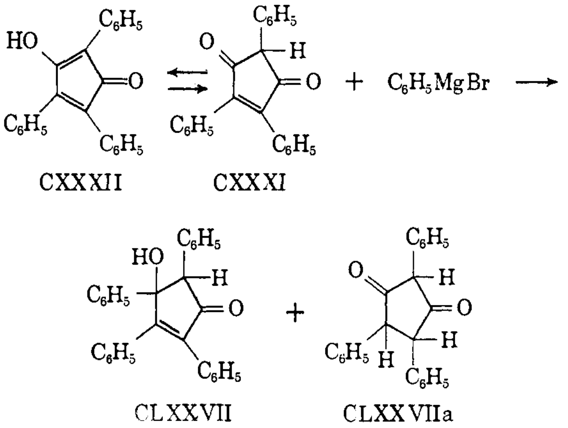


CXIX CXVII CLXXV



CXXXIV CXXXV CLXXVI

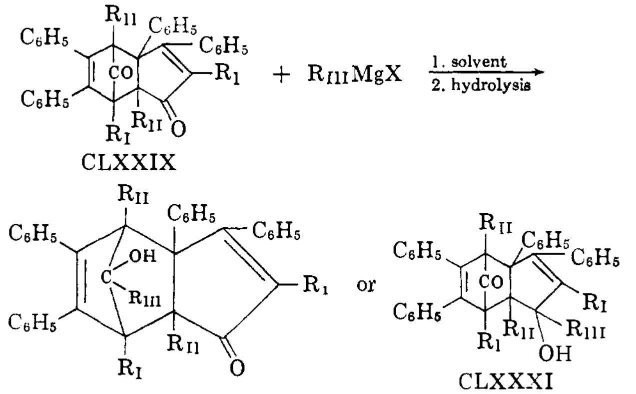
In the case of those hydroxycyclopentadienones which exist mainly in the diketo form 1,4-addition is also observed. This is observed (195) with 3-hydroxy-2,4,5-triphenylcyclopentadienone (CXXXII) which is stable as the diketone CXXXI. When this compound is treated with phenylmagnesium bromide, two products are formed. The first, 3-hydroxy-2,3,4,5-tetraphenylcyclopentenone (CLXXVII), is the product of normal 1,2-Grignard addition to one of the ketone groups and the second compound, CLXXVIIa, is the product of reduction of the double bond.



CXXXII CXXXI

CLXXVII CLXXVIIa

The cyclopentadienones which are not stable as monomers but which do exist as dimers have also been subjected to reaction with Grignard and organolithium reagents. In these reactions two possible monoaddition products may be formed according to the equation below, neglecting stereochemical considerations. Table XX summarizes the results.



CLXXIX CLXXX CLXXXI

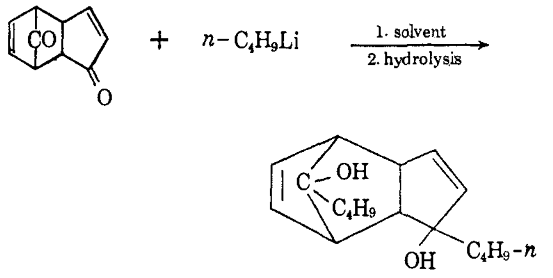
Cyclopentadienone dimer has also been treated with *n*-butyllithium to yield the diol (167).

Table XX

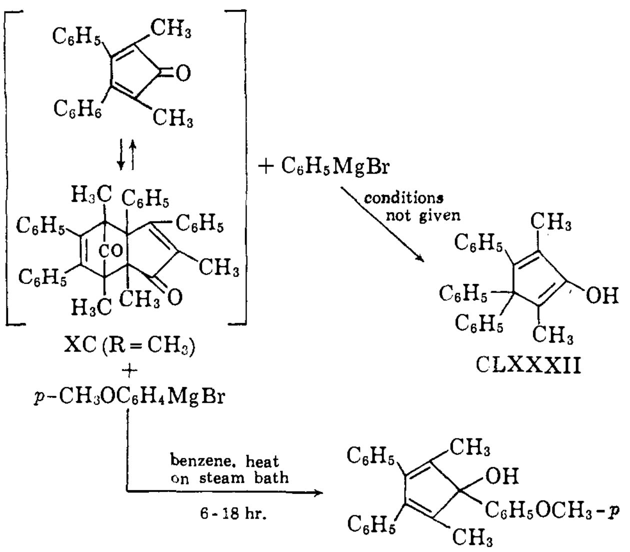
Grignard Reaction with Cyclones (Dimers)

R_I	R_{II}	R_{III}	MgX or Li	Product	M.p., °C.	Ref.
CH_3	CH_3	CH_3	MgBr	CLXXXI	205–206	35, 39
CH_3	H	CH_3	MgBr	CLXXX	286–288	39
CH_3	H	C_6H_5	MgBr	CLXXX	229	39
CH_3	H	p-$CH_3OC_6H_4$	MgBr	CLXXX	258	39
n-C_5H_{11}	H	C_6H_5	MgBr	CLXXX	180–181	39
CH_3	CH_3	C_6H_5	MgBr	CLXXX or CLXXXI[a]	223	16, 39
H	H	CH_3	MgBr	CLXXX[b]	262	16, 25
H	H	C_6H_5	MgBr	CLXXX[b]	226	16, 25
H	H	α-$C_{10}H_7$	MgBr	CLXXX[b]	295	16, 25
CH_3	CH_3	C_6H_5	Li	CLXXXI	205	35
CH_3	CH_3	CH_3	Li	CLXXXI	206	39
CH_3	CH_3	C_6H_5	Li	CLXXX or CLXXXI[c]	223	39

[a] In the original reference (39), the structure was not proved; however, in a later reference (16) structure CLXXXI is assigned on basis of infrared data (22, 23). [b] In the original reference (25), the 1-alkyl enol form of LXXXIII was assigned to the products, but in a later reference (16), structures of type CLXXXI were assigned to products on the basis of infrared data. [c] Structure not proved.

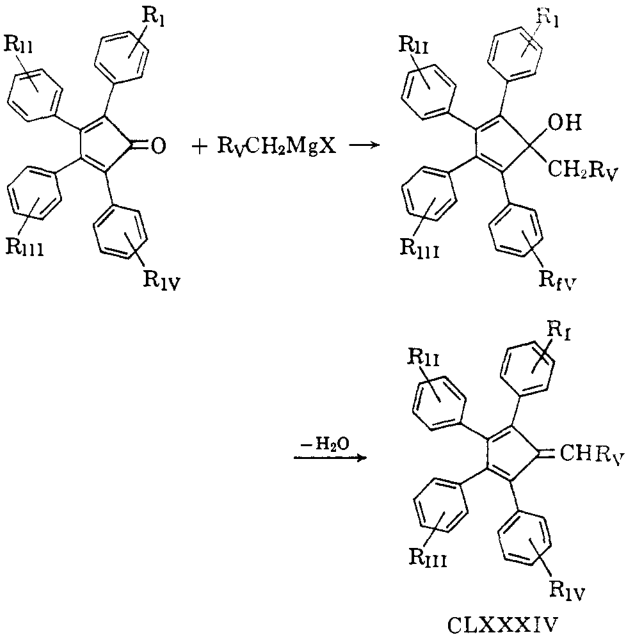


Two examples of abnormal products resulting from the reaction of Grignard reagents upon these dimers are known. In the first case the dimer of 1,4-dimethyl-2,3-diphenylcyclopentadienone (XC, R = CH_3) is treated with phenylmagnesium bromide to yield 2,5-dimethyl-3,4,4-triphenylcyclopentadienol (CLXXXII) under unspecified conditions (39). In the second case this same dimer (XC, R = CH_3) is treated with p-methoxyphenylmagnesium bromide under the conditions shown below to yield 1-(p-methoxyphenyl)-2,5-dimethyl-3,4-diphenylcyclopentadienol (CLXXXIII).



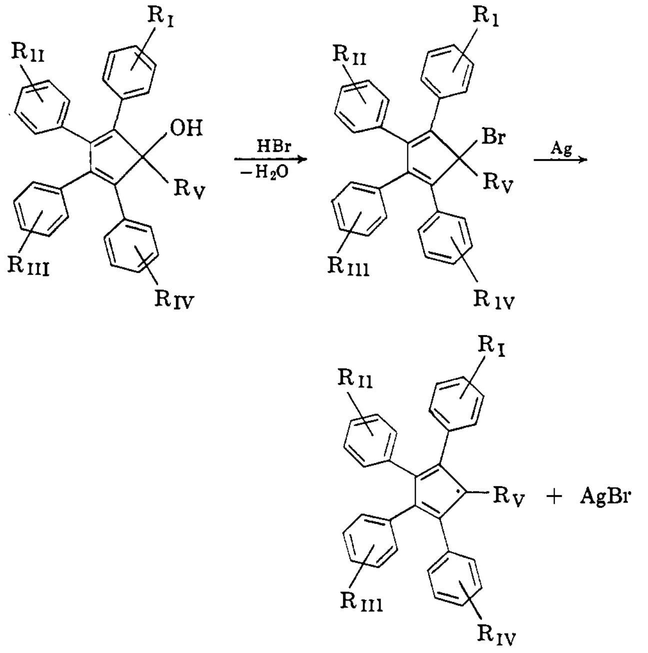
CLXXXIII

Once these alcohols are prepared they can be subjected to a variety of reactions to yield various members of other classes of organic compounds. For example, they may be dehydrated to produce fulvenes (CLXXXIV) (36, 75, 127, 207, 257, 263), provided that the alkyl group at C-1 has an α-carbon holding a hydrogen atom. The alcohol may be converted to a halide and, in turn, the halide may be removed with silver metal to produce a stable free radical (CLXXXV) (199, 287).

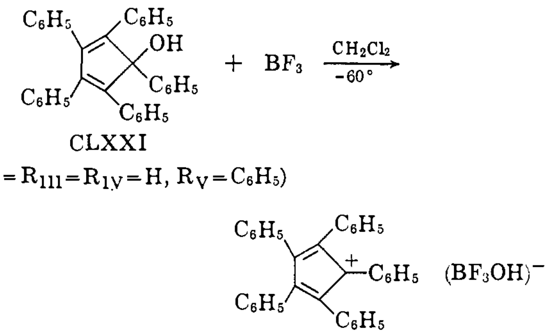


CLXXXIV

Another reaction which may be performed is preparation of a pentaphenylcyclopentadienyl cation (CLXXXVI) by treatment of pentaphenylcyclopentadienol with sulfuric acid (72, 287) or with boron trifluoride (78).



CLXXXV



CLXXXI

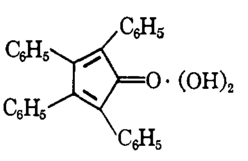
$(R_I = R_{II} = R_{III} = R_{IV} = H,\ R_V = C_6H_5)$

CLXXXVI

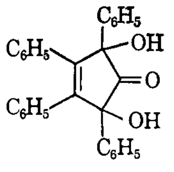
C. OXIDATION OF CYCLOPENTADIENONES

The oxidation of cyclopentadienones results in various products depending on the conditions used. The oxidation is accompanied by the loss of the characteristic purple, blue, or blue-green color.

The first reported oxidation was that of tetracyclone using either lead dioxide or nitric acid as the oxidizing agent. However, the structure of the colorless product that resulted was not given (133). Mild oxidation by refluxing tetracyclone (III) with nitric acid in dioxane gave a compound whose formula was CLXXXVII, and whose structure was given as CLXXXVIII (238, 239). Under slightly stronger oxidation conditions, namely nitric acid in acetic acid at 100°, both CLXXXVIII and tetraphenyl-2-pyrone (CLXXXIX) were obtained (238). Refluxing III with acetic acid, acetic anhydride, and hydrogen peroxide produced mainly CLXXXIX (238).

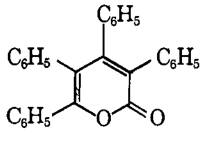


CLXXXVII

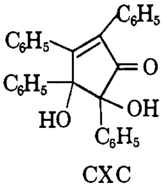


CLXXXVIII

Dioxane and nitric acid are reported to oxidize tetracyclone to both CLXXXVIII and CXC (285).

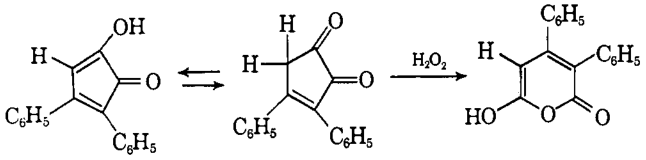


CLXXXIX



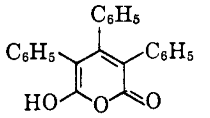
CXC

It is reported that 2-hydroxy-3,4-diphenylcyclopentadienone (CXIX), which exists as the ketone CXVII, is oxidized by hydrogen peroxide in alcohol containing sodium hydroxide to yield 6-hydroxy-3,4-diphenyl-2-pyrone (CXCI) (158), while similar treatment of 2-hydroxy-3,4,5-triphenylcyclopentadienone (CXXXIV), which exists in the keto form CXXXV, yields a similar product CXCII (194).



CXIX CXVII CXCI

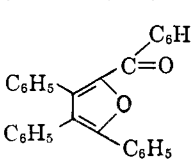
$\text{CXXXIV} \rightleftharpoons \text{CXXXV} \xrightarrow{H_2O_2}$



CXCII

It is interesting to note that CLXXXVIII could be dehydrated under a variety of conditions to yield 2-benzoyl-3,4,5-phenylfuran (CXCIII) (238, 239).

$\text{CLXXXVIII} \xrightarrow{-H_2O}$

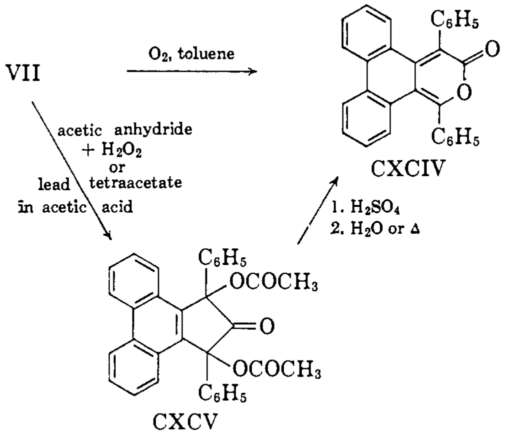


CXCIII

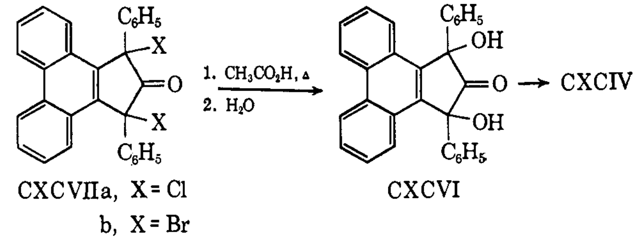
Therefore, 2,5-dihydroxytetraphenyl-3-cyclopenten-1-one (CLXXXVIII) has been suggested as the precursor of both CXCIII and CLXXXIX (123).

An oxidation of phencyclone (VII) in toluene yields a small amount of the 2-pyrone (CXCIV) (123). Oxidation of VII in acetic acid–acetic anhydride with hydrogen peroxide or with lead tetracetate in acetic acid, produced the diacetate CXCV which could be converted to CXCIV by treatment with sulfuric acid or by heat alone (123).

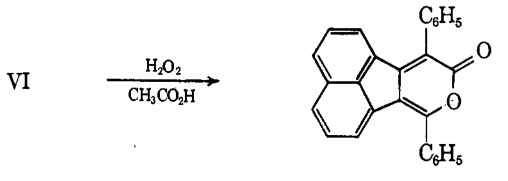
Although CXCVI, the phencyclone analog of CLXXXVIII, was not made by oxidation of phencyclone, it was made from CXCVII, and could be

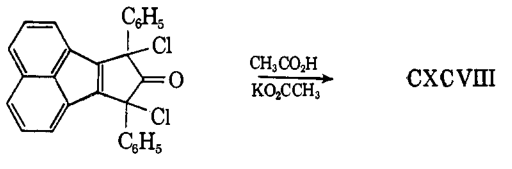


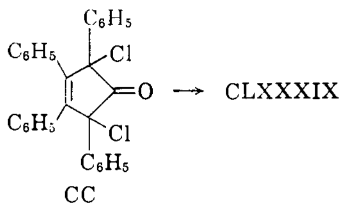
converted into CXCIV under various dehydrating conditions (123).



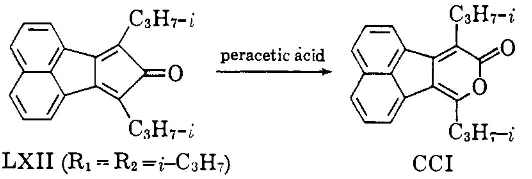
Oxidation of acecyclone (VI) with peroxide in acetic acid yielded CXCVIII (123). Compound CXCVIII could also be prepared from the dichloride CXCIX (123). It is noteworthy that the dichloride CC upon treatment with silver acetate and acetic acid yields CLXXXIX (238).

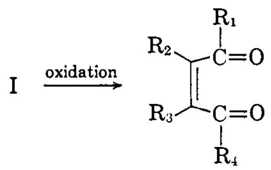




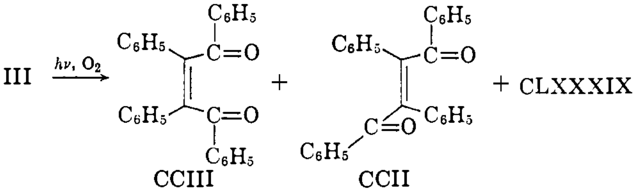


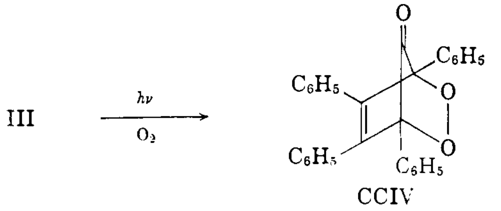
The cyclopentadienone CLXII (R_1 = R_2 = i-C_3H_7) upon oxidation with peracetic acid also yields a 2-pyrone (CCI) (44). Another course the oxidation may take is the formation of a diketone from I.

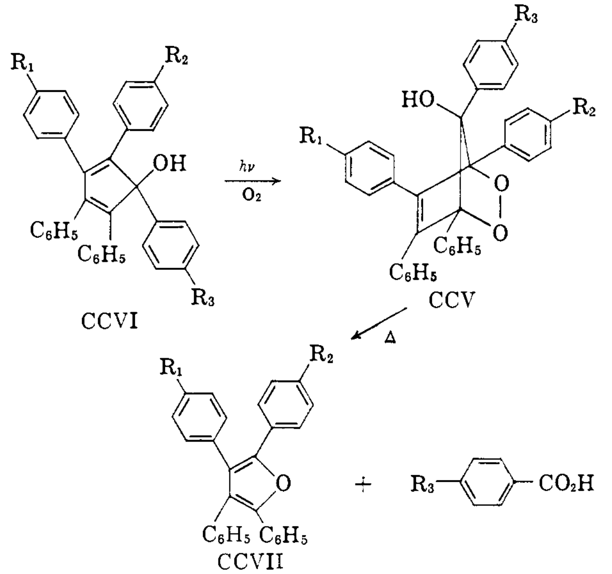




The oxidation of a solution of tetracyclone by air in the presence of light has been reported to yield *trans*-dibenzoylstilbene (CCII) (71, 87), *cis*-dibenzoylstilbene (CCIII) (71, 142, 143, 251), and tetraphenyl-2-pyrone (CLXXXIX) (71). The *trans*-dibenzoylstilbene (CCII) was reported as coming from the light-induced isomerization of *cis*-dibenzoylstilbene (CCIII) (71). A photooxide was proposed (CCIV) as a possible intermediate (57, 71, 143). A similar type of photooxide (CCV) was obtained by irradiation of pentaarylcyclopentadienols (CCVI) (57, 143, 241). This type of photooxide, upon heating, decomposed to an aromatic acid and a



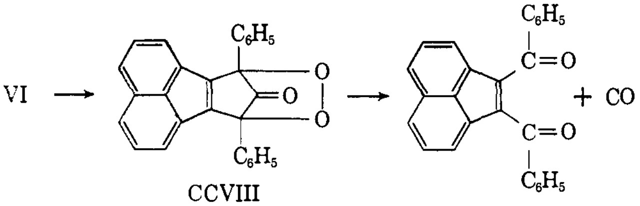




R_1	R_2	R_3	Ref.
H	H	H	57, 143
H	H	$N(CH_3)_2$	57, 143
$N(CH_3)_2$	H	H	57, 143
H	H	CH_3	241
H	CH_3	H	241
CH_3	H	H	241

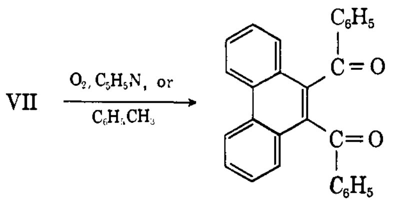
furan (CCVII) (57, 143, 241). The intermediate photooxides were stable and could be isolated (143, 241).

A similar peroxide, CCVIII, has been suggested as an intermediate for the oxidation of acecyclone (VI) (123).



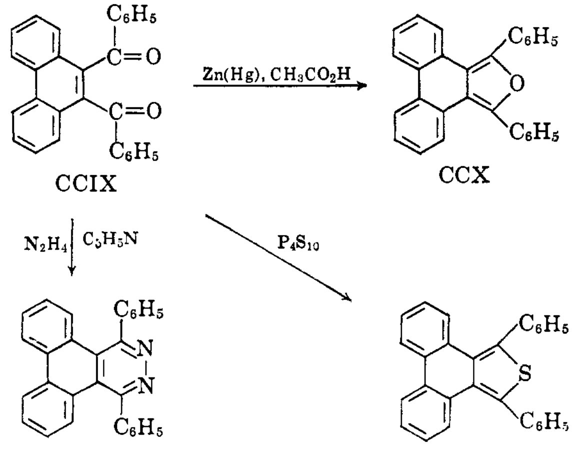
CCVIII

The oxidation of phencyclone (VII) in pyridine or toluene has been reported to yield dibenzoylphenanthrene (CCIX) (123).



CCIX

Compound CCIX could in turn be converted to a furan (CCX), a thiophene (CCXI), or to a pyridazine (CCXII) (123).

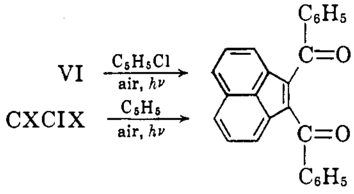


CCIX CCX

CCXII CCXI

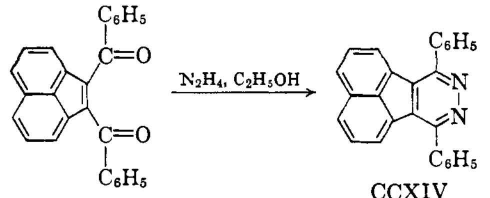
An oxidation of acecyclone (VI) in chlorobenzene by air in the presence of sunlight affords dibenzoylacenaphthylene (CCXIII) (123). A small amount of CCXIII could also be obtained by oxidation of VI with hydrogen peroxide in acetic acid, although the main product is CXCVIII (123).

The dichloride CXCIX has been shown to decompose partially to acecyclone and chlorine, and oxidation of it in benzene by air in the presence of light yields CCXIII as anticipated (123).



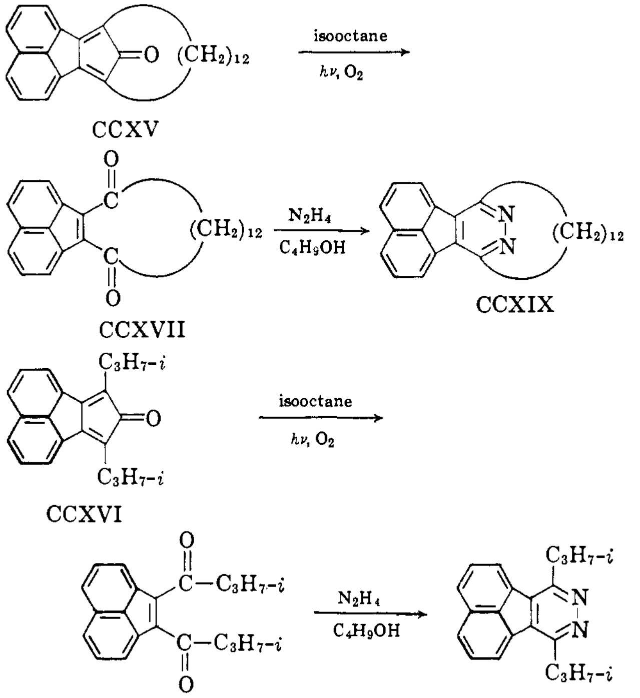
CCXIII

Compound CCXIII has also been converted to a pyridazine CCXIV (123).



CCXIII CCXIV

Oxidation of the cyclopentadienones CCXV and CCXVI by air in the presence of light yields the diketone CCXVII and CCXVIII (44). These diketones could also be converted to the pyridazines CCXIX and CCXX (44).



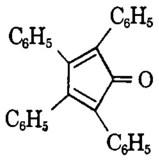
CCXVIII CCXX

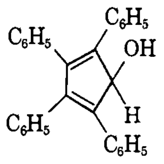
D. REDUCTION OF CYCLOPENTADIENONES

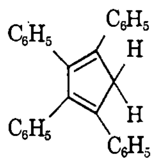
1. *Tetracyclone*

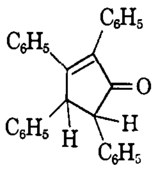
Tetracyclone (III) contains two double bonds and a carbonyl group. Reduction might be expected to proceed in several ways. The ketone may be reduced to an alcohol, CCXXI, or to a methylene group, CXXXVII; the double bond could be reduced to yield

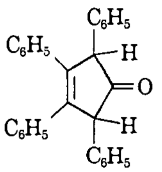
CXLVII or CXLVI; both double bonds could be reduced giving a ketone, CCXXII; or some combination of these reductions could occur such as CCXXIII, CCXXIV, CCXXV, or CCXXVI. Which ones are obtained depend upon the reaction conditions. The various conditions used are listed below.

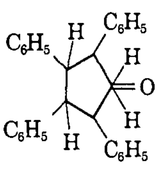

III

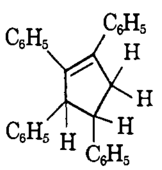

CCXXI

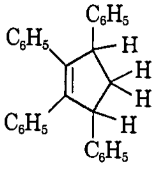

CXXXVII

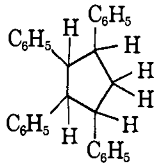

CXLVII

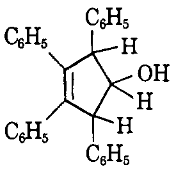

CXLVI


CCXXII


CCXXIII


CCXXIV

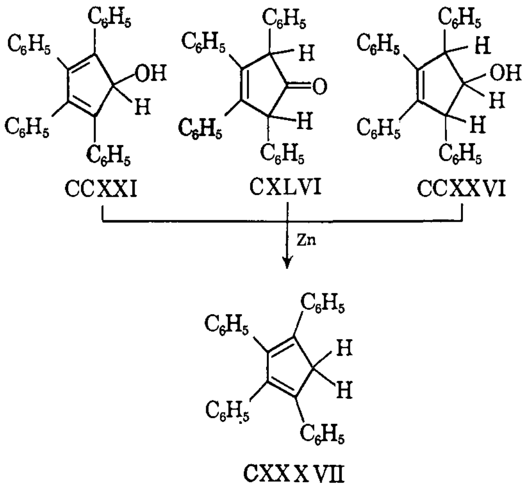

CCXXV


CCXXVI

a. Zinc Dust Distillation

Zinc dust distillation of III reduces the carbonyl group to a methylene group and yields CXXXVII (120, 263). Tetraphenylcyclopentadiene (CXXXVII) could be obtained by the zinc dust distillation of CCXXI, CXLVI, or CCXXVI (120).

$$\text{III} \xrightarrow[\text{distillation}]{\text{Zn dust}} \text{CXXXVII}$$

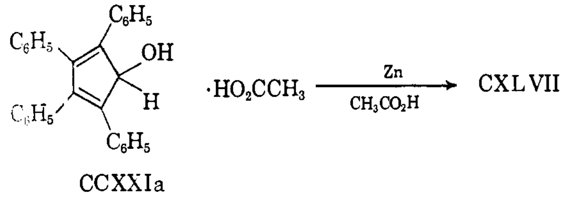


b. Zinc in Acetic Acid

The treatment of III with zinc in acetic acid was reported to give CCXXI and CXLVII (81, 133, 263), both compounds forming by the addition of 1 mole of hydrogen to III. Compound CXLVII could be oxidized back to III by treatment with bromine in acetic acid (133). Compound CCXXI exists both as

$$\begin{tikzcd} \text{III} \arrow[r, "\text{Zn, CH}_3\text{CO}_2\text{H}"] & \text{CXLVII} + \text{CCXXI} \arrow[l, bend left, "\text{Br}_2", "\text{CH}_3\text{COOH}"'] \end{tikzcd}$$

the structure given and as a solvate CCXXIa (263), which is converted to CXLVII on treatment with zinc and acetic acid (263). Therefore, it was suggested that in the reduction of III with zinc and acetic acid, CCXXI was first formed and CXLVII results from the rearrangement of CCXXIa (263). Compound CCXXI

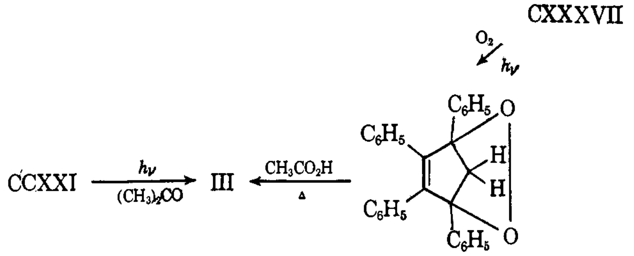


rearranges in acetic acid to CXLVI upon refluxing in a hydrogen atmosphere (120). It should be noted that both CXLVI and CXLVII result from this rearrangement and, since they both have the same melting point, they may be identical.

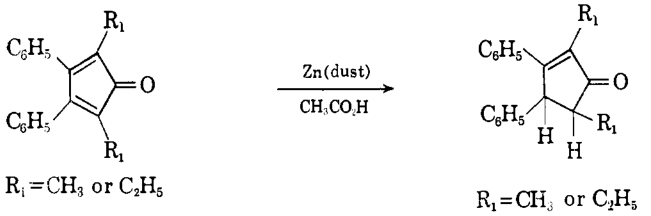
$$\text{CCXXI} \xrightarrow[\text{H}_2]{\text{CH}_3\text{CO}_2\text{H}} \text{CXLVI}$$

On the other hand, CXLVII has been rearranged to CCXXI by treatment with sodium (154), and irradiation of CCXXI in acetone oxidizes it back to III (133).

$$\text{CXLVII} \xrightarrow{\text{Na}} \text{CCXXI}$$



Tetraphenylcyclopentadiene (CXXXVII) can also be converted to tetracyclone (III) by going through the photooxide (57). 2,5-Dimethyl- and 2,5-diethyldiphenylcyclopentadienone have also been reduced by treatment with zinc dust and acetic acid (81).



c. Zinc in Acetic Acid with Hydrogen Chloride

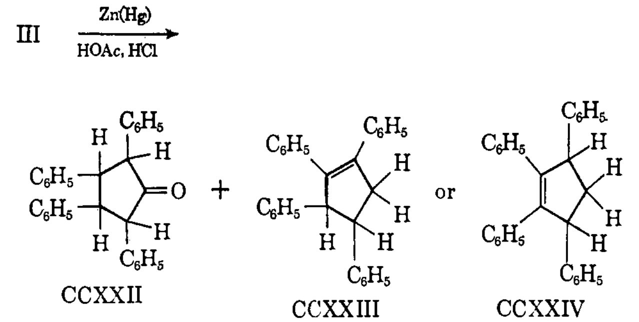
Treatment of III with amalgamated zinc in acetic acid followed by the addition of hydrogen chloride yields CCXXVI (120) by the reaction with 2 moles of hydrogen. Later it was observed that III under these

$$\text{III} \xrightarrow[\text{CH}_3\text{CO}_2\text{H, HCl}]{\text{Zn(Hg)}} \text{CCXXVI}$$

conditions added 1 mole of hydrogen to yield CXLVII when the reaction was run for about 10 min. (263).

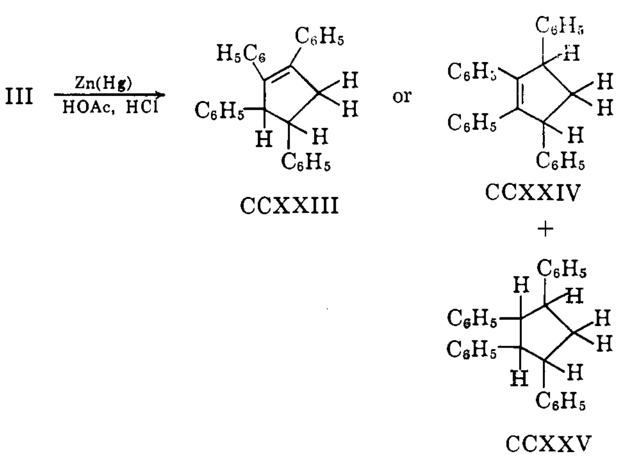
$$\text{III} \xrightarrow[\text{CH}_3\text{CO}_2\text{H, HCl}]{\text{Zn(Hg)}} \text{CXLVII}$$

If, on the other hand, the reaction was allowed to proceed for 1 hr., then 2 moles of hydrogen reacted to yield CCXXII, or 3 moles to yield either CCXXIII or CCXXIV, the position of the double bond being uncertain (263).



CCXXII CCXXIII CCXXIV

When the reaction was run for 8 hr., then 3 moles of hydrogen reacted to give either CCXXIII or CCXXIV, or 4 moles of hydrogen reacted to yield CCXXV (263).



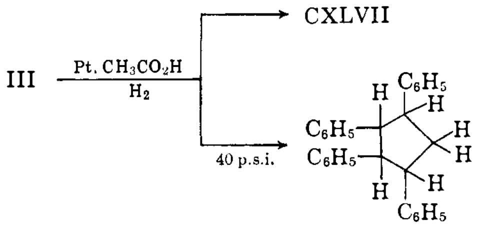
CCXXIII CCXXIV CCXXV

d. Catalytic Reduction

Catalytic reduction of III using palladium on barium sulfate in acetic acid gave CXLVII (133), while reduction with platinum black in acetic acid produced either CXLVII by reaction with 1 mole of hydrogen or

$$\text{III} \xrightarrow[\text{CH}_3\text{CO}_2\text{H}]{\text{Pd/BaSO}_4\text{, H}_2} \text{CXLVII}$$

CCXXV by reaction with 4 moles of hydrogen (263).



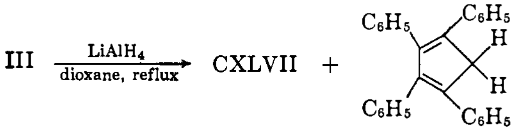
CCXXV

e. Lithium Aluminum Hydride

Reduction of III with lithium aluminum hydride in dioxane was reported to give CCXXI (64) which later was corrected to CXLVII (63), the conjugated "enone."

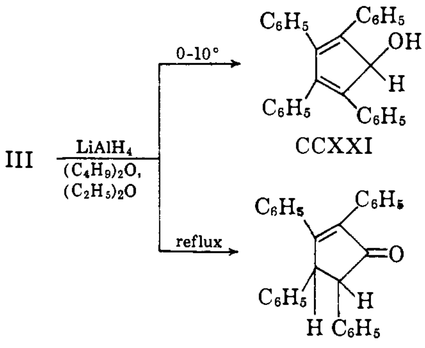
$$\text{III} \xrightarrow[\text{dioxane}]{\text{LiAlH}_4} \text{CXLVII}$$

It was later found that refluxing dioxane affords both CXLVII and a trace of CXXXVII (263), while use of



CXXXVII

equal amounts of butyl ether and ethyl ether as the solvent yielded CCXXI at 0–10° and CXLVII at the reflux temperature (263).



CCXXI CXLVII

f. Hydrazines

Refluxing a solution of hydrazine hydrate and ethanol with III yields CXLVII (263), and treatment

$$\text{III} \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{N}_2\text{H}_4} \text{CXLVII}$$

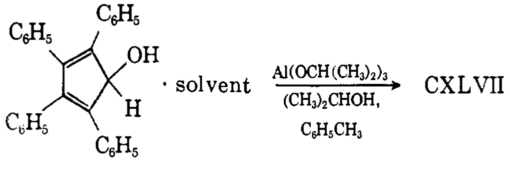
of III with phenylhydrazine at 140° also yields CXLVII (191).

$$\text{III} \xrightarrow[140°]{C_6H_5NHNH_2} \text{CXLVII}$$

g. Meerwein–Ponndorf–Verley Reduction

Aluminum isopropoxide in toluene and isopropyl alcohol reacted with III to produce CXLVII when the isopropyl alcohol was distilled (263). It was also found that, under the conditions of this reaction, solvated CCXXI is isomerized to CXLVII (263) and it was, therefore, suggested that in the reduction, as in the case of zinc in acetic acid, the enone (CXLVII) arises from isomerization of the initial reduction product, the dienol (CCXXI).

$$\text{III} \xrightarrow[(CH_3)_2CHOH,\ C_6H_5CH_3]{Al(OCH(CH_3)_2)_3} \text{CXLVII}$$



CCXXI

h. Reduction with Solvents

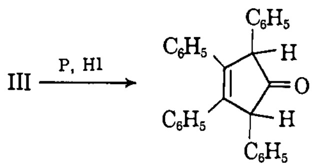
Heating III with xylene at 300°, tetralin at 140–200°, or absolute ethanol at 200–250° in a sealed tube was reported to yield CXLVI (49). Later, however (263), it was reported that toluene at 250° gave CXLVII and some benzaldehyde, while either 1,2- or 1,4-dihydronaphthalene when heated in a sealed tube with or without solvent also gave CXLVII (53). It should be noted that CXLVII was substantiated by infrared spectra (53, 263), while the only proof for the existence of CXLVI was a reduction of III with hydrogen iodide and phosphorus (49), the structure of CXLVI having been drawn mainly by analogy (120). It appears likely therefore that all reductions leading to CXLVI are questionable since they base this structure on ref. 120.

$$\text{III} \xrightarrow[\Delta]{\text{solvent}} \text{CXLVI}$$

$$\text{III} \xrightarrow[250°]{\text{toluene}} \text{CXLVII}$$

i. Reduction with Phosphorus and Hydrogen Iodide

Reduction of III with red phosphorus and hydrogen iodide was reported to give CXLVI (49, 120). However, it should be noted in the light of what was previously mentioned that CXLVI may actually be CXLVII.



CXLVI

j. Polarographic Reduction

Polarographic reduction of III proceeds by two additions of one electron each to yield CXLVII (159).

$$\text{III} \rightarrow \text{CXLVII}$$

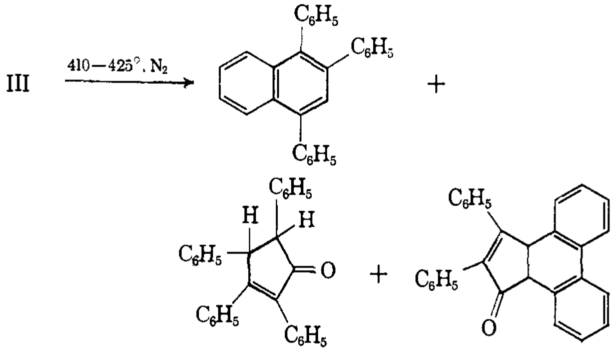
k. Stannous Chloride

Reduction of III with stannous chloride in hydrochloric and acetic acid has been found to give CXLVII (57). A 95% yield is obtained.

$$\text{III} \xrightarrow{SnCl_2,\ CH_3CO_2H,\ HCl} \text{CXLVII}$$

l. Pyrolysis

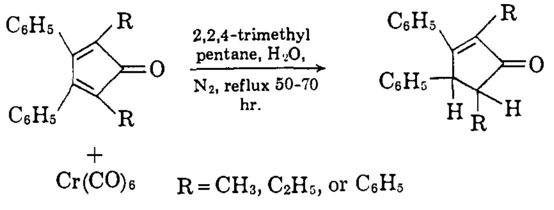
Pyrolysis of tetracyclone at 410–425° in a nitrogen atmosphere results in the preparation of three major compounds (217).



CXLVII

m. Metal Carbonyls

Chromium hexacarbonyl in the presence of refluxing 2,2,4-trimethylpentane, water, and under a nitrogen atmosphere has been used to reduce 2,5-dimethyl-, 2,5-diethyl-, and tetraphenylcyclopentadienone (81).

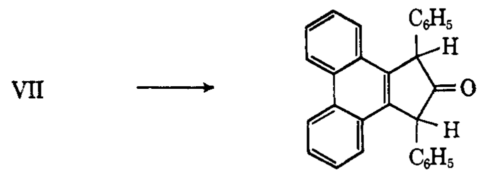


$R = CH_3, C_2H_5$, or C_6H_5

The author claims that the starting material used in the case of the 2,5-dimethyldiphenylcyclopentadienone is the monomer and that the product found is the enone of the monomer.

n. Other Cyclopentadienones

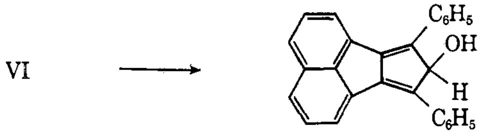
Phencyclone (VII) on treatment with excess alcoholic alkali, phosphorus and hydrogen iodide, or zinc dust in acetic acid, either hot or cold, is reduced to CCXXVII (126). With either xylene, toluene, benzene, tetralin, *n*-hexane, absolute ethanol, or 1,2- or 1,4-dihydro-



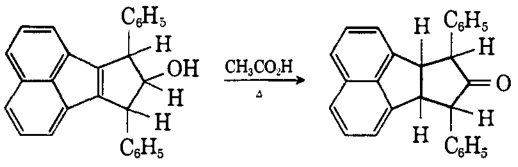
CCXXVII

naphthalene, at a high temperature in a sealed tube VII is also reduced to CCXXVII (49, 53).

Reduction of acecyclone (VI) with either zinc dust in acetic acid or hydrazine in pyridine yields CCXXVIII (123). With a larger quantity of zinc dust in acetic acid, CCXXIX can be obtained (123), which then isomerizes to CCXXX upon reflux in acetic acid (123).

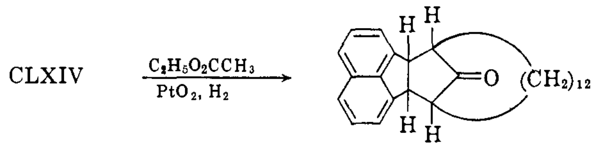


CCXXVIII

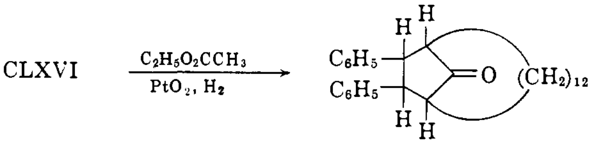


CCXXIX CCXXX

Using platinum oxide in ethyl acetate and hydrogen at atmospheric pressure, CLXIV and CLXVI were reduced to CCXXXI and CCXXXII, respectively (44).



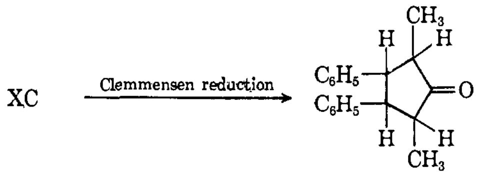
CCXXXI



CCXXXII

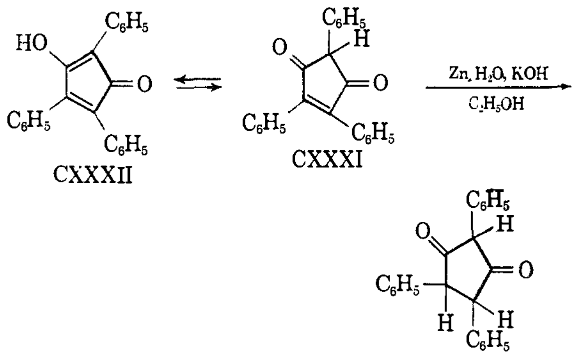
This reduction of CLXVI in which both double bonds are reduced might be compared to that of III in which only one bond is reduced at atmospheric pressure to give CXLVII (133, 263).

The dissociating dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (XC) is reduced under the conditions of the Clemmensen reduction by addition of 2 moles of hydrogen to yield CCXXXIII (35).



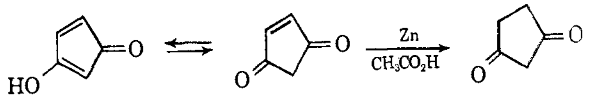
CCXXXIII

2,4,5-Triphenyl-3-hydroxycyclopentadienone (CXXXII), which exists mainly in the keto form CXXXI, is reduced to CCXXXIV, which exists mainly in the keto form CXXXI, is reduced to CCXXXIV by the addition of 1 mole of hydrogen using zinc dust in a basic solution (195).



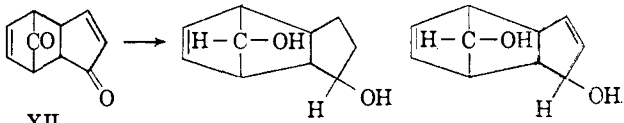
CXXXII CXXXI CCXXXIV

In a similar manner, reduction of 3-hydroxycyclopentadienone (XX), which exists as the diketone XIX, yields a cyclopentandione CCXXXV (105).

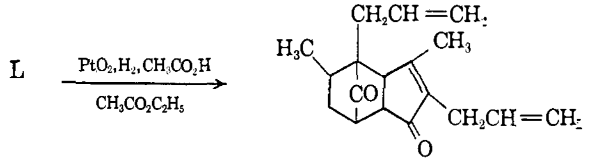


XX XIX CCXXXV

Reduction of cyclopentadienone, which exists as the dimer XII, yields a dialcohol CCXXXVI (166, 167) or CCXXXVII (167), while reduction of 2-allyl-3-methylcyclopentadienone, which also is dimeric L, yields a diketone CCXXXVIII (47).

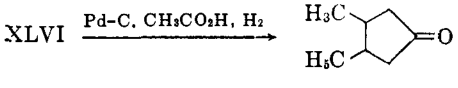


XII CCXXXVI CCXXXVII



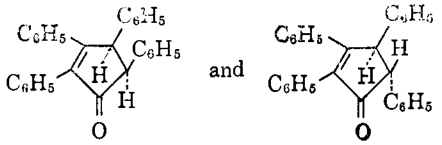
CCXXXVIII

3-Ethyl-4-methylcyclopentadienone (XLVI) is reported as the monomer (56, 226) even though one would expect it to be dimeric. Upon reduction it yields 3-ethyl-4-methylcyclopentanone (CCXXXIX) (56, 226).



CCXXXIX

As a general matter one aspect of the ring reduction of cyclones and of the halogen addition reactions of cyclones appears to have been neglected; namely, stereochemistry. The addition of two atoms of hydrogen to a substituted cyclone could result in the formation of a *trans-d,l* and a *cis-d,l* pair of isomers, *e.g.*

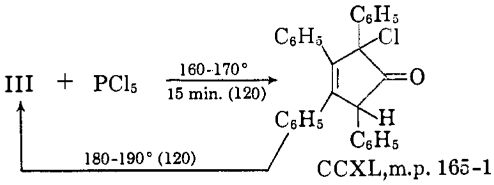


For the addition of four hydrogens, the reaction products could be more complex. For those additions of two atoms to the 3,4-position, a *cis-meso* and a *trans-d,l* pair could result. Since both chemical and catalytic reductions have been reported, the isomerism of the product(s) and their properties may indeed be dependent upon the synthetic route.

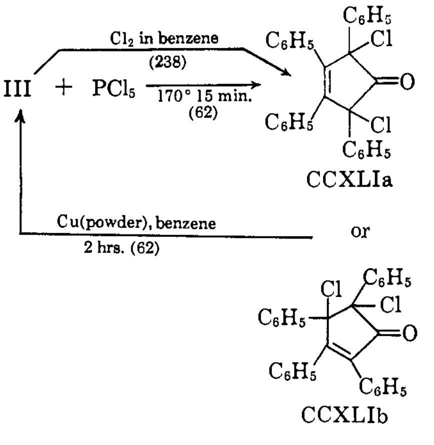
E. HALOGENATION OF CYCLOPENTADIENONES

Cyclopentadienones have been halogenated using iodine, phosphorus pentachloride, bromine, and chlorine. When tetracyclone is treated with phosphorus pentachloride, two different products are reported, the monochloro CCXL (120) addition product, and the dichloro CCXLIa or b (62) addition product, whose structure is uncertain. The initial compound CCXL most likely was obtained through the action of hydrogen chloride formed by partial hydrolysis of the reagent. Both products have been converted back to tetracyclone. Chlorine also reacts with tetracyclone to give a dichloro adduct CCXLIa.

The reaction of tetracyclone with bromine was reported (133) to give the dibromide CCXLII which was converted back to tetracyclone.

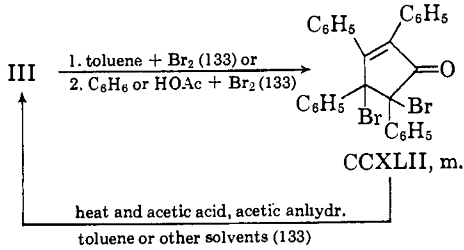


CCXL, m.p. 165-166°



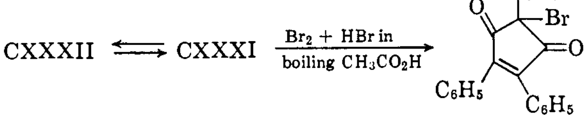
CCXLIa

CCXLIb

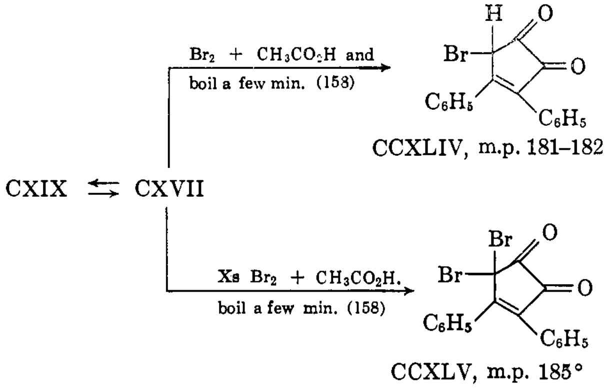


CCXLII, m.p. 169-170°

Bromine has been the only reagent used to prepare the halogen substitution products of hydroxycyclopentadienones, the products being diketones. Thus, reaction of bromine with 3-hydroxy-2,4,5-triphenylcyclopentadienone (CXXXII), which is stable as the diketone CXXXI, affords the monobromo diketone CCXLIII as the only product (195). This reaction is in agreement with another report of the substitution of bromine in hydroxycyclopentadienones (158). In this case, treatment of 2-hydroxy-4,5-diphenylcyclopentadienone (CXIX), stable as the diketone CXVII, with 1 mole of bromine gave the monobromo diketone CCXLIV. However, with an excess of bromine, the dibromo diketone CCXLV was obtained.



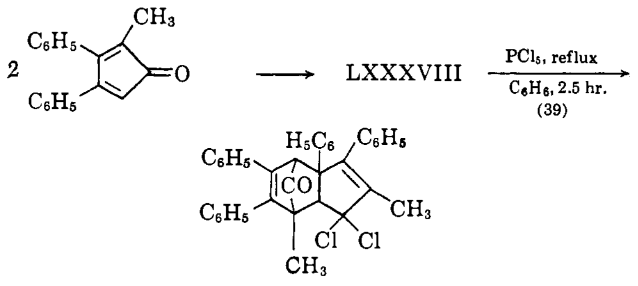
CCXLIII, m.p. 133-134°



CCXLIV, m.p. 181-182.5°

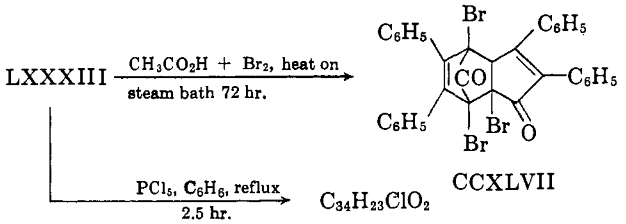
CCXLV, m.p. 185°

Some dimers of cyclopentadienones have also been treated with phosphorus pentachloride and bromine, namely, 2-methyl-3,4-diphenylcyclopentadienone and 3,4-diphenylcyclopentadienone. Treatment of the dimer LXXXVIII with phosphorus pentachloride gave a product thought to be 1,1-dichloro-8-keto-2,7-dimethyl-3,3a,5,6-tetraphenyl-4,7-methano-3a,4,7,7a-tetrahydroindene (CCXLVI) (39). Thus, the course of reaction is considerably different from that for the stable monomeric cyclopentadienones, which add chlorine and do not interchange chlorine for oxygen.



CCXLVI, m.p. 290°

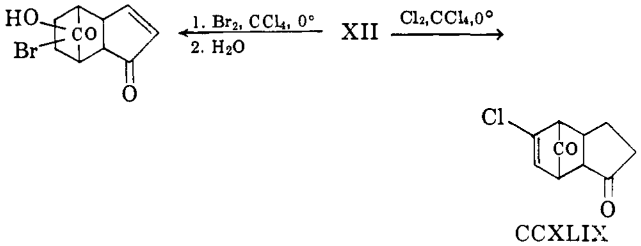
Treatment of the dimer LXXXIII with bromine affords the tribromo diketone CCXLVII, while treatment of the same dimer with phosphorus pentachloride gives a monochloro diketone CCXLVIII of empirical formula $C_{34}H_{23}O_2Cl$ whose structure is not given (25).



CCXLVII

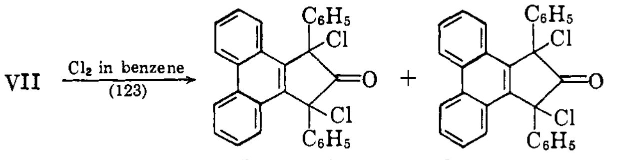
CCXLVIII

Treatment of cyclopentadienone dimer XII with 1 mole of chlorine in carbon tetrachloride affords a monochloro substitution product CCXLIX, while treatment of this same dimer with bromine and subsequent treatment with water affords a monobromo alcohol of undetermined structure (167).

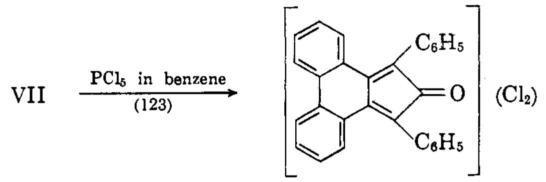


CCXLIX

In the condensed ring cyclone series both phencyclone and acecyclone have been halogenated successfully (123). Treatment of phencyclone with chlorine afforded two dichloro addition products, which may be accounted for as the *cis*-meso and *trans*-racemate stereoisomers CCL and CCLI. That the addition is 2,5- is quite likely since the phenanthrene-type resonance is obtained in this mode of addition. However, treatment of phencyclone with phosphorus pentachloride afforded a new dichloro ketone CCLII in which the position of the chlorine atoms is uncertain and whose mixture melting point with the two forms prepared above shows a depression (123).



CCL, m.p. 274° CCLI, m.p. 263°



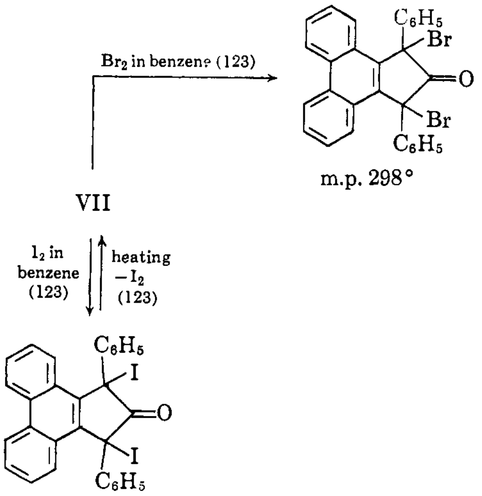
CCLII, m.p. 278°

position of chlorines uncertain

compound CCL plus compound CCLII, m.p. 258°
compound CCLI plus compound CCLII, m.p. 262°

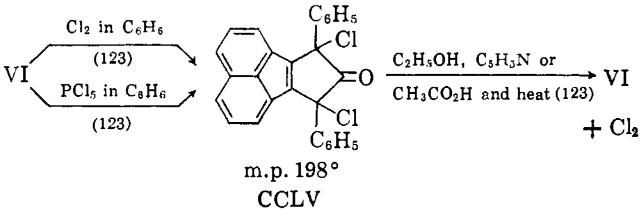
It is noteworthy that when any one of the three dichloro ketones (CCL, CCLI, or CCLII) is heated in inert solvent no chlorine is evolved.

In contrast to chlorination, treatment of phencyclone with bromine or iodine (123) affords only one product in each case. This is a clarification of a previous reference (126) which listed two products from bromination of phencyclone using the conditions shown. Heating the diiodo ketone CCLIII converts it back to phencyclone with the liberation of iodine.



CCLIII

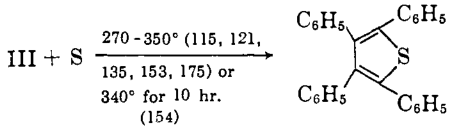
Treatment of acecyclone with either chlorine or phosphorus pentachloride affords only one dichloro ketone (CCLV), which, upon heating, is converted back to acecyclone with the liberation of chlorine; this contrasts with the behavior of the dichlorotetracyclones.

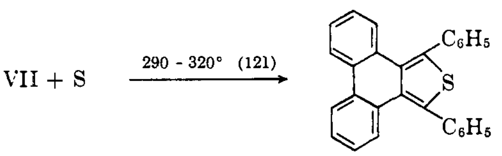


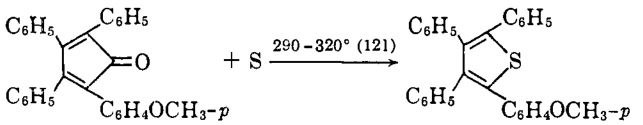
m.p. 198°
CCLV

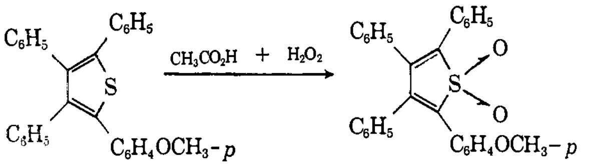
F. REACTION WITH CHALCOGENS

Tetracyclone, phencyclone, acecyclone, and 2-*p*-methoxyphenyl-3,4,5-triphenylcyclopentadienone have been treated with sulfur at high temperatures (121, 135). With the exception of acecyclone, the other cyclopentadienones gave the respective thiophenes, in which a sulfur atom replaced carbon monoxide. The work with tetracyclone and sulfur was later reinvestigated (115, 154, 175) and the earlier results substantiated. In the latter case the product was treated with hydrogen peroxide in acetic acid to yield the sulfone (121), a well-known reaction for arylated thiophenes.

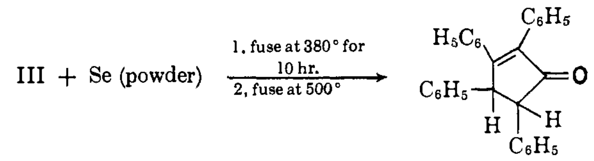








The reaction of the cyclopentadienones with selenium has been less thoroughly investigated. In the initial work (115) when tetracyclone was heated with selenium, a product was obtained whose structure was questionable. However, more recently (154) the reaction was reinvestigated and the product shown to be 2,3-dihydrotetraphenylcyclopentadienone (CXLVII). This surprising reduction probably involves hydrogen from another cyclone, possibly through the intervention of the selenium with accompanying formation of more highly condensed systems, but evidence on the details of the reaction is not available.



CXLVII

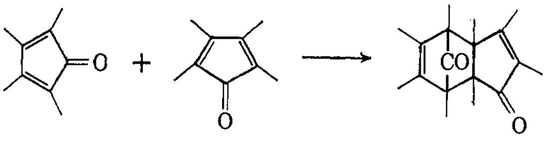
G. DIELS–ALDER REACTIONS

Several review articles have been written concerning the Diels–Alder reaction (11, 12, 84, 173, 193, 210, 219, 222, 231, 233, 234). These cover the general scope of the reaction along with some specific areas. This section, however, is concerned with only those Diels–Alder reactions which involve cyclopentadienones.

1. Cyclopentadienones as Dienophiles

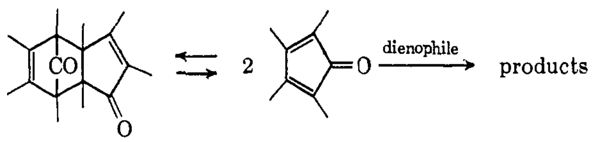
a. Dimerization of Cyclopentadienones and Decarbonylation of Adducts

Certain cyclopentadienones enter into a Diels–Alder dimerization reaction in which one molecule functions as the diene and the other as the dienophile. The position of this equilibrium depends upon the nature of the substituents on the cyclopentadienone so that some cyclopentadienones exist mainly as dimers, others as dissociating dimers, and still others strictly as monomers (41). Table XXI lists those cyclopentadienones which exist mainly in the dimeric form, while Table XXII lists those cyclopentadienones which exist as dissociating dimers. All the other cyclopentadienones which have been prepared are monomeric and show no tendency to dimerize.



The synthesis of those cyclopentadienones which exist as dimers has already been discussed. The monomers are not obtainable; instead upon attempted synthesis they immediately dimerize and the dimer or a reaction product of it is isolated.

The syntheses of the cyclopentadienones which exist as dissociating dimers have already been discussed in the section on synthesis. The dimers are generally colorless and the monomers are red, so that solutions of the dimer are colored, the color growing more intense as the temperature is raised. This equilibrium permits the cyclopentadienones to enter other Diels–Alder reactions as

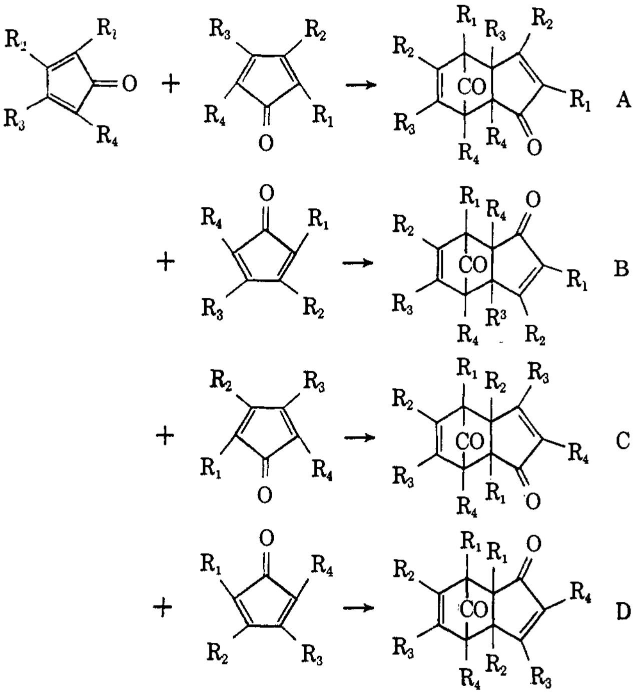


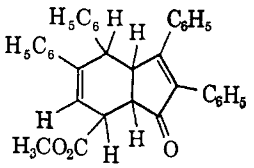
In the sections which cover these reactions, the monomer shall be listed as the reactive starting material.

Whether the monomer dimerizes appears to be determined by steric factors; those compounds which are dissociating dimers have groups no smaller than methyl in both the 2- and 5-positions of the monomer. It is interesting to note that tetrakis(trifluoromethyl)-cyclopentadienone is reported as a monomer (LX) (76, 108). The failure of this compound to dimerize may be due to the electron-withdrawing nature of the trifluoromethyl group as well as to the size of the trifluoromethyl group.

TABLE XXI

CYCLOPENTADIENONES WHICH EXIST MAINLY AS DIMERS



Monomer				Dimer	Ref.
R_1	R_2	R_3	R_4	Structure type	
H	H	H	H	A	13,[a] 96–98, 105, 166–168
1-Allyl	CH_3	H	H	A	47, 202
n-Propyl	CH_3	H	H	A	47
n-Butyl	CH_3	H	H	A	90[b]
n-C_5H_{11}	CH_3	H	H	A	90,[b] 264[b,c]
Cl	H	H	H	A or B	97
Cl	Cl	H	H	A or B	213
Br	H	Cl	Cl	C or D	213
Cl	Cl	Cl	Cl	A	220, 288,[c,d] 289,[a,d] 290, 291
Cl	Cl	Cl	CH_3	$C_{10}Cl_6(CH_3)_2O_2$	237[b]
Cl	Cl	CH_3	Cl	$C_{10}Cl_6(CH_3)_2O_2$	68[b]
Cl	CH_3	Cl	CH_3	$C_{10}Cl_4(CH_3)_4O_2$	155[b]
H	C_6H_5	C_6H_5	H	A	24,[e] 25,[e] 29, 32,[b] 33, 34, 161,[b] 179,[b] 182[b]
C_6H_5	C_6H_5	H	H		45[c]
Br	C_6H_5	C_6H_5	H	$C_{34}H_{22}Br_2O_2$	32[b]
Cl	C_6H_5	C_6H_5	H	$C_{34}H_{22}Cl_2O_2$	32[b]
CH_3	C_6H_5	C_6H_5	H	B	38, 161,[b] 183[b]
CH_2COOH	C_6H_5	C_6H_5	H	"Dihydroxylamine salt of dimer"	41[b]
n-C_5H_{11}	C_6H_5	C_6H_5	H	B	38
n-$C_{10}H_{21}$	C_6H_5	C_6H_5	H	B	41[b]
C_6H_5O	C_6H_5	C_6H_5	H	B	41[f]
C_6H_5	C_6H_5	C_6H_5	H	B	41,[b] 158

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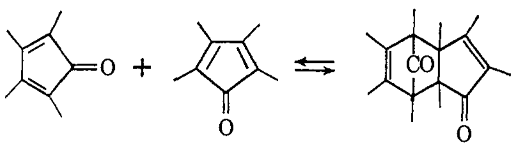
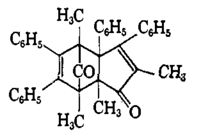
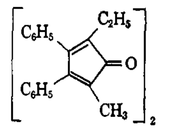
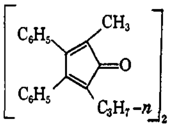
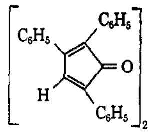
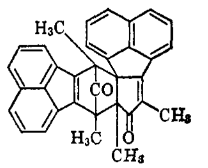
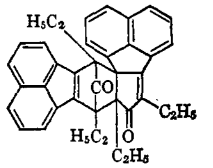
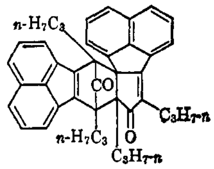
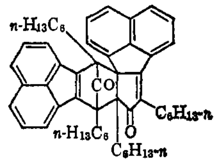
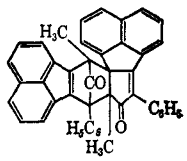
[a] Cyclone formed from pyrolysis of 3a,4,7,7a-tetrahydro-1,8-methanoinden-1-one at 360–380°. [b] Structure of dimer not given. [c] Cyclopentadienone formed in reaction mixture and derivative of dimer isolated. [d] Product is hexachloroindenone. [e] Product given as LXXXIII. [f] Dimer not isolated, derivative isolated was 7-phenoxy-2,3,5,6-tetraphenyl-1-indenone.

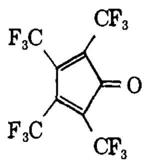
TABLE XXII

DISSOCIATING DIMERS



Monomer	Dimer	Ref.
Cyclopentadienone 2,5-Dimethyl-3,4-diphenyl-		161,^{a} 258
α-Ethyl-5-methyl-3,4-diphenyl-		258^a
2-Methyl-3,4-diphenyl-5-(*n*-propyl)-		41^a
2,3,5-Triphenyl-		134^a
Acecyclone 7,9-Dimethyl-		43
7,9-Diethyl-		43
7,9-Di(*n*-butyl)-		43
7,9-Di(*n*-hexyl)-		43
7-Methyl-9-phenyl-		43

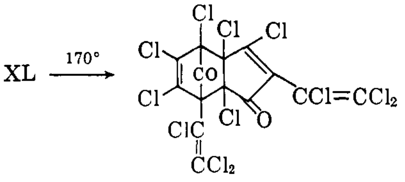
[a] Structure of dimer not given.



LX

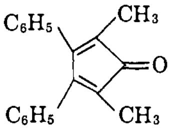
Although 2-*n*-propyl-3-methylcyclopentadienone (47), 2-*n*-butyl-3-methylcyclopentadienone (90), and 2-*n*-pentyl-3-methylcyclopentadienone (90, 264) are dimeric as expected, it is reported that 3-methylcyclopentadienone (230) and 3-methyl-4-ethylcyclopentadienone (56, 226) are monomeric. This is in direct conflict with what would be expected based on the properties of the other simple cyclopentadienones. It should be noted, however, that both compounds have unusually high boiling points for their proposed structures and molecular weights, being 218–220° (230) in the former and 115° (30 mm.) in the latter (226).

2,3,4-Trichloro-5-(trichlorovinyl)cyclopentadienone is reported as a red oil (XL) which dimerizes at 170° (214). This is a rather peculiar case in view of the fact that the other dimeric cyclopentadienones are formed at lower temperatures. This dimerization has been carried out at low temperature, although the position of the trichlorovinyl group is uncertain (221).

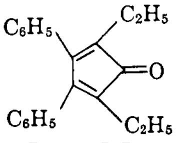


XLI

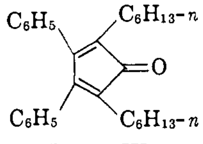
It appears that the steric requirements of the 3- and 4-groups also play a part in this dimerization. While LXXXIVa is a dissociating dimer (161, 258), compounds LXXXIVb and LXXXIVc are monomers (41).



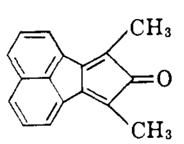
LXXXIVa



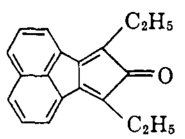
LXXXIVb



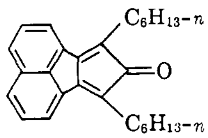
LXXXIVc



CLXIIa



CLXIIb



CLXIIc

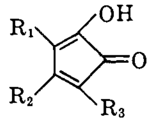
Compound CLXIIa is a dissociating dimer similar to LXXXIVa but, in contrast to the behavior of LXXXIVb and LXXXIVc, CLXIIb and CLXIIc are dissociating dimers (43). Apparently the fusing of the phenyl rings in LXXXIVa and LXXXIVb relieves the steric crowding sufficiently to permit dimerization.

A few of the nondissociating dimers have been heated, but rather than dissociate in a reverse Diels–Alder reaction the carbonyl bridge splits out as carbon monoxide. The initial product formed is a 3a,7a-dihydroindenone, but on further heating other products are obtained. These are presented in Table XXIII.

The dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone, a dissociable dimer, is also reported to evolve carbon monoxide upon heating, although the structure of the product is not given (161).

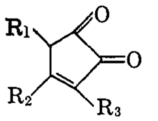
b. Reactions with Other Dienes

Hydroxycyclopentadienones of type XIII exist mainly as cyclopentendiones of type XV. As such, these cyclopentadienones react as dienophiles with



XIII

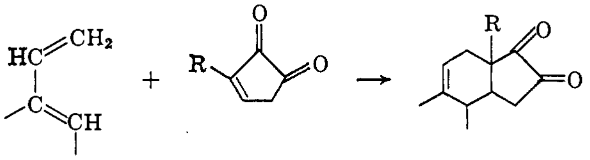
$R_1 = R_2 = H$; $R_3 = CH_3$, H



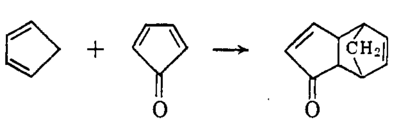
XV

$R_1 = R_2 = H$; $R_3 = CH_3$, H

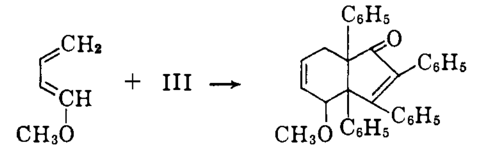
dienes according to the equation (92–95)



Cyclopentadienone has also been found to function as a dienophile in its reaction with cyclopentadiene (13, 96, 166–168). For the reaction the cyclopentadienone is generated *in situ.*



There is also one report in which tetracyclone functions as a dienophile (149); namely, in the reaction between it and 1-methoxy-1,3-butadiene. The reaction is in direct contrast to the normal reaction between tetracyclone and butadiene. An unequivocal proof of structure was not presented for the methoxybutadiene product.



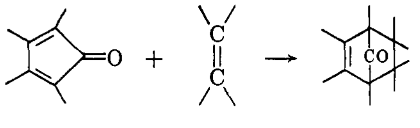
These reactions are presented in Table XXIV.

2. Cyclopentadienones as Dienes

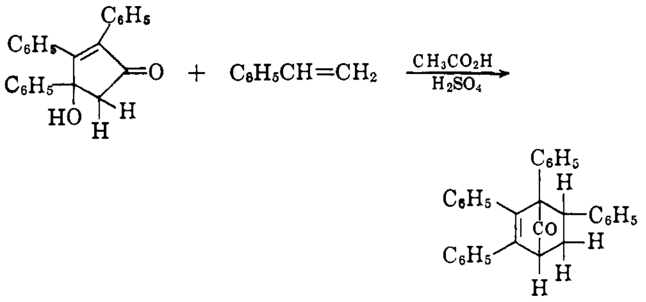
a. Reaction with Alkenes

(*1*) *Formation of Bridged Carbonyl Compounds.*—Two review articles (15, 16) have been written concerning bridged carbonyl compounds, so that their chemistry will not be discussed here.

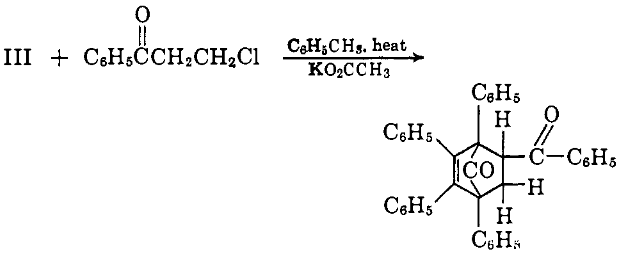
Cyclopentadienones can react as dienes in a Diels–Alder reaction (11, 222, 231, 233, 234). With alkenes the reaction can lead to the formation of bridged carbonyl compounds as



The cyclopentadienone can be either a monomer, or it may be produced from a dissociating dimer, or it can be generated *in situ* by dehydration of the 3-hydroxy-2-cyclopenten-1-one, *e.g.* (39)



The alkene can also be generated *in situ*, *e.g.* (20)



Quite a few alkenes have been allowed to react with cyclopentadienones (Table XXV). These have included monosubstituted ethylenes such as $H_2C{=}CHR$: R = H, CH_2OH, CH_2Cl, CN, CO_2CH_3, $CO_2C_4H_9$, O_2CCH_3, $NCOC_6H_5$, $Sn(CH_3)_3$, $Sn(C_2H_5)_3$, $Sn(C_6H_5)_3$, C_6H_5, $CH{=}CHC_6H_5$, $(CH_2)_3CH_3$, $(CH_2)_5CH_3$, $CH_2O_2CH_3$; disubstituted ethylenes such as $CH_2{=}CR_1R_2$ and $R_1CH{=}CHR_2$:

$CH_2{=}CR_1R_2$		$R_1CH{=}CHR_2$	
R_1	R_2	R_1	R_2
CH_3	OC_2H_5	NO_2	C_6H_5
C_6H_5	OC_2H_5	C_2H_5	CO_2H
CH_3	O_2CCH_3	CO_2H	CO_2H
CH_3	$CO_2CH(CH_3)_2$	CO_2CH_3	CO_2CH_3
CH_3	$CO_2CH_2CH_2C_6H_5$	OCC_6H_5	OCC_6H_5

Table XXIII

Decarbonylation of Cyclopentadienone Dimers

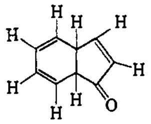
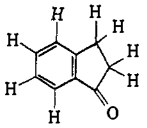
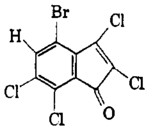
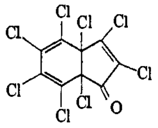
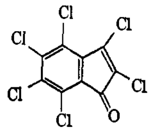
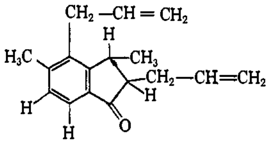
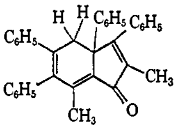
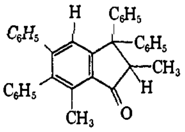
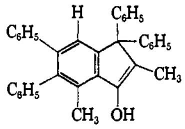
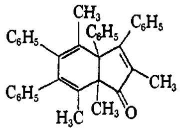
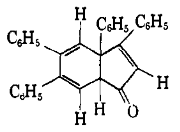
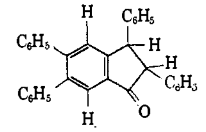
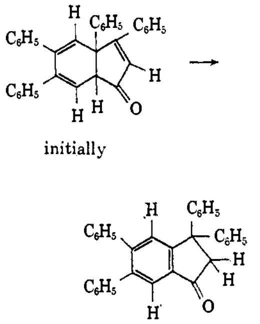
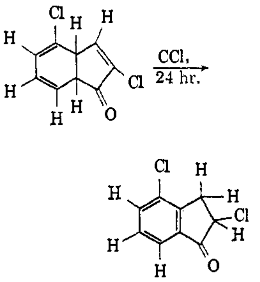
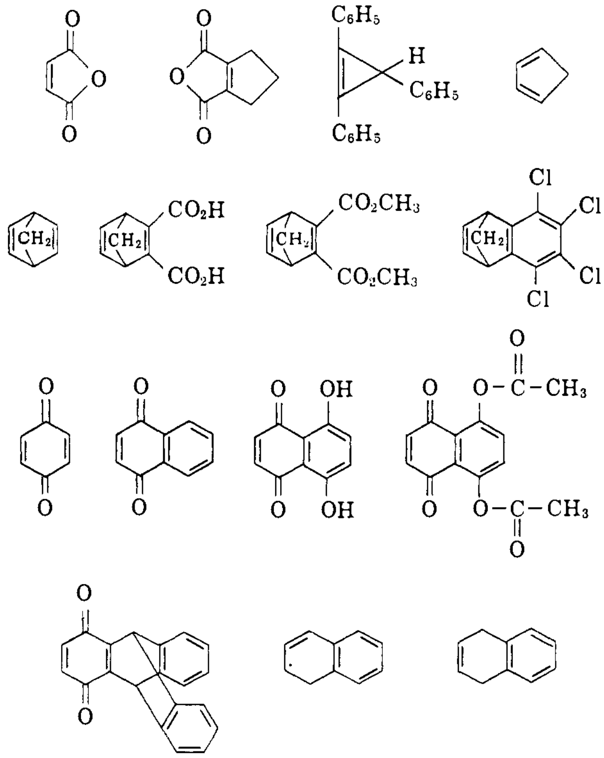
Dimer, -4,7-methanoindene-1,8-dione	Conditions	Product	Ref.
3a,4,7,7a-Tetrahydro-	360–380° (13)		13, 168[a]
3a,4,7,7a-Tetrahydro-	240° (166)		98, 166, 168
4,7a-Dibromo-2,3,6,7-tetrachloro-3a,7a-dihydro-	Reflux xylene (213)		213[b]
Octachloro-	Heat (291)		291
Octachloro-	Heat (290)		220, 290
3a,4,7,7a-Tetrahydro-3,5-dimethyl-2,4-di(2-propenyl)-	200–210° (202)		202
3a,4,7,7a-Tetrahydro-2,7-dimethyl-3,3a,5,6-tetraphenyl-	10 min. at 240° (40)		40
3a,4,7,7a-Tetrahydro-2,7-dimethyl-3,3a,5,6-tetraphenyl-	70 min. in quinoline or 7 hr. in $C_6H_3Cl_3$ (40)		40
3a,4,7,7a-Tetrahydro-2,7-dimethyl-3,3a,5,6-tetraphenyl-	3 hr. at 240° (40)		40
3a,4,7,7a-Tetrahydro-2,4,7,7a-tetramethyl-3,3a,5,6-tetraphenyl-	Heat (161)		161[c,d]
4,7,7a-Tetrahydro-3,3a,5,6-tetraphenyl-	10 min. at 210° (33), 200° (179)		33, 34, 179,[c,d] 182[c,d]

TABLE XXIII (*continued*)

Dimer, -4,7-methanoindene-1,8-dione	Conditions	Product	Ref.
3a,4,7,7a-Tetrahydro-3,3a,5,6-tetraphenyl-	Heating longer than 10 min. (33, 34)		33, 34
3a,4,7,7a-Tetrahydro-3,3a,5,6-tetraphenyl-	Heat (46)	 initially	46
2,7-Dichloro-3a,4,7,7a-tetrahydro- or 2,4-dichloro-3a,4,7,7a-tetrahydro- (uncertain)	15 min. at 180° (97)		97

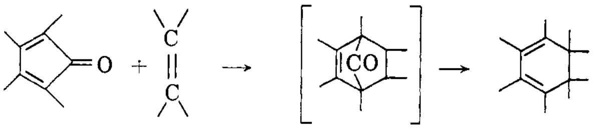
[a] Product postulated as a transient intermediate. [b] Structure of starting material and product uncertain. [c] Structure of dimer not given. [d] Structure of product not given.

and ring compounds such as

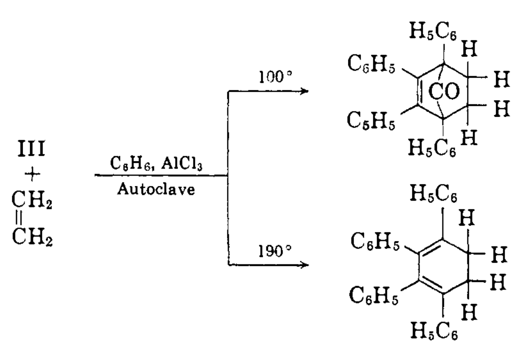


The conditions of the reaction depend upon the cyclopentadienone used and the dienophile.

(*2*) *Reaction with Simultaneous Evolution of Carbon Monoxide.*—Bridged carbonyl compounds lose carbon monoxide upon heating (15, 16), the temperature depending upon the structure of the compound. It follows, therefore, that the Diels–Alder reaction of cyclopentadienones could be carried out under conditions in which the carbonyl bridge is lost. The dihydrobenzene formed may react further with more alkene since it is a diene. Although a generalization



is difficult owing to the wide variety of reactants used, it appears that a higher temperature favors the loss of carbon monoxide. A few examples are listed below.

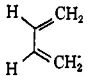
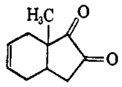
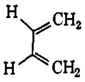
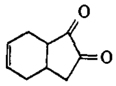
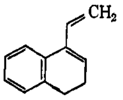
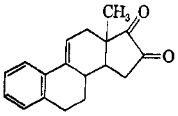
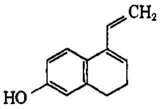
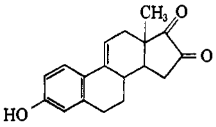
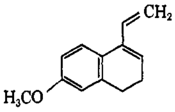
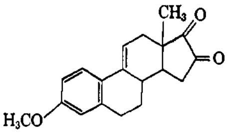
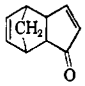
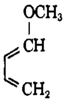
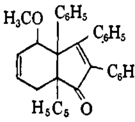
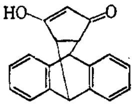
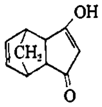


(30)

(30)

TABLE XXIV

REACTIONS OF CYCLOPENTADIENONES WITH DIENES

Cyclopentadienone	Diene	Product	Ref.
2-Hydroxy-5-methyl-			92,[a] 95[a]
2-Hydroxy-			92[b]
2-Hydroxy-5-methyl-			92[a]
2-Hydroxy-5-methyl-			92[a]
2-Hydroxy-5-methyl-			92,[a] 93,[a,c] 94[a]
Cyclopentadienone	Cyclopentadiene		13,[d,e] 96,[f] 97, 166,[e] 167,[e] 168[e]
Tetraphenyl-			149
3-Hydroxy-	Anthracene		98,[g] 104,[g,h] 105[g,h]
3-Hydroxy-	Cyclopentadiene		104,[d,e] 105[d]

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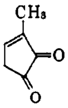
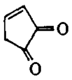
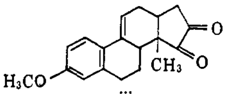
[a] Cyclone more stable as cyclopentenedione i. [b] Cyclone more stable as cyclopentenedione ii. [c] Authors uncertain as to the structure of the product; it could be iii. [d] Both starting materials formed in pyrolysis of XVII. [e] XVIII also formed. [f] Cyclone obtained from XII. [g] Cyclone more stable as cyclopentenedione XIX. [h] Structure of product not given.



i



ii



iii

TABLE XXV

FORMATION OF BRIDGED CARBONYL COMPOUNDS

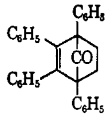
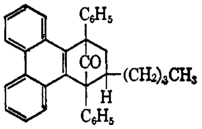
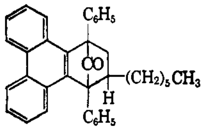
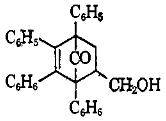
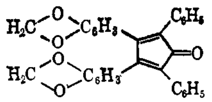
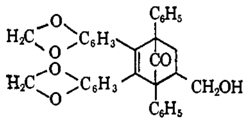
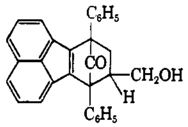
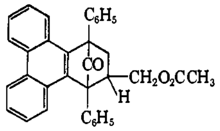
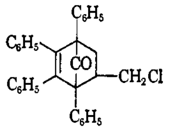
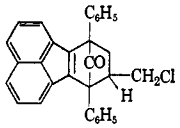
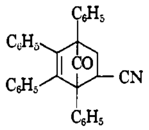
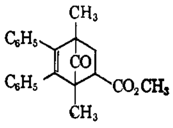
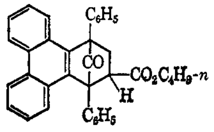
Cyclone	Dienophile	Conditions	Product	Ref.
III	$CH_2=CH_2$	C_6H_6 + $AlCl_3$ autoclave, 300 p.s.i., 24 hr. at 100° with shaking		30
VII	$CH_2=CH(CH_2)_3CH_3$			17
VII	$CH_2=CH(CH_2)_5CH_3$			17
III	$CH_2=CHCH_2OH$	Sealed tube, C_6H_6, 8 hr. at 180–200° (4, 5)		4, 5
	$CH_2=CHCH_2OH$	Sealed tube, C_6H_6, 4 hr. at 160–180°		51
VI	$CH_2=CHCH_2OH$	Sealed tube, C_6H_6, 30 hr. at 200–220°		10
VII	$CH_2=CHCH_2O_2CCH_3$			17
III	$CH_2=CHCH_2Cl$	Sealed tube, C_6H_6, 9 hr at 180–200° (4, 5)		4, 5
VI	$CH_2=CHCH_2Cl$	Sealed tube, C_6H_6, 36 hr. at 200–220°		10
III	$CH_2=CHCN$	C_6H_6, heat for 4.5 hr., large excess of dienophile necessary for good yield.		140
LXXXIV, $R_1 = R_2 = CH_3$	$CH_2=CHCO_2CH_3$	C_6H_6, heat		35
VII	$CH_2=CHCO_2C_4H_9$-*n*			17

TABLE XXV (*continued*)

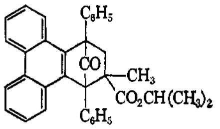
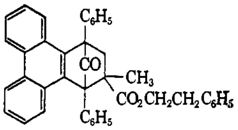
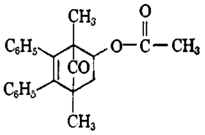
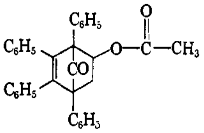
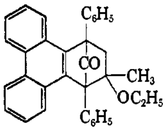
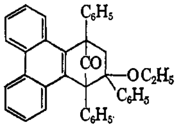
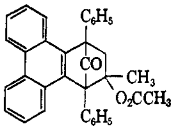
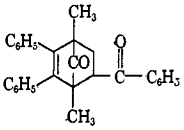
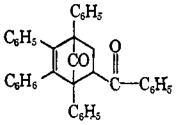
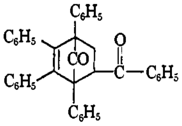
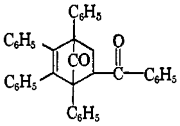
Cyclone	Dienophile	Conditions	Product	Ref.
VII	CH_2 ‖ $C—CH_3$ | $CO_2CH(CH_3)_2$			17
VII	CH_2 ‖ $C—CH_3$ | $CO_2CH_2CH_2C_6H_5$			17
LXXXIV, $R_1 = R_2 = CH_3$	CH_2 ‖ CH | $O—C{=}O$ | CH_3	Heat 24 hr.		30
III	CH_2 ‖ CH | $O—C{=}O$ | CH_3	Pressure bottle, 72 hr. at 95–100°		30
VII	CH_2 ‖ $C—CH_3$ | OC_2H_5	Sealed tube, C_6H_6, 34 hr. at 100°		6
VII	CH_2 ‖ $C—C_6H_5$ | OC_2H_5	Sealed tube, C_6H_6, 5 hr. at 120–150°		6
VII	CH_2 ‖ $C—CH_3$ | $O—C{=}O$ ‖ CH_3	Sealed tube, C_6H_6, 35 hr. at 100°		6
LXXXIV, $R_1 = R_2 = CH_3$	CH_2 ‖ CH | $C{=}O$ | C_6H_5	C_6H_6, heat		35
III	CH_2 ‖ CH | $C{=}O$ | C_6H_5	130° or C_6H_6, heat for 2 hr.		20
III	CH_2Cl | CH_2 | $C{=}O$ | C_6H_5	KOAc, $C_6H_5CH_3$ heat 3 hr.		20[a]
III	$CH_2N(CH_3)_2HCl$ | CH_2 | $C{=}O$ | C_6H_5	KOAc, $C_6H_5CH_3$ heat 24 hr.		20

TABLE XXV (*continued*)

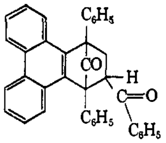
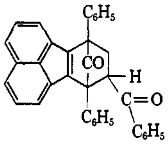
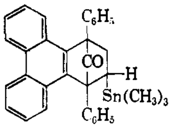
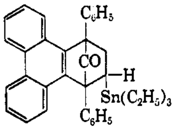
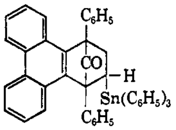
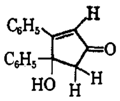
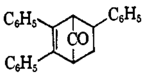
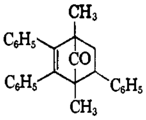
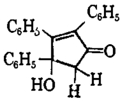
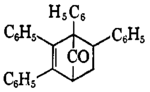
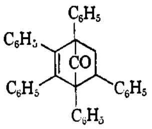
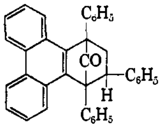
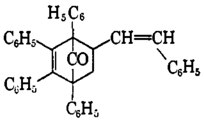
Cyclone	Dienophile	Conditions	Product	Ref.
VII	CH_2Cl | CH_2 | $C{=}O$ | C_6H_5	KOAc, $C_6H_5CH_3$ heat 2 hr.		20
VI	CH_2Cl | CH_2 | $C{=}O$ | C_6H_5	KOAc, $C_6H_5CH_3$ heat 2 hr.		20
VII	CH_2 ‖ CH | $Sn(CH_3)_3$	Sealed tube, CO_2, 6 hr. at 120–127°		52
VII	CH_2 ‖ CH | $Sn(C_2H_5)_3$	Sealed tube, C_6H_6, CO_2, 10 hr. at 120–130°		52
VII	CH_2 ‖ CH | $Sn(C_6H_5)_3$	Sealed tube, C_6H_6, CO_2, 43 hr. at 140–150°		52
	CH_2 ‖ CH | C_6H_5	$KHSO_4$, reflux 2.5 hr.		172, 228, 244
LXXXIV, $R_1 = R_2 = CH_3$	CH_2 ‖ CH | C_6H_5	C_6H_6, heat		35
	CH_2 ‖ CH | C_6H_5	H_2SO_4–HOAc		39
III	CH_2 ‖ CH | C_6H_5	C_6H_6		36
VII	CH_2 ‖ CH | C_6H_5			17
III	CH_2 ‖ CH | CH ‖ $HC{-}C_6H_5$	Phenyl-β-naphthylamine, C_6H_6, reflux 4 hr.		163

TABLE XXV (*continued*)

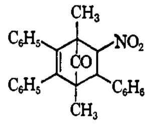
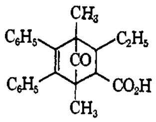
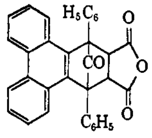
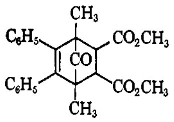
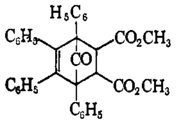
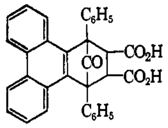
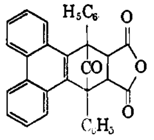
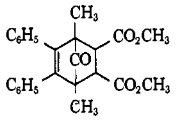
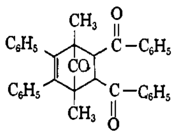
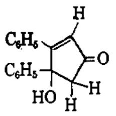
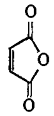
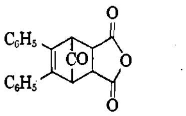
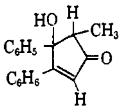
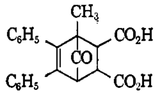
Cyclone	Dienophile	Conditions	Product	Ref.
LXXXIV, $R_1 = R_2 = CH_3$	$\begin{array}{l} CHNO_2 \\ \| \\ HC{-}C_6H_5 \end{array}$	C_6H_6, heat		35
LXXXIV, $R_1 = R_2 = CH_3$	$\begin{array}{l} CHC_2H_5 \\ \| \\ HC{-}CO_2H \end{array}$	C_6H_6, heat		35
VII	$\begin{array}{l} HCCO_2H \\ \| \\ HO_2CCH \end{array}$	C_6H_5Cl, reflux, 5 hr. C_6H_6, reflux, 50 hr. $C_6H_5CH_3$, reflux, 36 hr.		125
LXXXIV, $R_1 = R_2 = CH_3$	$\begin{array}{l} HCCO_2CH_3 \\ \| \\ H_3CO_2CCH \end{array}$	C_6H_6, heat, 15 hr.	 *trans*	35
III	$\begin{array}{l} CH_3O_2C{-}CH \\ \| \\ HCCO_2CH_3 \end{array}$	170°	 *trans*	31
VII	$\begin{array}{l} HC{-}CO_2H \\ \| \\ HC{-}CO_2H \end{array}$	C_6H_5Cl, reflux, 20 min.		125
VII	$\begin{array}{l} HC{-}CO_2H \\ \| \\ HC{-}CO_2H \end{array}$	C_6H_5Cl, reflux, more than 20 min.		125
LXXXIV, $R_1 = R_2 = CH_3$	$\begin{array}{l} HC{-}CO_2CH_3 \\ \| \\ HC{-}CO_2CH_3 \end{array}$	C_6H_6, heat	 *cis*	35
LXXXIV, $R_1 = R_2 = CH_3$	$\begin{array}{l} C_6H_5{-}C{=}O \\ \quad\quad\ \| \\ \quad\quad CH \\ \quad\quad \| \\ \quad\quad HC \\ \quad\quad\ \| \\ \quad O{=}C \\ \quad\quad\ \| \\ \quad\quad C_6H_5 \end{array}$	C_6H_6, reflux. 4 hr.		18,[b] 22
	 (M.A.)	7% KOH, 3-5 hr. at 131°		31
	M.A.	Reflux 5 hr., HOAc, then alkali		38

TABLE XXV (*continued*)

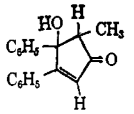
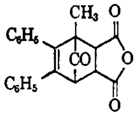
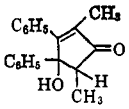
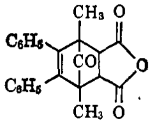
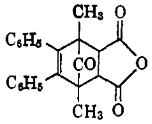
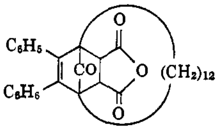
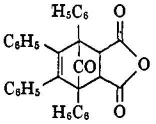
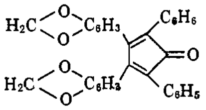
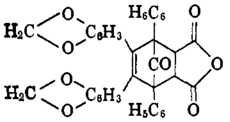
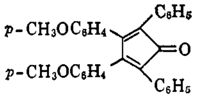
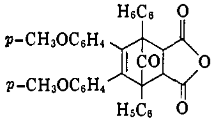
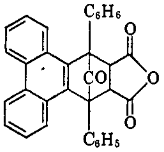
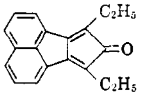
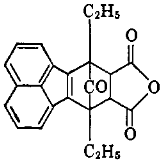
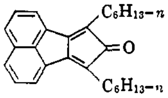
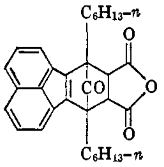
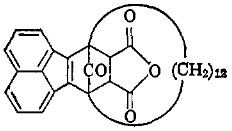
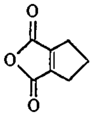
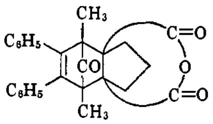
Cyclone	Dienophile	Conditions	Product	Ref.
	M.A.	Reflux 5 hr., HOAc		38
	M.A.	C_6H_6 + one drop H_2SO_4, heat		35
LXXXIV, $R_1 = R_2 = CH_3$	M.A.	C_6H_6, heat		35
CLXVI	M.A.	C_6H_6, room temp., 4 days		44
III	M.A.	Conditions not given (34, 136), 155–160° (31); 190–200° (119); C_6H_6, heat, 7 days (137); dioxane (250)		31, 34,[b] 111, 113, 116, 119, 136, 137, 250 (k_2 obtained)
	M.A.	C_6H_6, reflux, 8 hr.		51
	M.A.	100° or reflux C_6H_6, 4–5 hr. or 8–10 hr.		232
VII	M.A.	100° or reflux C_6H_6 or reflux C_6H_5Cl (latter is best)		125
	M.A.	C_6H_6, room temp., 2 days		43[c]
	M.A.	C_6H_6, room temp., 2 days		43[c]
CCXV	M.A.	C_6H_6, room temp., 4 days		44
XXXIV, $R_1 = R_2 = CH_3$		Xylene, 140–148° for 4 hr. then stand overnight		258[c]

TABLE XXV (*continued*)

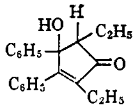
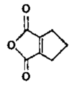
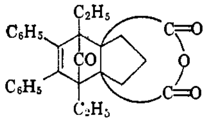
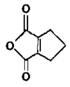
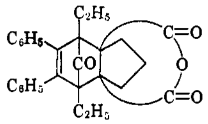
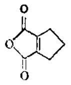
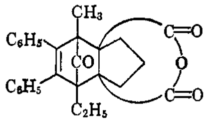
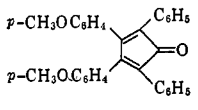
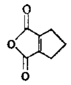
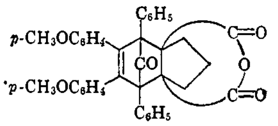
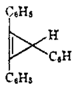
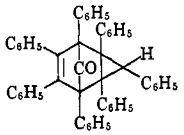
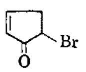
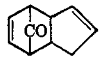
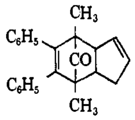
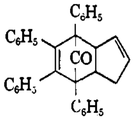
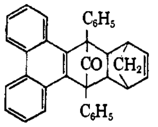
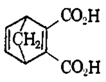
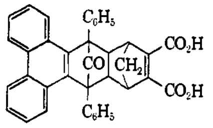
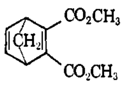
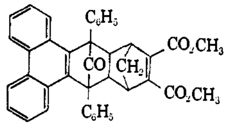
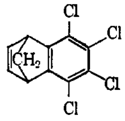
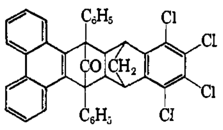
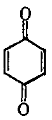
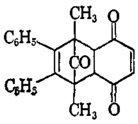
Cyclone	Dienophile	Conditions	Product	Ref.
		Acetic anhydride + H_2SO_4, heat 1 hr.		258
LXXXIV, $R_1 = R_2 = C_2H_5$		Xylene, 140–145° for 4 hr.		258[c]
LXXXIV, $R_1 = CH_3$, $R_2 = C_2H_5$		Xylene, 140–145° for 4 hr.		258[c]
		Xylene, 140–145° for 4 hr.		258
III		Room temp., 6 days		58
X	Cyclopentadiene	360–380° (13)  + $(C_2H_5)_2NH$ (166–168)		13,[d,e] 166,[e] 167,[e] 168[e]
LXXXIV, $R_1 = R_2 = CH_3$	Cyclopentadiene	C_6H_6, reflux for 4 hr.		26
III	Cyclopentadiene	C_6H_6, reflux for 4 hr.		164[f]
VII		C_6H_5Cl, reflux for 1–2 hr.		208
VII		C_6H_5Cl, boil for 30 min.		208
VII		C_6H_5Cl, boil for 45 min.		208
VII		C_6H_5Cl, heat 45 min.		208
LXXXIV, $R_1 = R_2 = CH_3$		C_6H_6, reflux 4 hr.		18

TABLE XXV (*continued*)

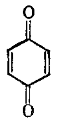
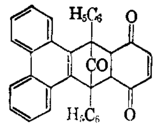
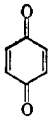
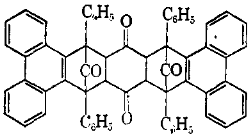
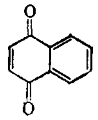
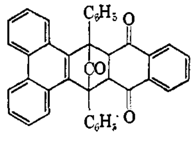
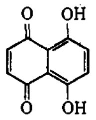
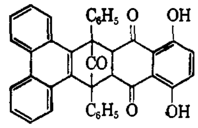
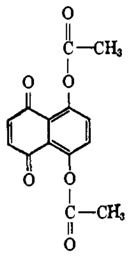
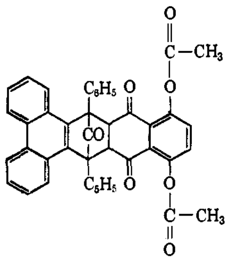
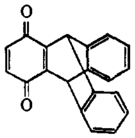
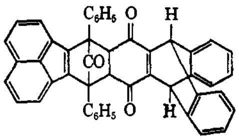
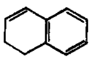
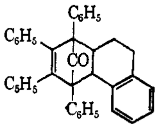
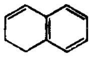
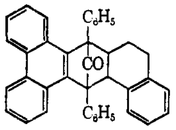
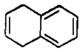
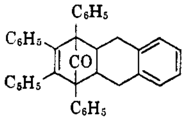
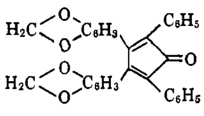
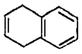
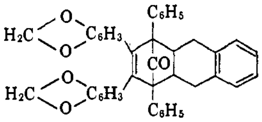
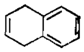
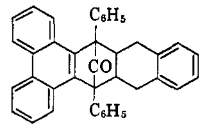
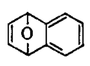
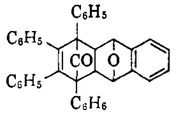
Cyclone	Dienophile	Conditions	Product	Ref.
VII		C_6H_5Cl, heat under CO_2 (131); $C_6H_5NO_2$, 100° (48)		48, 131
VII		$C_6H_5NO_2$, 100° for 1.5–2 hr.		48
VII		C_6H_5Cl, heat under CO_2 (131); $C_6H_5NO_2$ 100° for 4 hr. or room temp. for 12–14 hr. (48)		48, 131
VII		C_6H_6, reflux under CO_2		131
VII		C_6H_5Cl, heat under CO_2		131
VI		Sealed tube, C_6H_6 200–220° for 36 hr.		10
III		Sealed tube, C_6H_6 230—240° for 12 hr. or sealed tube, xylene, 230–240° for 8 hr. (50)		50, 53[g]
VII		Sealed tube, xylene 180–200° (50)		50, 53[g]
III		Sealed tube, xylene, 230–240° for 8 hr. (50)		50, 53[g]
		Sealed tube, xylene, 230–240° for 8–9 hr.		50
VII		Sealed tube, xylene, 140–150° for 5–6 hr. (50)		50, 53[g]

TABLE XXV (*continued*)

Cyclone	Dienophile	Conditions	Product	Ref.
III		Refluxing benzene		153a

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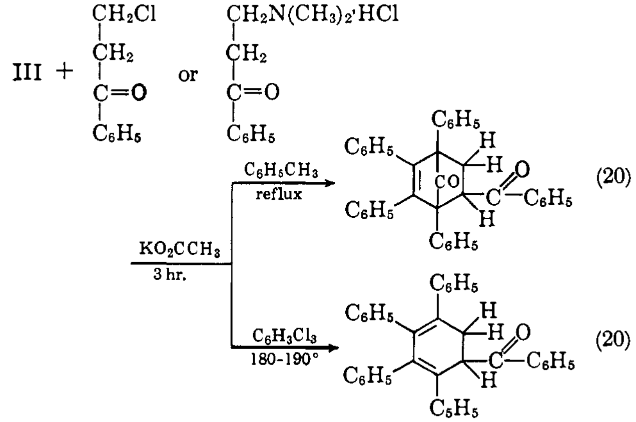
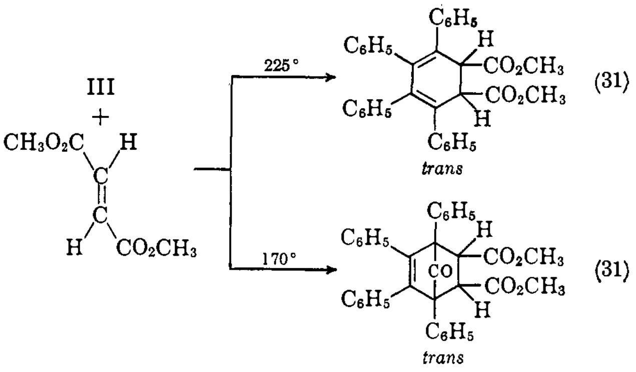
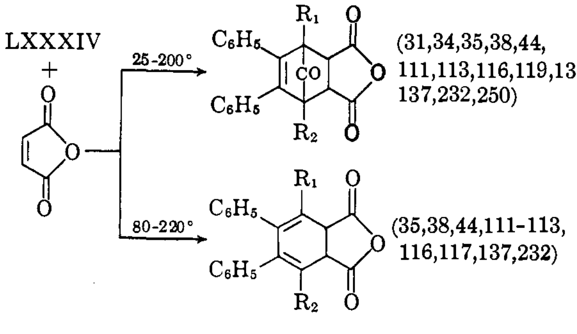
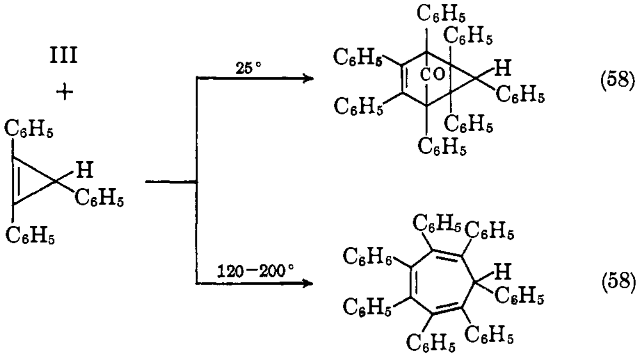
[a] Dienophile formed in reaction mixture. [b] Structure of product not given. [c] Cyclone exists as dimer. [d] Both starting materials formed from pyrolysis of 3a, 4,7,7a-tetrahydromethanoindenone (i) at 360–380° and the decarbonylated product isolated. [e] i also formed. [f] The authors also tried the following unsuccessfully: furan, pyrrole, N-methylpyrrole, thiophene, and diphenylcyclopentadiene. [g] Products in error; should be CXLVII and CCXXVII.

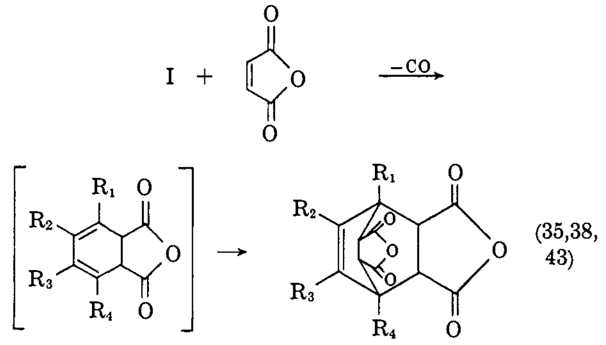




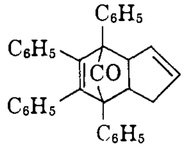


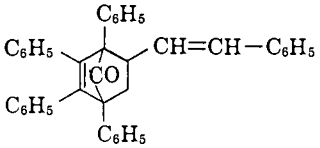


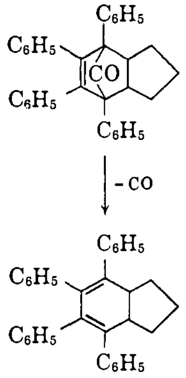
In some cases, maleic anhydride added to the dihydrobenzene that resulted from the decarbonylation of the initial addition product.



Two reactions are known in which the presence or not of unsaturation in the adduct determines whether the adduct will dissociate or eliminate carbon monoxide. Cyclopentadiene (164) and 1-phenyl-1,3-butadiene (163) form the 1:1 adducts as expected with tetracyclone. Heating either of these adducts results in incomplete dissociation. However, if the corresponding dihydro compounds are heated, carbon monoxide is smoothly evolved. Table XXVI lists all reactions leading to dihydrobenzenes.







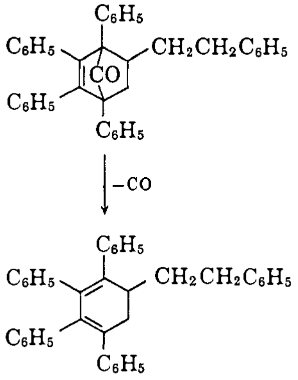


TABLE XXVI

FORMATION OF DIHYDROBENZENES

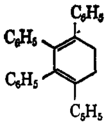
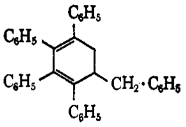
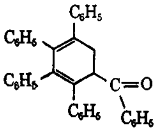
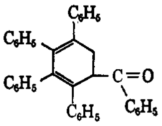
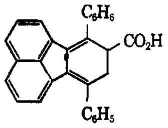
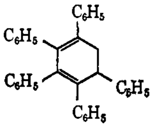
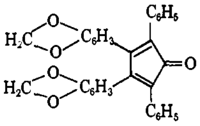
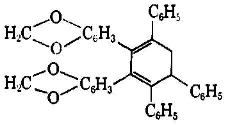
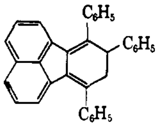
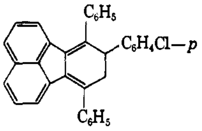
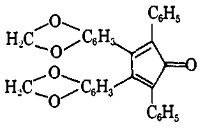
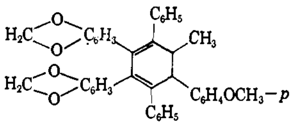
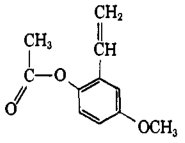
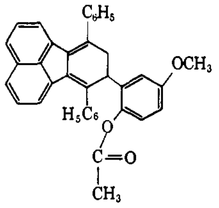
Cyclone	Dienophile	Conditions	Product	Ref.
III	$CH_2{=}CH_2$	Autoclave, C_6H_6, 190°, shake for 16 or 24 hr.		30
III	$CH_2{=}CH{-}CH_2C_6H_5$	Sealed tube, C_6H_6, 150–180° for 8 hr.		4
III	$CH_2Cl{-}CH_2{-}C({=}O){-}C_6H_5$	$C_6H_3Cl_3$, KOAc, 180–190° for 3 hr. or KOAc, $C_6H_5NO_2$[a]		20[b]
III	$N(CH_3)_2\cdot HCl{-}CH_2{-}C({=}O){-}C_6H_5$	$C_6H_3Cl_3$, KOAc, 180–190° for 3 hr. or KOAc, $C_6H_5NO_2$[a]		20[b]
VI	$CH_2{=}CH{-}CO_2H$	Xylene, reflux 2 hr.		43
III	$CH_2{=}CH{-}C_6H_5$	Sealed tube, C_6H_6, 160–190° for 5 hr. (4, 5)		4, 5
	$CH_2{=}CH{-}C_6H_5$	Sealed tube, C_6H_6, 180–190° for 25 hr.		51
VI	$CH_2{=}CH{-}C_6H_5$	Xylene, reflux 2 hr.		43
VI	$CH_2{=}CH{-}C_6H_4Cl\text{-}p$	Xylene, reflux 2 hr.		43
	$CH_3{-}CH{=}CH{-}C_6H_4OCH_3\text{-}p$	Sealed tube, C_6H_6, 180–200° for 34 hr.		51
VI		$C_6H_5CH_3$, reflux 24 hr.		276

TABLE XXVI (*continued*)

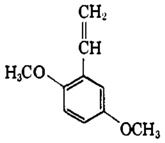
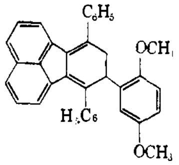
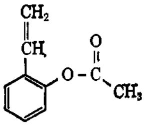
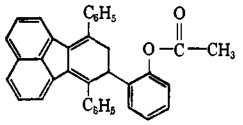
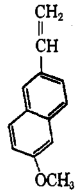
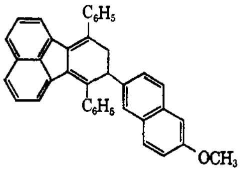
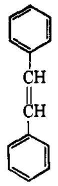
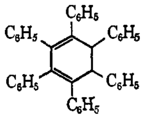
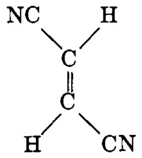
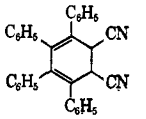
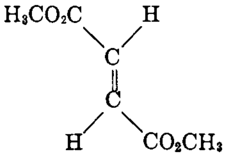
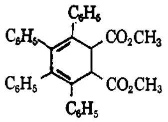
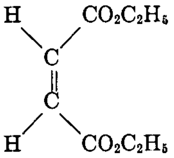
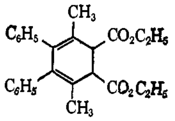
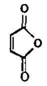
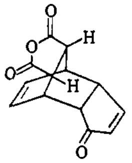
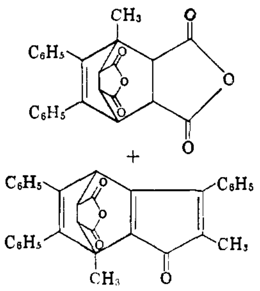
Cyclone	Dienophile	Conditions	Product	Ref.
VI		$C_6H_5CH_3$, reflux 24 hr.		276
VI		$C_6H_5CH_3$, reflux 24 hr.		276
VI		$C_6H_5CH_3$, reflux 24 hr.		276
III		305° (111–113, 116, 119)		111-113, 116, 119
III		C_6H_5Br, reflux 5.25 hr.		140
III		275°	 *trans*	31
LXXXIV, $R_1 = R_2 = CH_3$		Heat		35
XII	 (M.A.)	Heat		167
LXXXVIII	M.A.	220°		38, 40[b]

TABLE XXVI (*continued*)

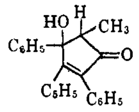
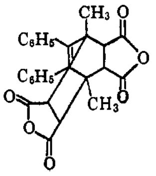
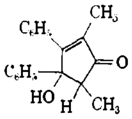
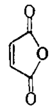
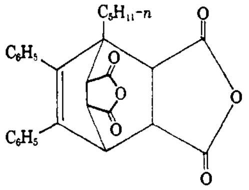
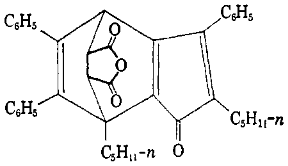
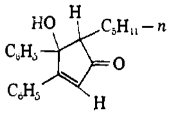
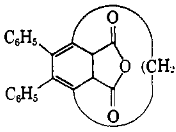
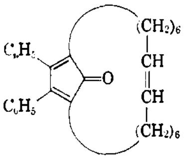
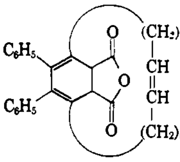
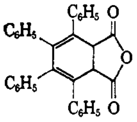
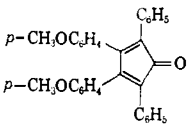
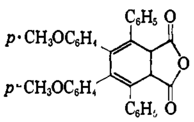
Cyclone	Dienophile	Conditions	Product	Ref.
	M.A.	190–200°	Same products as above	38
LXXXIV, $R_1 = R_2 = CH_3$	M.A.	C_6H_6, heat in excess maleic anhydride		35[d]
	M.A.	C_6H_5, heat in excess  + drop H_2SO_4	Same product as above	35
LXXXIX	M.A.	190–200° (38)	 + 	38,140[c,d]
	M.A.	$C_6H_3Cl_3$ + H_2SO_4 reflux 0.5 hr.	Same products as above	38
CLXVI	M.A.	Xylene, reflux		44
	M.A.	Xylene, reflux		44
III	M.A.	C_6H_5Cl, reflux (111–113, 116, 119, 137)		111–113, 116, 119, 137
	M.A.	C_6H_5Br, reflux 4 hr.		232

TABLE XXVI (*continued*)

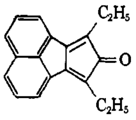
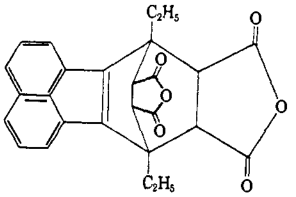
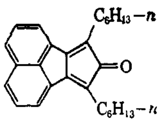
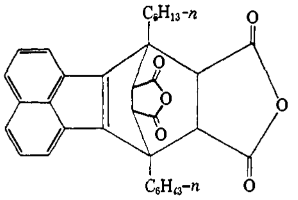
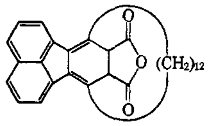
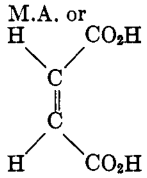
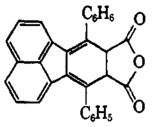
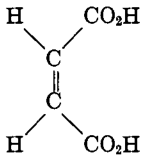
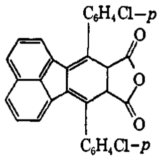
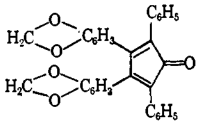
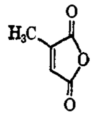
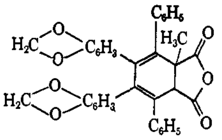
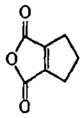
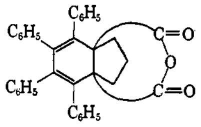
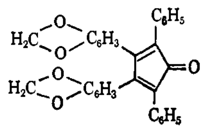
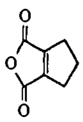
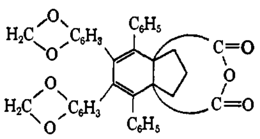
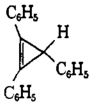
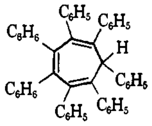
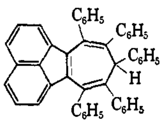
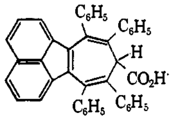
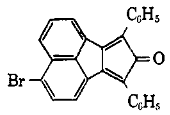
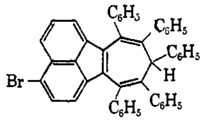
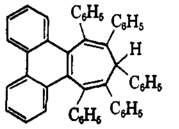
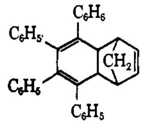
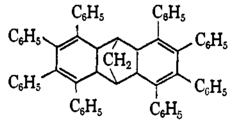
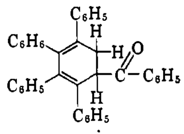
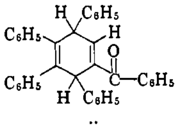
Cyclone	Dienophile	Conditions	Product	Ref.
	M.A.	HOAc, reflux 3 hr.		43[c,d]
	M.A.	HOAc, reflux 3 hr.		43[c,d]
CCXV	M.A.	Xylene, reflux		44
VI	M.A. or 	C_6H_5Cl, heat, 2 hr.		122
CLXI		C_6H_5Cl, reflux 7 hr.		268
		Sealed tube, C_6H_6, 180–200° for 32 hr.		51
III		Xylene, reflux, 3 hr.		258
		Xylene, heat at 140–145° for 4 hr. then let stand overnight		258
III		120–200°, or C_6H_6, reflux 2 days; or xylene, reflux 3 hr.		58
VI	Same as above	(1) Reflux xylene 4–7 hr. (2) Reflux benzene (3) Benzene–chloroform		59

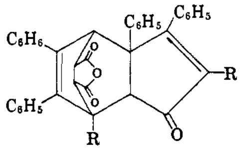
TABLE XXVI (*continued*)

Cyclone	Dienophile	Conditions	Product	Ref.
VI	Same as above	Reflux xylene		59
	Same as above	Reflux xylene		59
VII	Same as above	Reflux xylene		59
III		$CHCl_3$, heat 48 hr.		208
III	Same as above	$CHCl_3$, heat 48 hr.		208

[a] Product may be i or ii but is still different from the product obtained from the reaction performed in $C_6H_3Cl_3$. [b] Product may be ii;

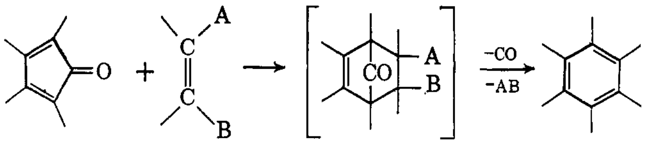

i


ii

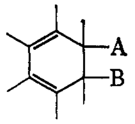

iii

authors uncertain. [c] A product iii, R = CH_3, n-C_5H_{11}, reported only. [d] Cyclone exists as dissociating dimer.

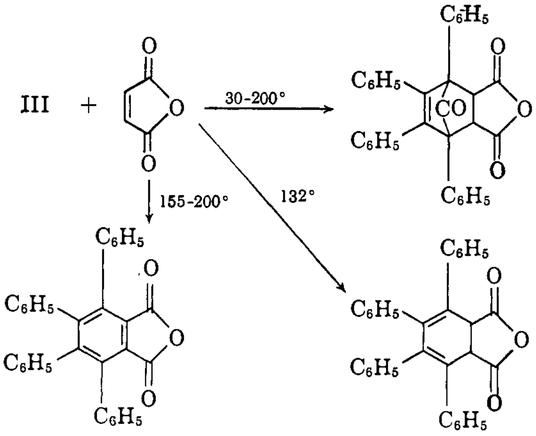
(*3*) *Reaction with Simultaneous Evolution of Carbon Monoxide and Aromatization.*—Under suitable conditions, cyclopentadienones react with alkenes to yield aromatic products as follows (Table XXVII).



Since dihydrobenzenes have been isolated, it seems reasonable to suppose that the carbon monoxide is lost first to yield dihydrobenzenes such as



Perhaps the best example of this stepwise reaction is the reaction between tetracyclone and maleic anhydride which can yield either the bridged carbonyl compound, the dihydrobenzene, or the aromatic tetraphenylphthalic anhydride.



The elements A–B which have been eliminated in this reaction are H–H, H–Br, H–Cl, H–NO_2, H–OR, H–O_2CH, H–O_2CCH_3, H–NR_1R_2, H–SnR_3, cyclopentadiene, cyclopentadienedicarboxylic acid, and tetrachloroindene. Hydrogen itself can be split out by running the reaction at a high temperature (20, 30, 31, 35, 38, 50, 111–113, 116, 119, 122, 124, 135, 136, 284), using an oxidizing agent (43, 111–113, 116, 119, 140, 162, 232), or palladium on charcoal (43). The remaining com-

TABLE XXVII

FORMATION OF AROMATIC COMPOUNDS FROM ALKENES

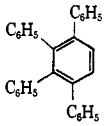
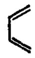
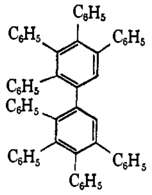
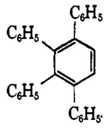
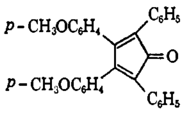
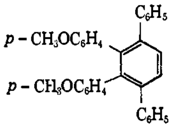
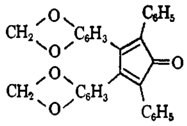
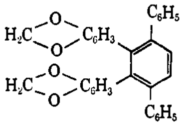
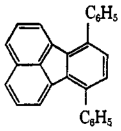
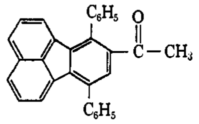
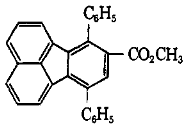
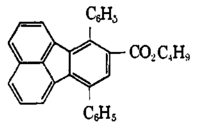
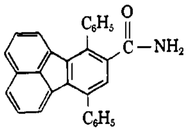
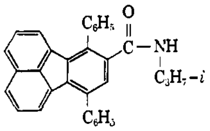
Cyclone	Dienophile	A–B	Conditions	Product	Ref.
III	$CH_2=CH_2$	H-H	C_6H_6, autoclave, 190°, shaking 24 hr.		30
III		H-H H-H	260–290°		135
III	$CH_2=CHBr$	H–Br	Sealed tube, C_6H_6, 150° for more than 20 hr.		1, 2
	$CH_2=CHBr$	H–Br	10 hr. at 120° and 10 hr. at 150° (9)		2, 9
	$CH_2=CHBr$	H–Br	$C_6H_5CH_3$, sealed tube, 180–200° for 15–18 hr.		1, 2
VI	$CH_2=CHBr$	H–Br	Sealed tube, C_6H_6 180–200° for 24 hr.		2, 10
VI	$CH_2=CH-C(=O)-CH_3$	H–H	(1) Xylene, reflux for 2 hr. (2) Pd–C or $KMnO_4$ in acetone (43)		43
VI	$CH_2=CH-CO_2CH_3$	H–H	(1) Xylene, reflux for 2 hr. (2) Pd–C or $KMnO_4$ in acetone (43)		43
VI	$CH_2=CH-CO_2C_4H_9$	H–H	(1) Xylene, reflux for 2 hr. (2) Pd–C or $KMnO_4$ in acetone		43
VI	$CH_2=CH-C(=O)-NH_2$	H–H	(1) Xylene, reflux for 2 hr. (2) Pd–C or $KMnO_4$ in acetone		43
VI	$CH_2=CH-C(=O)-NH-C_3H_7\text{-}i$	H–H	(1) Xylene, reflux 2 hr. (2) Pd–C or $KMnO_4$ in acetone		43

TABLE XXVII (*continued*)

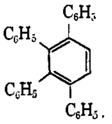
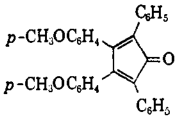
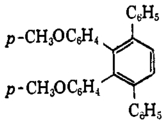
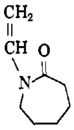
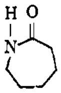
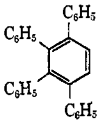
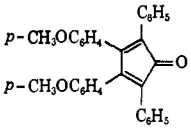
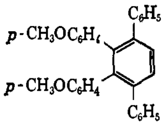
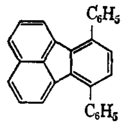
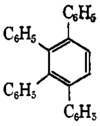
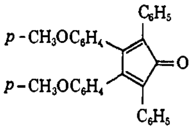
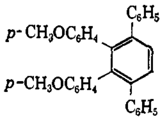
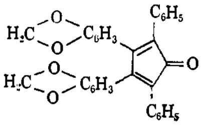
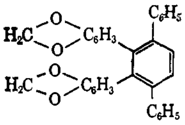
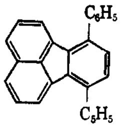
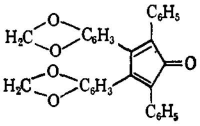
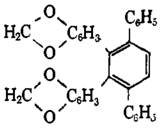
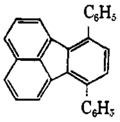
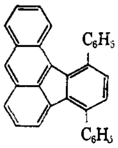
Cyclone	Dienophile	A-B	Conditions	Product	Ref.
III	$CH_2{=}CH{-}NH{-}CH_2{-}CH_2OH$	$\underset{NH_2}{CH_2}CH_2OH$	10 hr. at 100° and 8 hr. at 168°		9
	$CH_2{=}CH{-}NH{-}CH_2{-}CH_2OH$	$\underset{NH_2}{CH_2}CH_2OH$	10 hr. at 170°		9
III			10 hr. at 160° and 10 hr. at 180°		9
	Same as above		10 hr. at 160° and 10 hr. at 180°		9
VI	$CH_2{=}CH{-}OC_2H_5$	C_2H_5OH	C_6H_6, sealed tube, 180–200° for 14 hr.		2, 10
III	$CH_2{=}CH{-}OC_4H_9\text{-}n$	$n\text{-}C_4H_9OH$	C_6H_6, sealed tube, 170–180°, 8 hr. (1) C_6H_6, sealed tube, 135–145°, 60 hr. (2)		1, 2
	Same as above		150–160° for 14 hr. (9)		2, 9
	Same as above		C_6H_6, sealed tube, 180–200° for 8 hr.		1, 2
VI	Same as above		C_6H_6, sealed tube, 180–200° for 12 hr.		2, 10
	Same as above		C_6H_6, sealed tube, 180–200° for 8 hr.		1, 2
VI	Same as above		Xylene, sealed tube, 18 hr. at 220° or 12 hr. at 310° (74)		2, 74
VIII	Same as above		C_6H_6, sealed tube, 180–200°, for 25 hr.		1, 2

TABLE XXVII (*continued*)

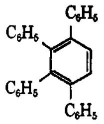
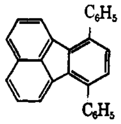
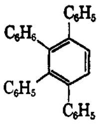
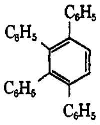
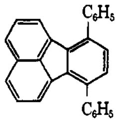
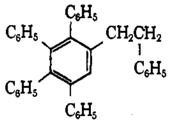
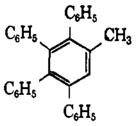
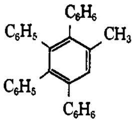
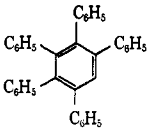
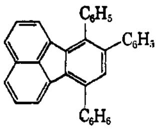
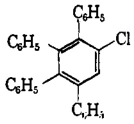
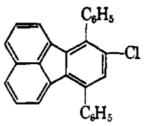
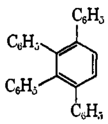
Cyclone	Dienophile	A-B	Conditions	Product	Ref.
III	CH_2 ‖ CH | $Sn(CH_3)_3$	$(CH_3)_3SnH$	C_6H_6, sealed tube, under CO_2, 16 hr. at 180–190°		52
VI	Same as above		C_6H_6, sealed tube, under CO_2, 20 hr. at 170–190° and 10 hr. at 200–230°		52
III	CH_2 ‖ CH | $Sn(C_2H_5)_3$	$(C_2H_5)_3SnH$	C_6H_6, sealed tube, under CO_2, 5 hr. at 190–200°		52
III	CH_2 ‖ CH | $Sn(C_6H_5)_3$	$(C_6H_5)_3SnH$	C_6H_5Br, reflux (245, 246) $C_6H_5NO_2$, reflux for 13 hr. (246)		245,[a] 246
VI	Same as above		C_6H_6, sealed tube, under CO_2, 50 hr. at 200–230°		52
III	CH_2 ‖ CBr | CH_2 | $CH_2C_6H_5$	H–Br	*p*-Cymene, reflux, 29.5 hr. at 180°		163
III	CH_2 ‖ CCH_3 | OC_2H_5	C_2H_5OH	C_6H_6, sealed tube, 75 hr. at 180–200°		6
III	CH_2 ‖ CCH_3 | O_2CCH_3	CH_3CO_2H	C_6H_6, sealed tube, 130–160° for 10 hr. or 23 hr. at 180–200°		6
III	CH_2 ‖ CC_6H_5 | OC_2H_5	C_2H_5OH	C_6H_6, sealed tube, 5 hr. at 120–150° and 62 hr. at 180–200°		6
VI	Same as above		C_6H_6, sealed tube, 5 hr. at 120–150° and 180–200° for 24 hr.		6
III	$CHCl$ ‖ $CHCl$	H–Cl	C_6H_6, sealed tube, 200–220° for 30 hr.		1
VI	Same as above		Xylene, 15 hr. at 220° or 6 hr. at 260°		74
III	$CHCl$ ‖ $CHHgCl$	$HgCl_2$	C_6H_6, sealed tube, 180–200° for 7 hr.		1

TABLE XXVII (*continued*)

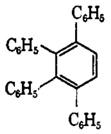
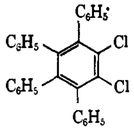
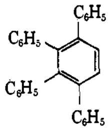
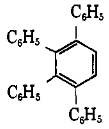
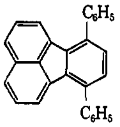
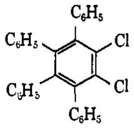
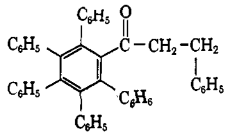
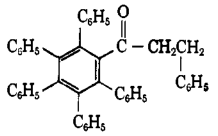
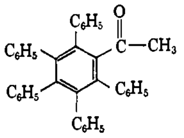
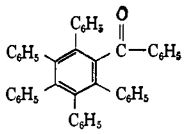
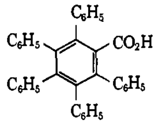
Cyclone	Dienophile	A-B	Conditions	Product	Ref.
III	$CHCl{=}CHAsCl_2$	$AsCl_3$	C_6H_6, sealed tube, 150° for 36 hr.		1
III	$CCl_2{=}CHCl$	H–Cl	C_6H_6, sealed tube, 180–200° for 17 hr.		7
III	$CH_2Cl{-}CH_2Cl$	H–Cl	C_6H_6, sealed tube, 155° for 4.5 hr. or 12 hr. at 200–220°		7[b]
III	$CH_2Br{-}CH_2Br$	H–Br	C_6H_6, sealed tube, 250–270° for 35 hr.		7[b]
VI	Same as above		C_6H_6, sealed tube, 200–240° for 54 hr.		7[b]
III	$CHCl_2{-}CHCl_2$	H–Cl	C_6H_6, sealed tube, 250–270° for 35 hr.		7[b]
III	$CHC_6H_5{=}CH{-}C{=}O{-}CH_2{-}CH_2C_6H_5$	H–H	310–320° for 5 min.		284
III	$CHC_6H_5{=}CH{-}C{=}O{-}CH{=}CHC_6H_5$	H–H	310–320° for 20 min.		284
III	$CHC_6H_5{=}CH{-}C{=}O{-}CH_3$	H–H	240–260° or C_6H_5Br, heat, 84.5 hr. or C_6H_5Br, CCl_3CO_2H, heat, 86–89 hr.		284
III	$CHC_6H_5{=}CH{-}C{=}O{-}C_6H_5$	H–H	$C_6H_3Cl_3$, reflux, 24 hr. at 210–213°		20
III	$CH{-}C_6H_5{=}CH{-}CO_2H$	H–H	C_6H_5Br, heat, 47 hr.		284

TABLE XXVII (*continued*)

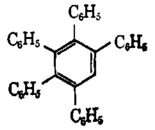
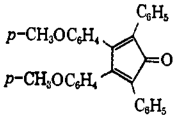
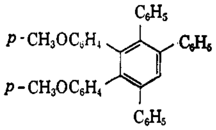
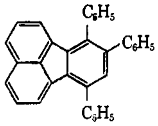
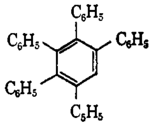
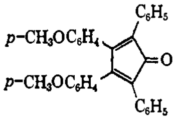
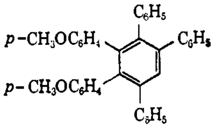
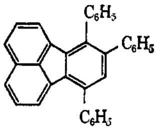
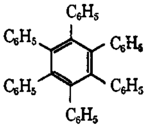
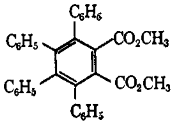
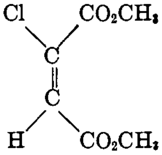
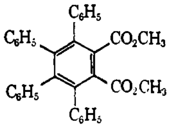
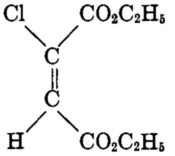
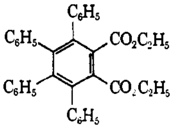
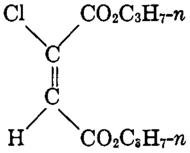
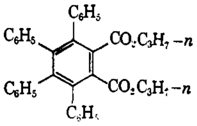
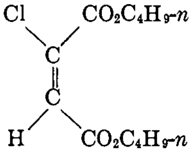
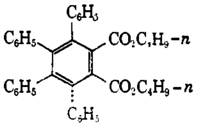
Cyclone	Dienophile	A-B	Conditions	Product	Ref.
III	CHBr ‖ CHC$_6$H$_5$	H–Br	17 hr. at 150–160° and 15 hr. at 180–190°		9
	Same as above		150–160° for 15 hr. and 10 hr. at 180–190°		9
VI	Same as above		12 hr. at 115–160° and 15 hr. at 180–190°		9
III	CHNO$_2$ ‖ CHC$_6$H$_5$	H–NO$_2$	C$_6$H$_3$Cl$_3$, heat 30 hr. at 170°		9, 19, 21
	Same as above		10 hr. at 160° and 10 hr. at 180°		9
VI	Same as above		30 hr. at 170°		9
III	CHC$_6$H$_5$ ‖ CHC$_6$H$_5$	H–H	Heat		136
III	HCCO$_2$CH$_3$ ‖ HCCO$_2$CH$_3$	H–H	165°		31
III		H–Cl	Heat		243
III		H–Cl	C$_6$H$_5$Br, heat, 3 hr.		243
III		H–Cl			256
III		H–Cl			256

TABLE XXVII (*continued*)

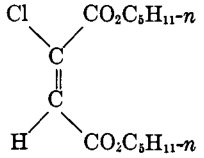
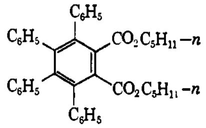
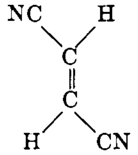
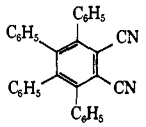
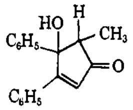
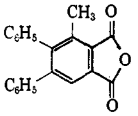
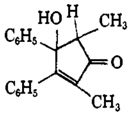
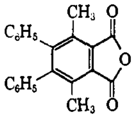
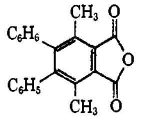
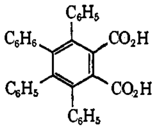
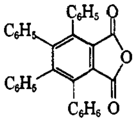
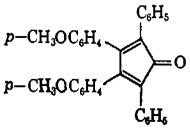
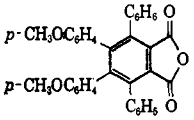
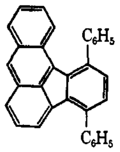
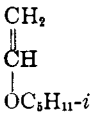
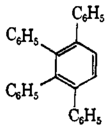
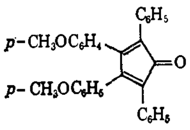
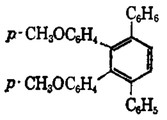
Cyclone	Dienophile	A-B	Conditions	Product	Ref.
III		H–Cl			256
III		H–H	(1) C_6H_5Br, reflux, 2 hr. (2) Br_2, heat, 3 hr.		140
	M.A.	H–H	HOAc, heat then distil		38
	Same as above		$C_6H_3Cl_3$, heat, with a drop of H_2SO_4		35
LXXXIV, $R_1 = R_2 = CH_3$	Same as above		$C_6H_3Cl_3$, reflux		35
III	Same as above		240–250°		31
III	Same as above		190–200° (111–113, 116, 119) (1) C_6H_5Br, reflux, 3.5 hr. (2) C_6H_5Br, Br_2, reflux 3 hr. (162)		111–113, 116, 119, 162
	Same as above		$C_6H_5NO_2$, reflux 2 hr.		232
VIII	Same as above		C_6H_6, sealed tube, 180–200° for 25–28 hr.		1, 2
III	 $CH_2{=}CH{-}OC_5H_{11}\text{-}i$	$i\text{-}C_5H_{11}OH$	C_6H_6, sealed tube, 160–180° for 16 hr.		1, 2
	Same as above		23 hr. at 150–160°		2, 9

TABLE XXVII (*continued*)

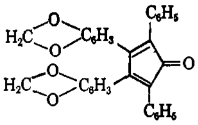
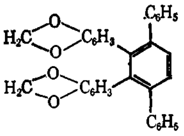
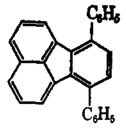
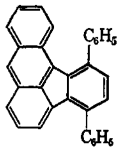
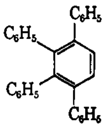
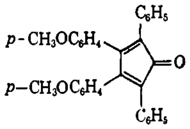
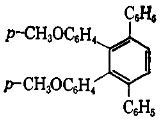
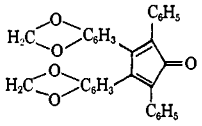
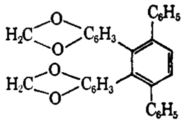
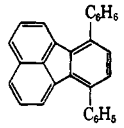
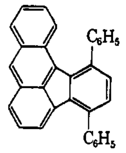
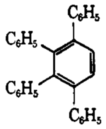
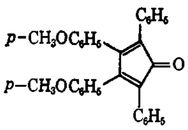
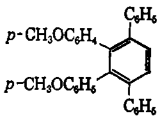
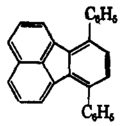
Cyclone	Dienophile	A–B	Conditions	Product	Ref.
	Same as above		C_6H_6, sealed tube, 180–200° for 6 hr.		1, 2
VI	Same as above		Xylene, sealed tube (74) 18 hr. at 220° or 12 hr. at 310° (2)		2, 74
VIII	Same as above		C_6H_6, sealed tube, 180–200° for 30 hr.		1, 2
III	$CH_2{=}CH{-}OC_6H_5$	C_6H_5OH	C_6H_6, sealed tube, 170–180° for 8 hr. (1) or C_6H_6, sealed tube, 135–145° for 60 hr. (1)		1, 2
	Same as above		147° for 70 hr. (9)		2, 9
	Same as above		C_6H_6, sealed tube, 180–200° for 13 hr.		1, 2
VI	Same as above		C_6H_6, sealed tube, 180–200° for 12 hr.		2, 10
VIII	Same as above		C_6H_6, sealed tube, 180–200° for 30 hr.		1, 2
III	$CH_2{=}CH{-}OCH_2$ $CH_2{=}CH{-}OCH$ $CH_2{=}CH{-}OCH_2$	CH_2OH $CHOH$ CH_2OH	C_6H_6, sealed tube, 180–200° 5 hr. (1) or C_6H_6, sealed tube, 180–200° 55 hr. (1)		1, 2
	Same as above		110–120° for 20 hr. and 140–150° for 20 hr. (9)		2, 9
VI	Same as above		Xylene, sealed tube, 18 hr. at 220° or 12 hr. at 310° (74)		2, 74

TABLE XXVII (*continued*)

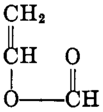
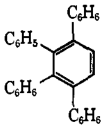
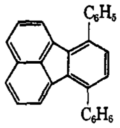
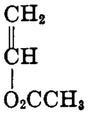
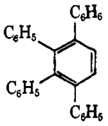
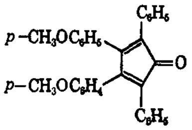
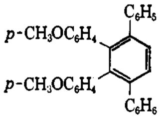
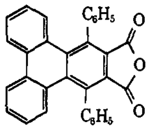
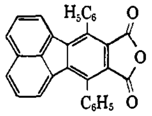
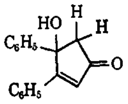
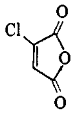
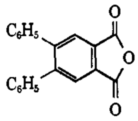
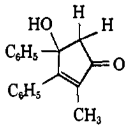
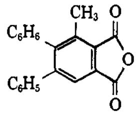
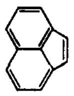
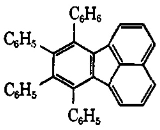
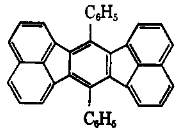
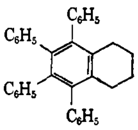
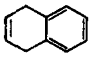
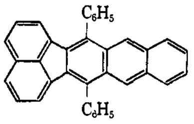
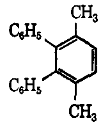
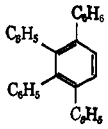
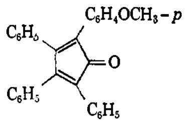
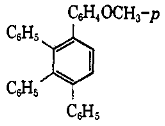
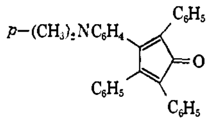
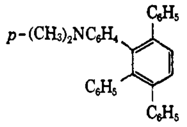
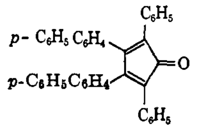
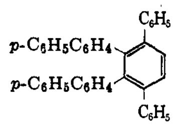
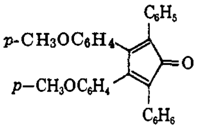
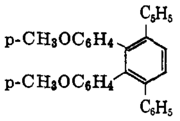
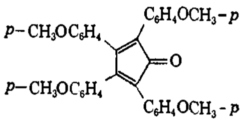
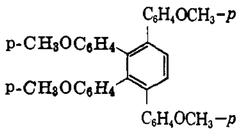
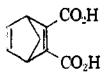
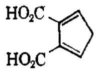
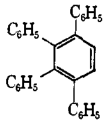
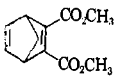
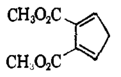
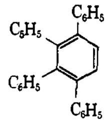
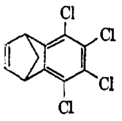
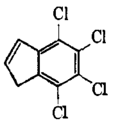
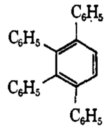
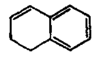
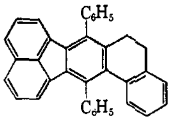
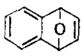
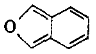
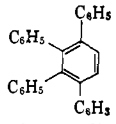
Cyclone	Dienophile	A-B	Conditions	Product	Ref.
III	 $CH_2{=}CH{-}O{-}CHO$	HCO_2H	C_6H_6, sealed tube, 180–200° for 5 hr.		1, 2
VI	Same as above		C_6H_6, sealed tube, 180–200° for 16 hr.		2, 10
III	 $CH_2{=}CH{-}O_2CCH_3$	CH_3CO_2H	C_6H_6, sealed tube, 150–180° for 14 hr.		1, 2
	Same as above		155–165° for 30 hr. (9)		2, 9
VII	Same as above		$C_6H_5NO_2$, boil		111–113, 116, 119
VI	Same as above		Heat		122
		H–Cl	200° for 1 hr. with 1 drop of H_2SO_4		42
	Same as above		Trace H_2SO_4, C_6H_5Br reflux 7 hr., then stand room temp. several days		42
III		H–H	250°		124
VI	Same as above		250–300°		124
III		H–H	280° 10–12 hr.		135
VI		H–H	(1) Xylene, reflux 2 hr. (2) Pd–C or $KMnO_4$ in acetone		43

TABLE XXVII (*continued*)

Cyclone	Dienophile	A-B	Conditions	Product	Ref.
LXXXIV, $R_1 = R_2 = CH_3$			C_6H_5Cl, reflux 2 hr.		208
III	Same as above		Xylene, maleic anhydride[b] 3.5 hr.		208[c]
	Same as above		$o\text{-}Cl_2C_6H_4$, reflux 6–10 hr.		208
	Same as above		$o\text{-}Cl_2C_6H_4$, reflux 6–10 hr.		208
	Same as above		$o\text{-}Cl_2C_6H_4$, reflux 6–10 hr.		208
	Same as above		$o\text{-}Cl_2C_6H_4$, reflux 6–10 hr.		208
	Same as above		$o\text{-}Cl_2C_6H_4$, reflux 6–10 hr.		208
III			$o\text{-}Cl_2C_6H_4$, heat 14 hr.		208
III			$o\text{-}Cl_2C_6H_4$, heat 14 hr.		208
III			$o\text{-}Cl_2C_6H_4$, reflux 7 hr.		208
VI		H-H	Xylene, sealed tube, 240–280°, 2 hr. and 280–300° for 3 hr.		50[d]
III			165°, diglyme		153a

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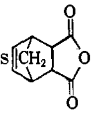
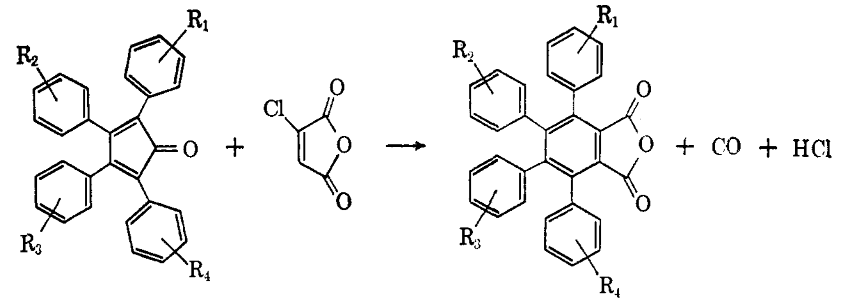
[a] $(C_6H_5)_3SnH$ reacted further with C_6H_5Br and tetracyclone to give reduction products. [b] Under the conditions of the reaction, an olefin is first formed. [c] Cyclopentadiene trapped with maleic anhydride as  [d] No structure for product given.

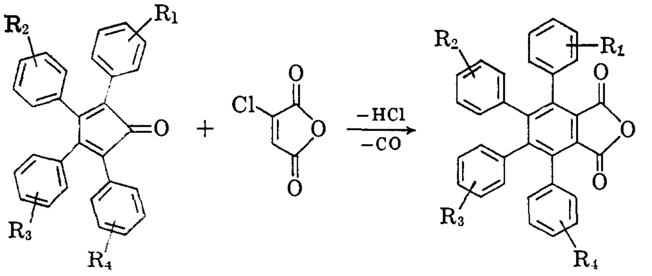
TABLE XXVIII



R1	R2	R3	R4	Conditions	Ref.
o-Cl	H	H	H	C_6H_5Br, reflux	260
H	o-Cl	H	H	C_6H_5Br, reflux	260
o-Cl	H	H	o-Cl	C_6H_5Br, reflux	260
H	o-Cl	o-Cl	H	C_6H_5Br, reflux	260
H	H	H	H	C_6H_5Br, reflux	88
p-CH_3	H	H	H	C_6H_5Br, reflux	88
H	p-CH_3	H	H	C_6H_5Br, reflux	88
p-CH_3	H	H	p-CH_3	C_6H_5Br, reflux	88
H	p-CH_3	p-CH_3	H	C_6H_5Br, reflux	88
p-Cl	H	H	H	C_6H_5Br, reflux	88
p-F	H	H	H	C_6H_5Br, reflux	88
p-Br	H	H	H	C_6H_5Br, reflux	88
H	p-Br	H	H	C_6H_5Br, reflux	88
p-Br	H	H	p-Br	C_6H_5Br, reflux	88
H	p-Br	p-Br	H	C_6H_5Br, reflux	88
p-Br	p-Br	p-Br	p-Br	C_6H_5Br, reflux	88
H	p-OCH_3	H	H	C_6H_5Br, reflux	88
p-OCH_3	H	H	p-OCH_3	C_6H_5Br, reflux	88
H	p-OCH_3	p-OCH_3	H	C_6H_5Br, reflux	88
p-OCH_3	p-OCH_3	p-OCH_3	p-OCH_3	C_6H_5Br, reflux	88
p-SCH_3	H	H	H	C_6H_5Br, reflux	88
p-SO_2CH_3	H	H	H	C_6H_5Br, reflux	88
H	p-SO_2CH_3	H	H	C_6H_5Br, reflux	88
H	H	H	H	C_6H_5Br, reflux 1 hr.	266
p-Cl	H	H	p-Cl	C_6H_5Br, reflux 10 hr.	269
p-Cl	p-Cl	p-Cl	p-Cl	C_6H_5Br, reflux 6 hr	269
m-CH_3	m-CH_3	m-CH_3	m-CH_3	C_6H_5Br, reflux 14 hr.	54
m-CH_3	H	H	m-CH_3	C_6H_5Br, reflux 14 hr	54
H	3,5-di-CH_3	3,5-di-CH_3	H	C_6H_5Br, reflux 14 hr.	54
H	p-Cl	p-Cl	H	C_6H_5Br, reflux 8 hr.	269
H	m-CH_3	m-CH_3	H	C_6H_5Br, reflux 14 hr.	54

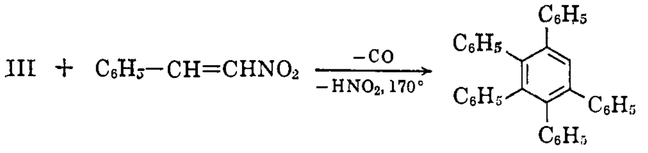
pounds have been cleaved off by thermal means. The temperature required for the cleavage depends on the structure of the adducts, the elements to be cleaved off, and varies from 100 to 310°.

For example, the decarbonylated adduct of stilbene and tetracyclone apparently survives as the dihydrobenzene even at 305°, while the decarbonylated adduct of maleic anhydride and tetracyclone loses two hydrogens at 190–200°.

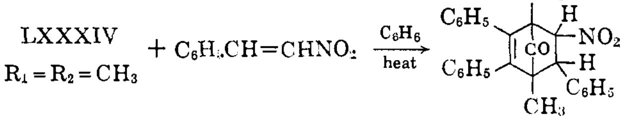


Chloromaleic anhydride has served as a derivatizing agent for substituted tetracyclones (Table XXVIII). Both CO and HCl are eliminated in one reaction (see bottom of left-hand column).

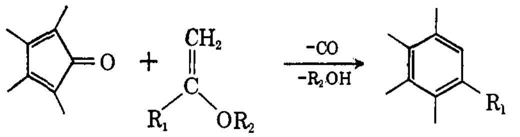
The elements of H–NO_2 have been removed in the reaction of β-nitrostyrene and tetracyclone (9, 19, 21).



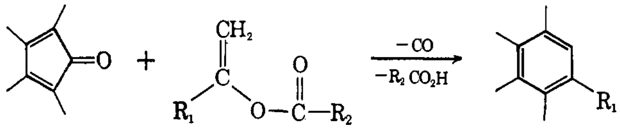
If 2,5-dimethyl-3,4-diphenylcyclopentadienone and a lower temperature is used, then the initial adduct can be isolated (35).



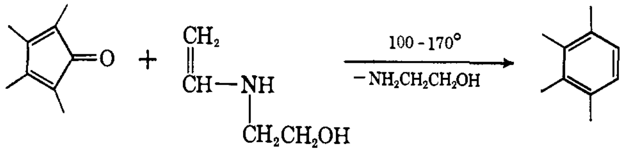
Alcohols have also been split out when vinyl ethers are used (1, 2, 6, 9, 10, 74).



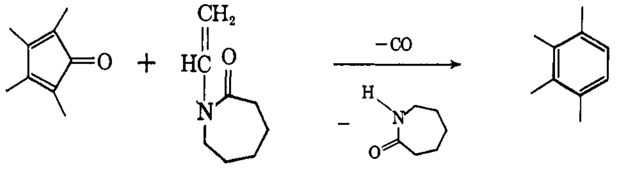
Acetic acid (1, 2, 6, 9, 74) and formic acid (1, 2, 10) have also been evolved.



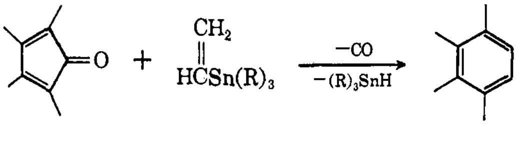
The reaction between cyclopentadienones and N-vinyl-2-hydroxyethylamine evolves ethanolamine (9).



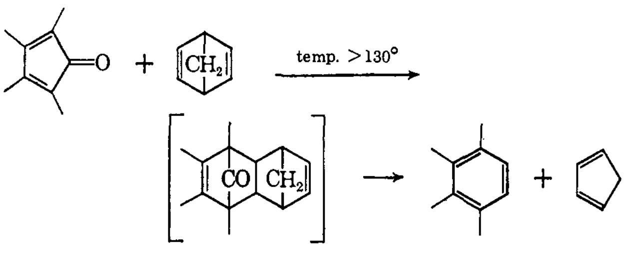
In a similar manner, N-vinylcaprolactam evolves caprolactam (9).



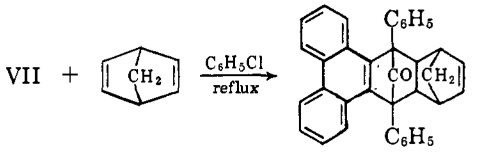
Trimethylvinylstannane, triethylvinylstannane, and triphenylvinylstannane have been allowed to react at elevated temperatures, *i.e.*, 180–200°, and found to evolve trialkyl- or triphenylstannane (52, 245, 246).



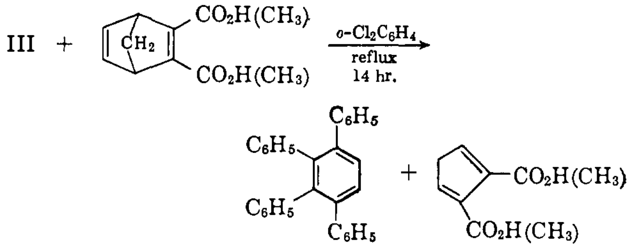
When norbornadiene reacts with cyclopentadienones at elevated temperatures cyclopentadiene is evolved (208).

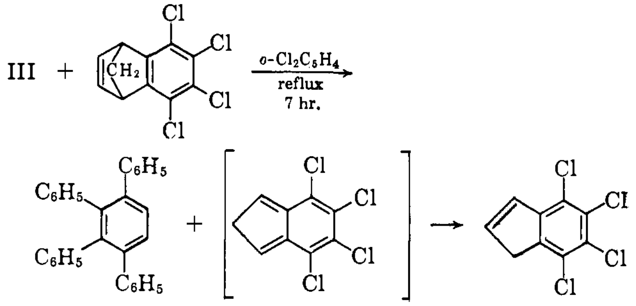


That an adduct is first formed which later decomposes may be implied from the reaction of phencyclone and norbornadiene (208).

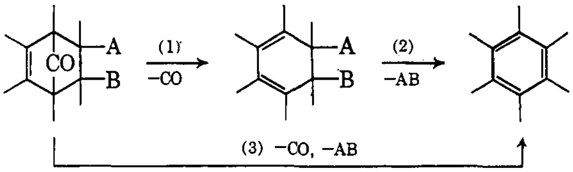


Derivatives of norbornadiene also react in a similar manner (208).





(*4*) *Decarbonylation of the Bridged Carbonyl Compounds and Subsequent Aromatization.*—The bridged carbonyl compounds which result from the addition of alkenes to cyclopentadienones have been converted to aromatic compounds as



The decarbonylation of the bridged carbonyl compounds has already been covered in two review articles (15, 16). Table XXIX lists those bridged carbonyl compounds which have been decarbonylated having originally been formed from the Diels–Alder reaction of cyclopentadienones and alkenes. Table XXX lists the dihydrobenzenes which have been aromatized. The dihydrobenzenes were prepared either from the decarbonylation of the bridged carbonyl compounds or from the Diels–Alder reaction of cyclopentadienones and alkenes with simultaneous evolution of carbon monoxide. Table XXXI lists those bridged carbonyl compounds which have been directly converted to aromatic compounds.

b. Reaction with Alkynes

(*1*) *Formation of Bridged Carbonyl Compounds.*—When 5-bromo-2-cyclopenten-1-one is treated with diethylamine, cyclopentadienone is produced. If

TABLE XXIX

DECARBONYLATION OF BRIDGED CARBONYL COMPOUNDS

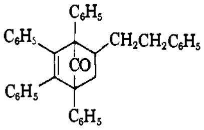
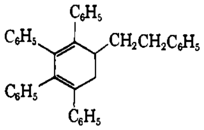
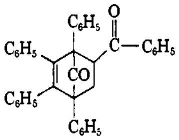
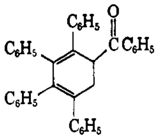
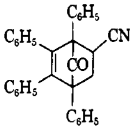
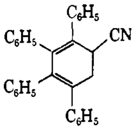
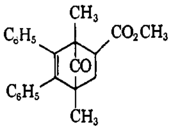
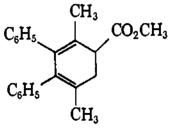
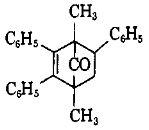
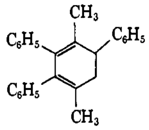
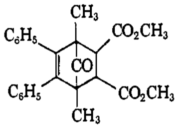
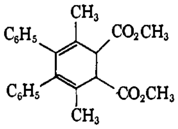
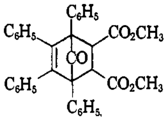
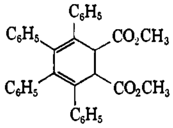
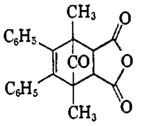
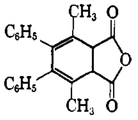
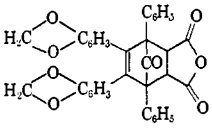
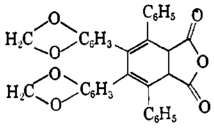
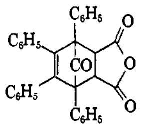
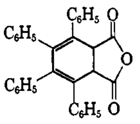
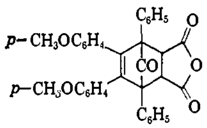
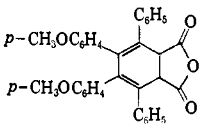
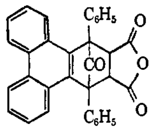
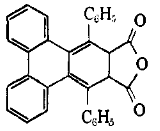
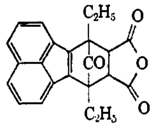
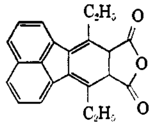
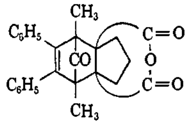
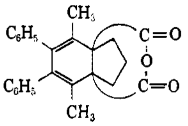
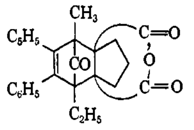
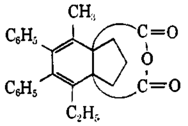
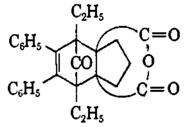
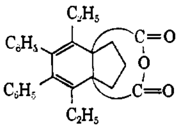
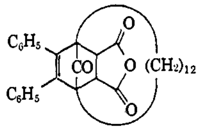
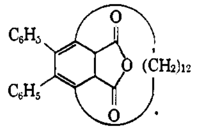
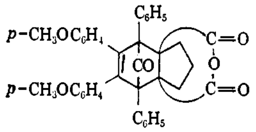
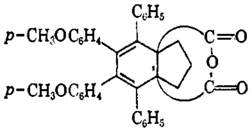
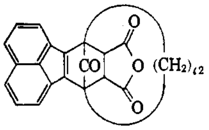
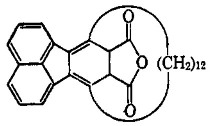
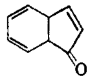
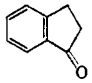
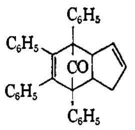
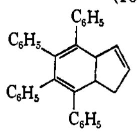
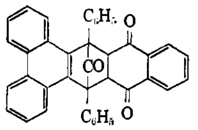
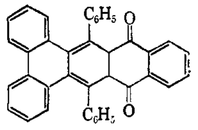
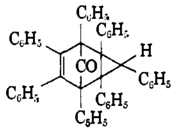
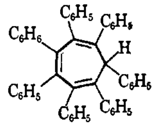
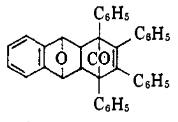
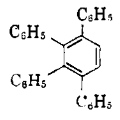
Bridged carbonyl compd.	Conditions	Product	Ref.
	p-Cymene, reflux for 12 hr. (180°) or 220–225° for 1 hr.		163[a]
	10 min. at 215°		20[b]
	$C_6H_5NO_2$ or p-cymene, reflux 10 hr. in presence of $CH_2{=}CHCN$		140
	Heat		35
	Heat		35
 *trans* or *cis*	200°	 *trans* or *cis*	35
 *trans*	Heat	 *trans*	31
	200°		35
	Sealed tube, xylene, 230–250° for 4 hr.		51
	Heat (136); 10 min. at 235–240° (31); CH_3OH, HCl, reflux (31)[c]; 260–270° with or without S_8 (31)[d]; C_6H_5Cl reflux (137); $C_6H_5NO_2$ (137)[e]		31, 111, 113, 116, 119, 136, 137
	C_6H_5Br, heat 1 hr.		232

TABLE XXIX (*continued*)

Bridged carbonyl compd.	Conditions	Product	Ref.
	Naphthalene, heat for 30 hr.		125
	Heat, steam bath 70°, reflux 10 min. in C_6H_6		43
	Tetralin, reflux for 2 hr.		258
	Tetralin, reflux for 2 hr.		258
	Tetralin, reflux for 2 hr.		258
	Heat		44
	Tetralin, reflux for 2 hr.		258
	240° for 10 min.		44
XII	360–380° (13) 240° (167)	 (13)  (167)	13,167
	HOAc or C_6H_5Cl reflux		164
	C_5H_5N, $NH_2OH \cdot HCl$, heat for 2 days (131); 10% KOH in ethanol, reflux 4 hr. (27)		27,131
	C_6H_6, reflux 24 hr.		58
	180°		153a

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[a] Carbonyl compound from ref. 163. [b] Product may be 1-benzoyl-2,3,4,5,6-pentaphenylcyclohexa-1,3-diene; authors uncertain. [c] Product is the dimethyl ester of *cis*-1,2-dihydro-3,4,5,6-tetraphenylphthalic acid. [d] Product is tetraphenylphthalic acid. [e] Product is tetraphenylphthalic anhydride.

TABLE XXX

AROMATIZATION OF DIHYDROBENZENES

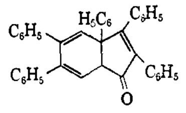
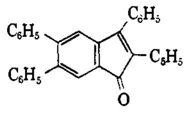
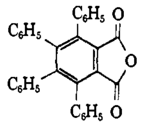
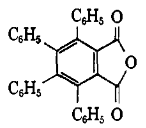
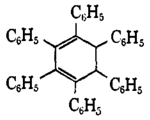
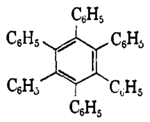
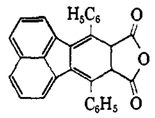
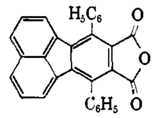
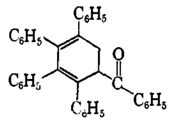
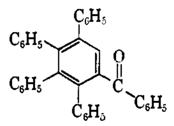
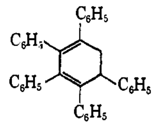
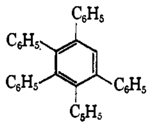
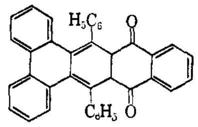
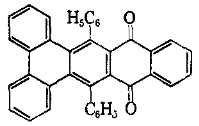
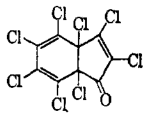
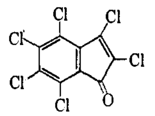
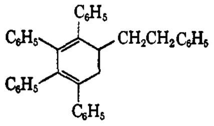
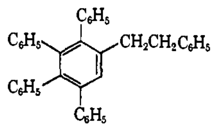
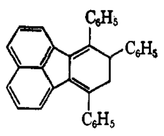
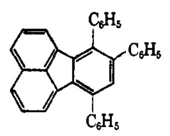
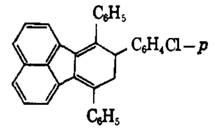
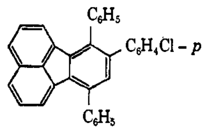
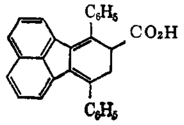
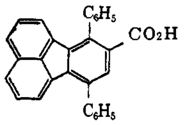
Reactant (from decomposition of bridged carbonyl compound)	A-B	Conditions	Product	Ref.
	C_6H_6 (C_6H_5SH)	S_8 at 325°		33
	H-H	Temp. 200° (111–113, 116, 119, 136); 260–270° (31); with or without S_8, $C_6H_5NO_2$ (137); S_8, 250–300°, 2 hr. (137)		31, 111–113, 116, 119, 136, 137
	H-H	Zn dust or Se, heat		111–113, 116, 119
	H-H	Heat		122
	H-H	Br_2, $KMnO_4$, or S_8		20[a]
	H-H	300–320°, Se		4, 5
	H-H	C_6H_5N, CH_3OH, KOH		131
	Cl-Cl	HOAc, NaOAc, or $SnCl_2$		291
	H-H	Chloranil, xylene, reflux 24 hr. or Pd–C, 1-methylnaphthylene, reflux 6 hr.		163
	H-H	Pd–C or $KMnO_4$ in acetone		43
	H-H	Pd–C or $KMnO_4$ in acetone		43
	H-H	Pd–C or $KMnO_4$ in acetone		43

Table XXX (*continued*)

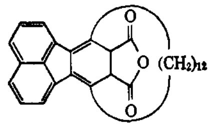
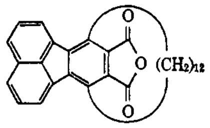
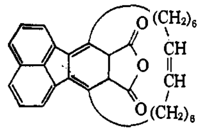
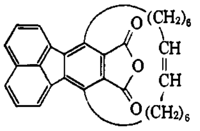
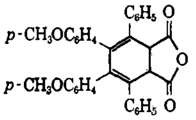
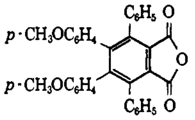
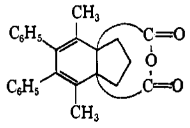
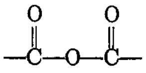
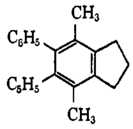
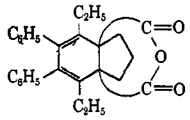
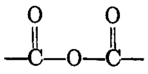
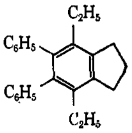
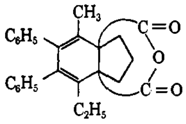
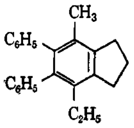
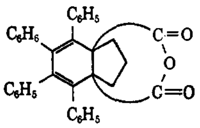
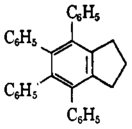
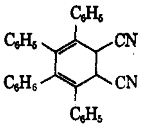
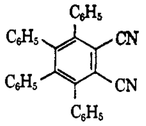
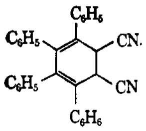
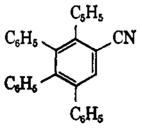
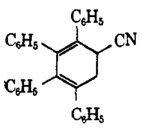
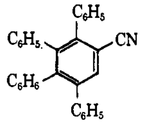
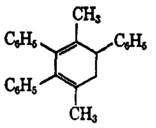
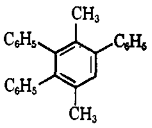
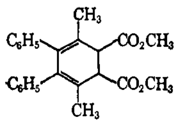
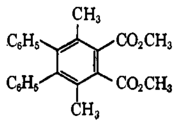
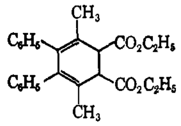
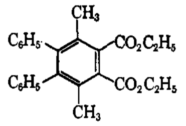
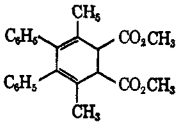
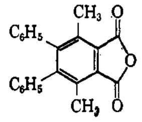
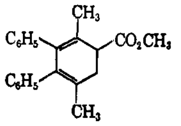
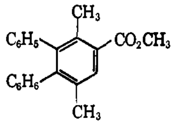
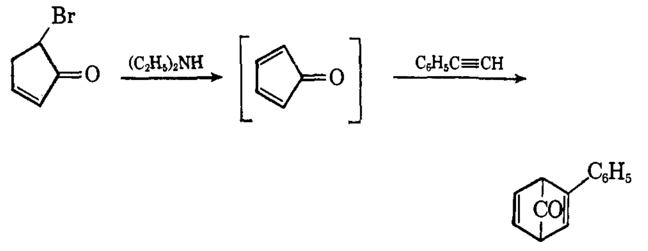
Reactant (from decomposition of bridged carbonyl compound)	A–B	Conditions	Product	Ref.
	H–H	Pd–C		44
	H–H	Pd–C		44
	H–H	Br_2 in C_6H_5Br, 2 hr. at room temp. or heat, $C_6H_5NO_2$, 1 hr.		232
	 $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	Soda lime, heat		258
	 $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	Soda lime, heat		258
	Same as above	Soda lime, heat		258
	Same as above	Soda lime, heat		258
	H–H	C_6H_5Br, Br_2 reflux 3.5 hr.		140
	H–CN	Merck basic alumina or 240–250° for 15 min., or diethylenetetramine, C_6H_5Br, heat 1 hr.		140
	H–H	C_6H_5Br, Br_2, reflux 6 hr.		140
	H–H	Br_2 in CCl_4		35
	H–H	Br_2 in CCl_4		35

TABLE XXX (*continued*)

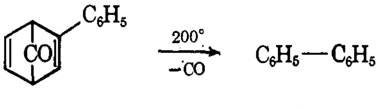
Reactant (from decomposition of bridged carbonyl compound)	A-B	Conditions	Product	Ref.
	H-H	Br_2 in CCl_4		35
	H-H	100% H_2SO_4		35
	H-H	$KMnO_4$		35

[a] Starting material may be 1-benzoyl-3,4,5,6-tetraphenylcyclohexa-1,3-diene; authors uncertain.

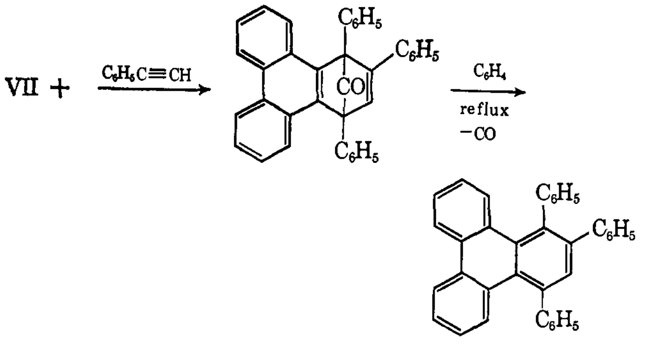
phenylacetylene is present, the cyclopentadienone is trapped (167, 168). This bridged carbonyl compound,



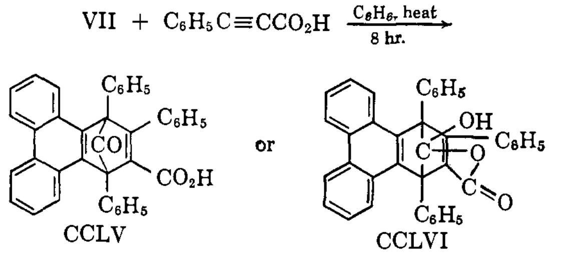
upon heating to 200°, loses carbon monoxide to yield biphenyl (167, 178).



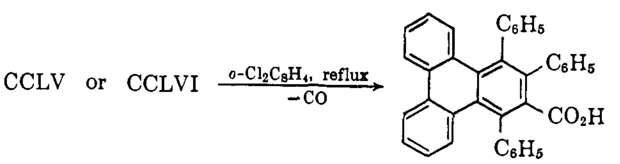
Phencyclone also reacts with phenylacetylene to yield a bridged carbonyl compound, which upon refluxing in benzene loses carbon monoxide (124).



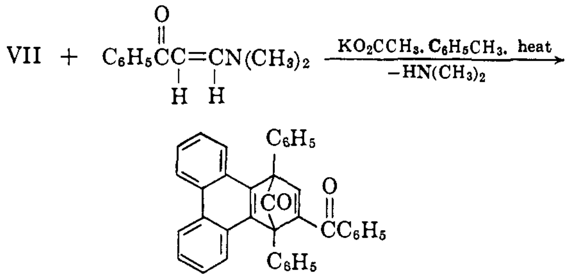
With phenylpropiolic acid, the structure of the product is uncertain, CCLV or CCLVI, but upon refluxing in *o*-dichlorobenzene it is decarbonylated (124).



CCLV CCLVI



Using *ω*-dimethylaminoacrylophenone, phencyclone forms a bridged carbonyl compound, which does not contain the dimethylamino group (20). Whether the alkene is first converted to the acetylene followed by reaction with phencyclone or whether the dimethylamino group is lost from the adduct of the alkene and phencyclone is not stated.



(*2*) *Reaction with Simultaneous Evolution of Carbon Monoxide.*—The usefulness of the reaction of cyclopentadienones with acetylenes lies in the direct formation of the aromatic compounds, generally under milder conditions than those required for the corresponding

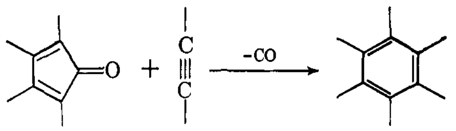
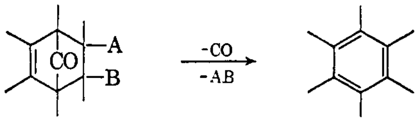


TABLE XXXI

DECARBONYLATION AND AROMATIZATION OF BRIDGED CARBONYL COMPOUNDS FROM DIELS–ALDER REACTIONS OF CYCLOPENTADIENONES



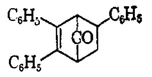
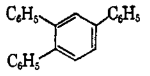
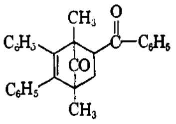
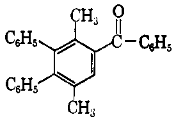
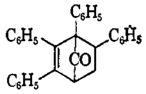
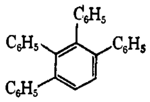
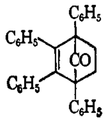
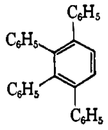
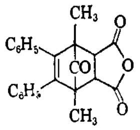
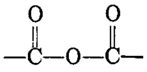
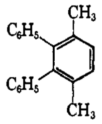
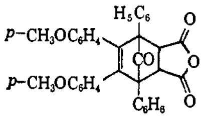
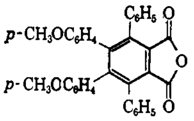
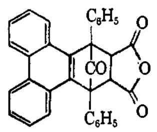
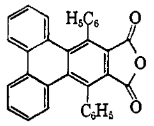
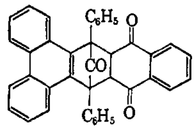
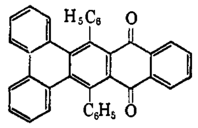
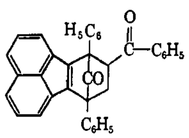
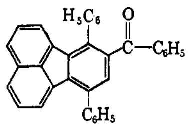
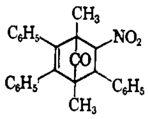
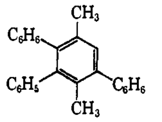
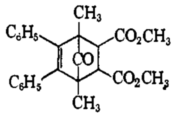
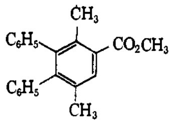
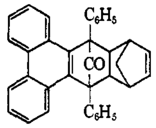
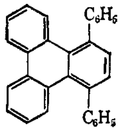
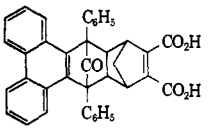
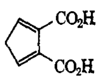
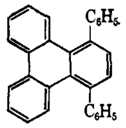
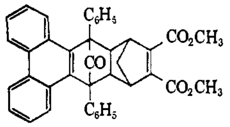
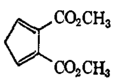
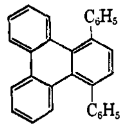
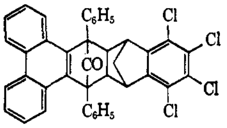
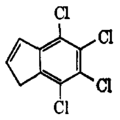
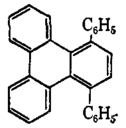
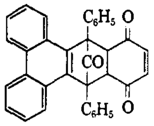
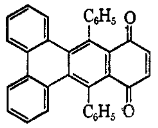
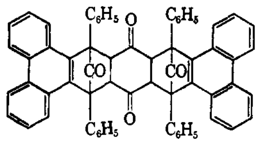
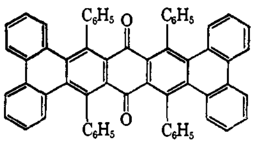
Bridged carbonyl compound from cyclone reaction	A–B	Conditions	Product	Ref.
	H–H	(1) 220–230° (2) S_8, 250° for 4 hr.		172, 228, 244
	H–H	200°		35
	H–H	(1) 4 hr. KOH–ethanol (2) K_2CO_3, heat, $KMnO_4$ (3) Br_2–CCl_4		39
	H–H	Mass spectrometry		30
	 $-\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}-$	$Ba(OH)_2$ or soda lime		35
	H–H	$C_6H_5NO_2$, heat 1 hr.		232
	H-H	(1) 300–320° (2) S_8, heat (3) $C_6H_5NO_2$, heat		125
	H–H	CH_3CO_2H, CrO_3, 10 hr. or C_5H_5N, heat, 3 days, (131); $C_6H_5NO_2$, reflux 4 hr. (48)		48, 131
	H–H	HOAc, heat		20
	HNO_2	Br_2 in CCl_4		35
	HCO_2CH_3	Heat		35

TABLE XXXI (*continued*)

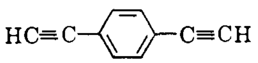
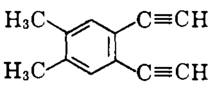
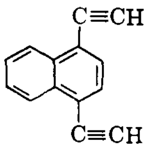
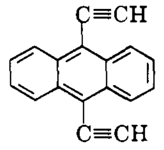
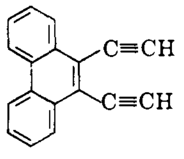
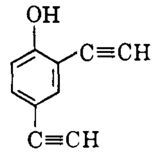
Bridged carbonyl compound from cyclone reaction	A-B	Conditions	Product	Ref.
	Cyclo- pentadiene	200° for 20 min.		208
		Heat, 2 hr.		208
		$C_6H_5NO_2$ and maleic anhydride, boil 1 hr.		208
		200°, 2 hr.		208
	H-H	$C_6H_5NO_2$, reflux 6 hr.		48
	H-H	$C_6H_5NO_2$, reflux 6 hr.		48

reactions with olefins. Table XXXII summarizes the reactions of cyclopentadienones with acetylenes which lose carbon monoxide simultaneously. The acetylenes which have been used include

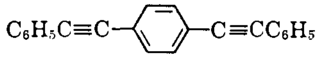
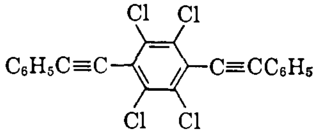
$HC\equiv HC$
$(CH_3)_3CC\equiv CH$
$C_6H_5CH_2CH_2C\equiv CH$
$HOCH_2C\equiv CH$
$HO_2CC\equiv CH$
$C_6H_5C\equiv CH$
$CH_3C\equiv CCO_2H$
$CH_3C\equiv CCO_2C_2H_5$
$HO_2CC\equiv CCO_2H$
$CH_3O_2CC\equiv CCO_2CH_3$
$C_2H_5O_2CC\equiv CCO_2C_2H_5$
$n\text{-}C_4H_9O_2CC\equiv CCO_2C_4H_9\text{-}n$
$C_6H_5C\equiv CCH_3$
$C_6H_5C\equiv CCH_2OH$

$C_6H_5C\equiv CCH(OC_2H_5)_2$
$C_6H_5C\equiv CCHO$
$C_6H_5C\equiv C\underset{\underset{O}{\|}}{C}C_6H_5$
$C_6H_5C\equiv CCN$
$C_6H_5C\equiv CCO_2H$
$C_6H_5C\equiv CCO_2CH_3$
$XC_6H_4C\equiv CCO_2CH_3$
$C_6H_5C\equiv CCO_2C_2H_5$
$C_6H_5C\equiv CBr$
$C_6H_5C\equiv CC_6H_5$
$CH_3HgC\equiv CHgCH_3$
$C_2H_5HgC\equiv CHgC_2H_5$
$C_6H_5HgC\equiv CHgC_6H_5$

Several bisacetylenes have also been used.

$C_6H_5C\equiv CC\equiv CC_6H_5$

Except for diphenylbutadiyne, these bisacetylenes form products from reaction with 2 moles of cyclopentadienone.

Among the more unusual types of acetylenes have been cyclooctyne, which was determined by titration with tetracyclone, and several benzynes which were

Table XXXII
Reactions with Acetylenes

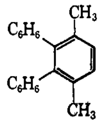
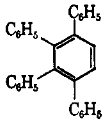
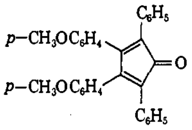
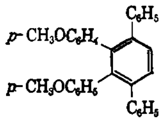
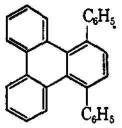
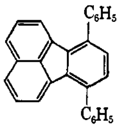
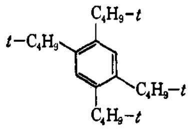
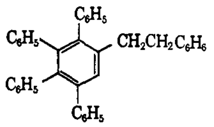
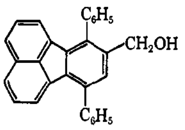
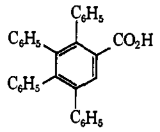
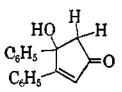
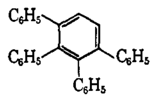
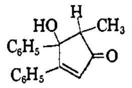
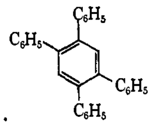
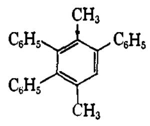
Cyclone	Acetylene	Conditions	Product	Ref.
LXXXIV, $R_1 = R_2 = CH_3$	HC≡CH	o-$Cl_2C_6H_4$, heat (208); C_6H_6, heat (35)		35, 208
III	HC≡CH	Naphthalene, 150–180° (20, 111–113, 116, 119)		20, 111–113, 116, 119, 129, 136
	HC≡CH			208
VII	HC≡CH	o-$Cl_2C_6H_4$, heat for 3 hr.		208
VI	HC≡CH	Phenanthrene, 250–280° for 1 hr.		124
XVII	$(CH_3)_3CC≡CH$	C_6H_6, sealed tube, 250° for 3 hr.		174
III	$C_6H_5CH_2CH_2C≡CH$	p-Cymene, reflux at 180° for 5.5 hr. or dioxane, reflux 204 hr.		163
VI	$HOCH_2≡CH$	140° for 20 min. or o-$Cl_2C_6H_4$, reflux for 4 hr.		43
III	$HO_2CC≡CH$	C_6H_5Br, heat		140
	$C_6H_5C≡CH$	$KHSO_4$, 180–185° for 7.5 hr., then 230–240°		172
	$C_6H_5C≡CH$	5 hr. at 160–170° then distil		38
LXXXIV, $R_1 = R_2 = CH_3$	$C_6H_5C≡CH$	Heat		35

TABLE XXXII (*continued*)

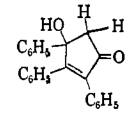
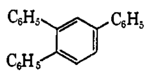
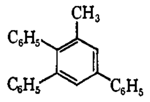
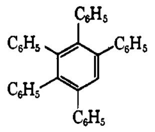
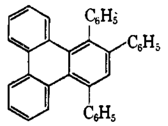
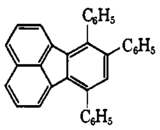
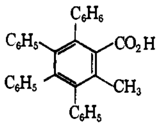
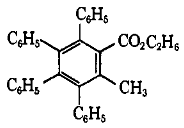
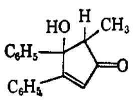
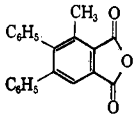
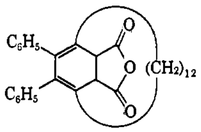
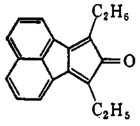
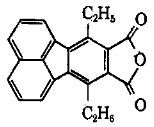
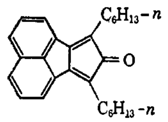
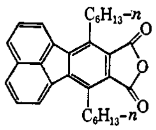
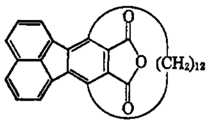
Cyclone	Acetylene	Conditions	Product	Ref.
	$C_6H_5C\equiv CH$	2.5 hr., at 280°		129
CXXI	$C_6H_5C\equiv CH$			129
III	$C_6H_5C\equiv CH$	160° (111–113, 116, 119); *p*-cymene or toluene, reflux (141)		111–113, 116, 119, 129, 136, 141
VII	$C_6H_5C\equiv CH$	Heat or 3 days at room temp.		124
VI	$C_6H_5C\equiv CH$	250–300°		124
III	$CH_3C\equiv CCO_2H$	Sealed tube, 200° for 1 hr.		137
III	$CH_3C\equiv CCO_2C_2H_5$	Sealed tube, 200° for 1 hr.		137
	$HO_2CC\equiv CCO_2H$	160–170° then 190° for 5 min.		38
CLXVI	$HO_2CC\equiv CCO_2H$	225° for 3 min.		44
	$HO_2CC\equiv CCO_2H$	220–225° for 3 min.		43
	$HO_2CC\equiv CCO_2H$	220–225° for 3 min.		43
CCXV	$HO_2CC\equiv CCO_2H$	225° for 3 min.		44

TABLE XXXII (*continued*)

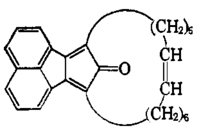
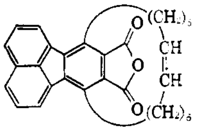
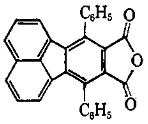
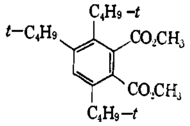
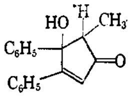
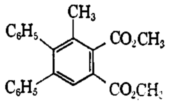
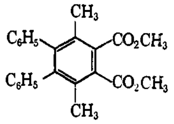
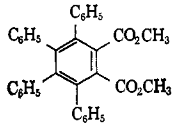
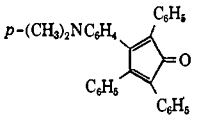
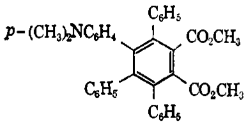
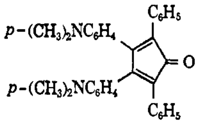
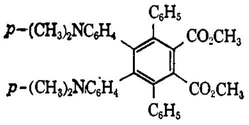
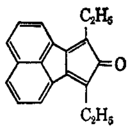
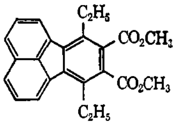
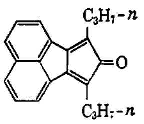
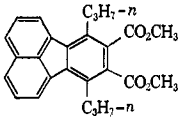
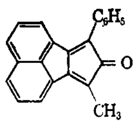
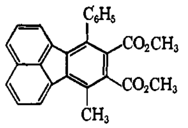
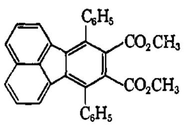
Cyclone	Acetylene	Conditions	Product	Ref.
	$HO_2CC{\equiv}CCO_2H$	225° for 3 min.		44
VI	$HO_2CC{\equiv}CO_2H$			43
LVII	$CH_3O_2CC{\equiv}CO_2CH_3$	200° for 10 min.		174
	$CH_3O_2CC{\equiv}CCO_2CH_3$	Distillation		38
LXXXIV $R_1 = R_2 = CH_3$	$CH_3O_2CC{\equiv}CCO_2CH_3$	Heat, 10 min.		35
III	$CH_3O_2CC{\equiv}CCO_2CH_3$	Heat (31, 137); *o*-$Cl_2C_6H_4$ reflux (153); C_6H_6, reflux 9–10 hr. (57)		31, 57, 137, 153
	$CH_3O_2CC{\equiv}CCO_2CH_3$	C_6H_6, reflux for 11 hr.		57
	$CH_3O_2CC{\equiv}CCO_2CH_3$	C_6H_6, reflux for 3 hr.		57
	$CH_3O_2CC{\equiv}CCO_2CH_3$	20 min. at 140° or 4 hr. reflux *o*-$Cl_2C_6H_4$		43
	$CH_3O_2CC{\equiv}CCO_2CH_3$	20 min. at 140° or 4 hr. reflux *o*-$Cl_2C_6H_4$		43
	$CH_3O_2CC{\equiv}CCO_2CH_3$	20 min. at 140° or 4 hr. reflux in *o*-$Cl_2C_6H_4$		43
VI	$CH_3O_2CC{\equiv}CCO_2CH_3$	240°		122

TABLE XXXII (*continued*)

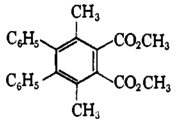
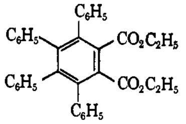
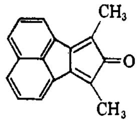
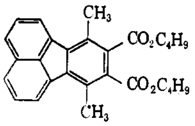
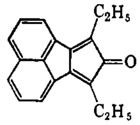
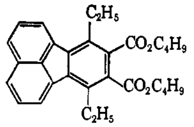
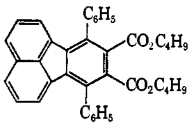
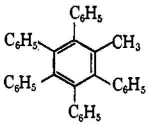
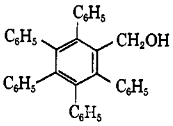
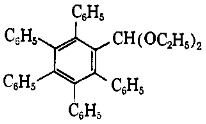
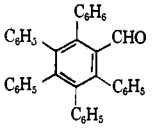
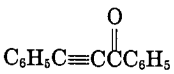
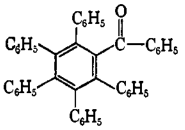
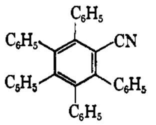
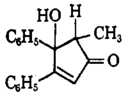
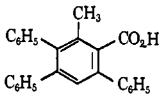
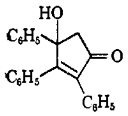
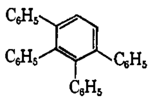
Cyclone	Acetylene	Conditions	Product	Ref.
LXXXIV, $R_1 = R_2 = CH_3$	$C_2H_5O_2CC{\equiv}CCO_2C_2H_5$	Heat, 10 min.		35
III	$C_2H_5O_2CC{\equiv}CCO_2C_2H_5$	Sealed tube, 300–310° for 2 hr. (31); 130–160° (137)		31, 137
	$C_4H_9O_2CC{\equiv}CCO_2C_4H_9$	20 min. at 140° or 4 hr. reflux in o-$Cl_2C_6H_4$		43
	$C_4H_9O_2CC{\equiv}CCO_2C_4H_9$	20 min. at 140° or 4 hr. reflux in o-$Cl_2C_6H_4$		43
VI	$C_4H_9O_2CC{\equiv}CCO_2C_4H_9$	20 min. at 140° or 4 hr. reflux in o-$Cl_2C_6H_4$		43
III	$C_6H_5C{\equiv}CCH_3$	*p*-Cymene, heat		141
III	$C_6H_5C{\equiv}CCH_2OH$	*p*-Cymene, reflux		141
III	$C_6H_5C{\equiv}CCH(OC_2H_5)_2$	$Cl_3C_6H_3$ at 200°		111–113, 116, 119
III	$C_6H_5C{\equiv}CCHO$	*p*-Cymene, reflux (141)		136, 141
III	 $C_6H_5C{\equiv}C\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5$	Sealed tube, 195° for 5 min.		31
III	$C_6H_5C{\equiv}CCN$			136
	$C_6H_5C{\equiv}CCO_2H$	50 min. at 160–170°		38
	$C_6H_5C{\equiv}CCO_2H$			129

TABLE XXXII (*continued*)

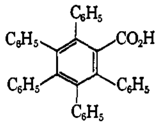
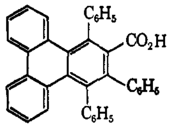
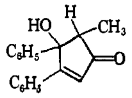
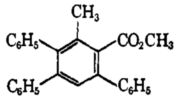
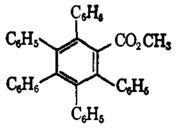
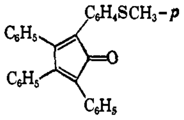
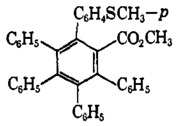
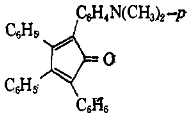
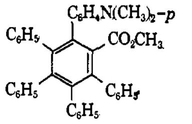
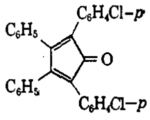
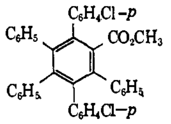
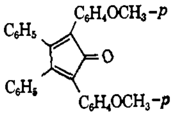
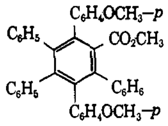
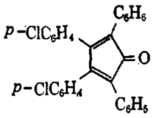
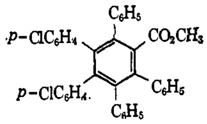
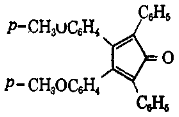
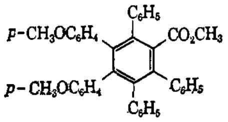
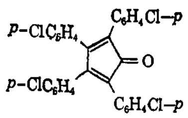
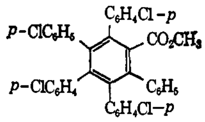
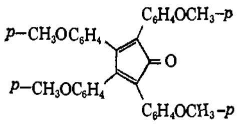
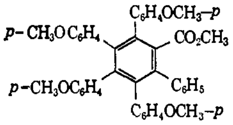
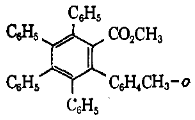
Cyclone	Acetylene	Conditions	Product	Ref.
III	$C_6H_5C\equiv CCO_2H$	190° (137); *p*-cymene or toluene reflux (141)		136, 137, 141
VII	$C_6H_5C\equiv CCO_2H$	150–170°		124
	$C_6H_5C\equiv CCO_2CH_3$	Distilled		38
III	$C_6H_5C\equiv CCO_2CH_3$	170–175° for 0.5 hr. and then at 190° (137); *p*-cymene, reflux (141); phenylcyclohexane, 170° (61, 211, 242)		61, 137, 141, 211, 242
	$C_6H_5C\equiv CCO_2CH_3$	*p*-Cymene, reflux for 16.5 hr.		203[a]
	$C_6H_5C\equiv CCO_2CH_3$	*p*-Cymene, reflux overnight		157[b]
	$C_6H_5C\equiv CCO_2CH_3$	Phenylcyclohexane, 176°		242
		Same as above		242
		Same as above		242
		Same as above		242
		Same as above		242
		Same as above		242
III	*o*-$CH_3C_6H_4C\equiv CO_2CH_3$	Same as above		211

TABLE XXXII (*continued*)

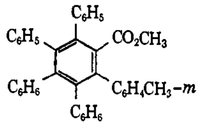
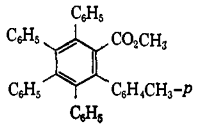
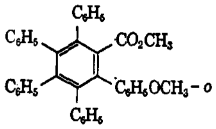
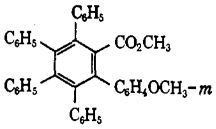
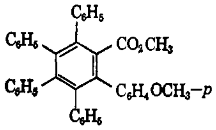
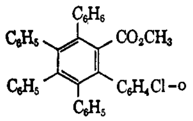
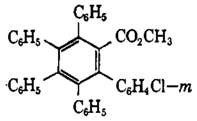
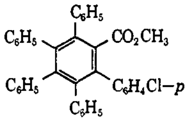
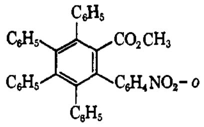
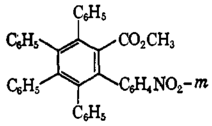
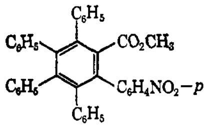
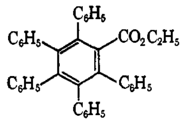
Cyclone	Acetylene	Conditions	Product	Ref.
III	$m\text{-}CH_3C_6H_4C\equiv CO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$p\text{-}CH_3C_6H_4C\equiv CO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$o\text{-}CH_3OC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$m\text{-}CH_3OC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$p\text{-}CH_3OC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$o\text{-}ClC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$m\text{-}ClC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$p\text{-}ClC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$o\text{-}O_2NC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$m\text{-}O_2NC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$p\text{-}O_2NC_6H_4C\equiv CCO_2CH_3$	Phenylcyclohexane, 175° (61); kinetics (211)		61, 211
III	$C_6H_5C\equiv CCO_2C_2H_5$	$C_6H_5NO_2$, boil		111–113, 116, 119

TABLE XXXII (*continued*)

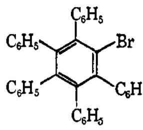
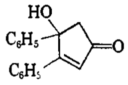
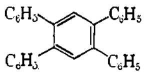
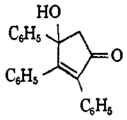
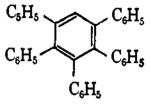
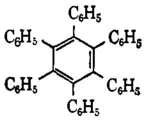
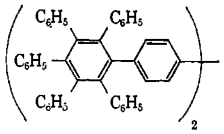
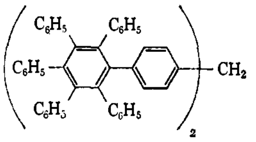
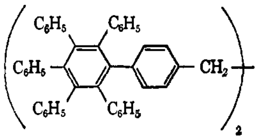
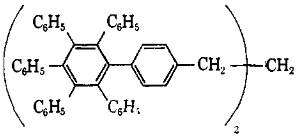
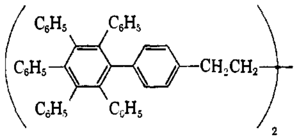
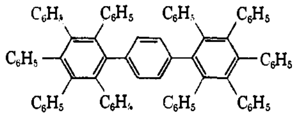
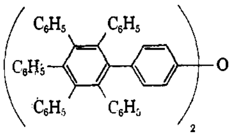
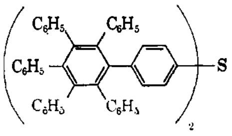
Cyclone	Acetylene	Conditions	Product	Ref.
III	$C_6H_5C\equiv CBr$	Nitrogen, 160°		135
	$C_6H_5C\equiv CC_6H_5$	275°, 1 hr. (129)		128, 129
	$C_6H_5C\equiv CC_6H_5$	280° (129)		128, 129
III	$C_6H_5C\equiv CC_6H_5$	225–315° (129); 225–325° (111, 112, 113, 116, 119, 153)		111–113, 116, 119, 128, 129, 136, 153
IXa	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr. (225)		152, 225
IXb	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr. (225)		152, 225
IXe	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr.		224
IXf	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr.		224
IXg	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr.		224
IXh	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr.		224
IXc	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr. (152)		152, 225
IXd	$C_6H_5C\equiv CC_6H_5$	Heat, 1 hr. (152)		152, 225

TABLE XXXII (*continued*)

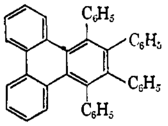
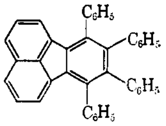
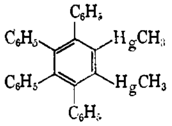
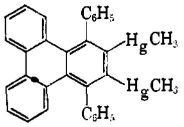
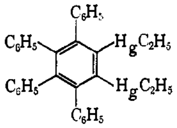
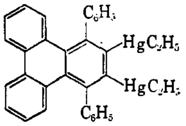
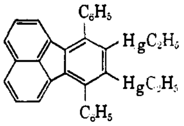
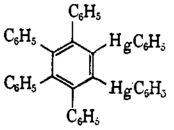
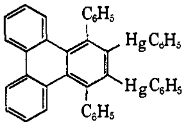
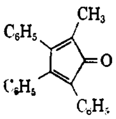
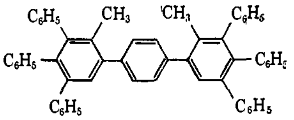
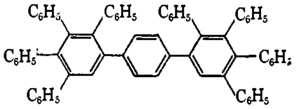
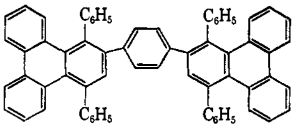
Cyclone	Acetylene	Conditions	Product	Ref.
VII	$C_6H_5C{\equiv}CC_6H_5$	180 or 230° for 5 min.		124
VI	$C_6H_5C{\equiv}CC_6H_5$	230–300° then 60–70° in H_2SO_4 (111, 112, 113, 116, 119); 250–270° (124)		111–113, 116, 119, 124
III	$CH_3HgC{\equiv}CHgCH_3$	Sealed tube, C_6H_6, 112–115° for 10 hr.		8
VII	$CH_3HgC{\equiv}CHgCH_3$	Sealed tube, C_6H_6 for 4 hr.		8
III	$C_2H_5HgC{\equiv}CHgC_2H_5$	Sealed tube, C_6H_6, 112–115° for 15 hr.		8
VII	$C_2H_5HgC{\equiv}CHgC_2H_5$	Sealed tube, C_6H_6, 112–115° for 15 hr.		8
VI	$C_2H_5HgC{\equiv}CHgC_2H_5$			8
III	$C_6H_5HgC{\equiv}CHgC_6H_5$	Sealed tube, C_6H_6, 112–115°		8
VII	$C_6H_5HgC{\equiv}CHgC_6H_5$	Sealed tube, C_6H_6 for 7 hr.		8
	*p*-Diethynylbenzene	β-Decalol, boil		240
III	Same as above			240
VII	Same as above			240

TABLE XXXII (*continued*)

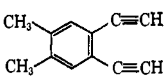
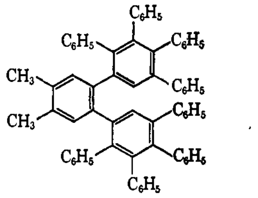
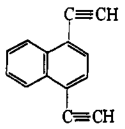
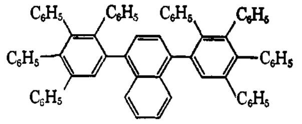
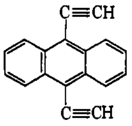
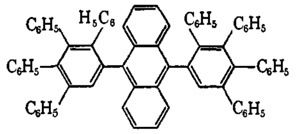
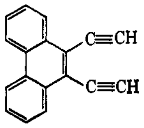
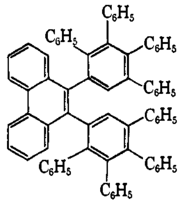
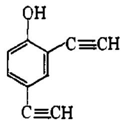
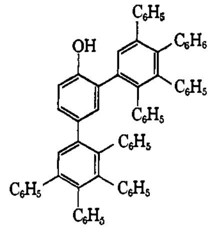
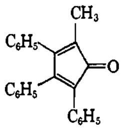
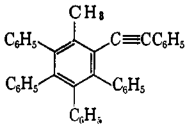
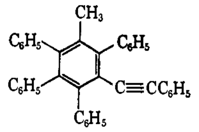
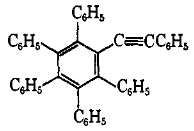
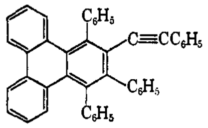
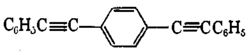
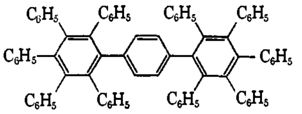
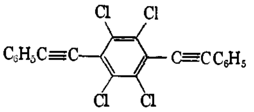
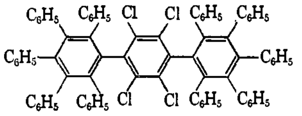
Cyclone	Acetylene	Conditions	Product	Ref.
III		β-Decalol, boil		240
III		β-Decalol, boil		240
III		β-Decalol, boil		240
III		β-Decalol, boil		240
III		β-Decalol, boil		240
	$C_6H_5C{\equiv}CC{\equiv}CC_6H_5$	Heat 20–30 min.	 or 	240
III	$C_6H_5C{\equiv}CC{\equiv}CC_6H_5$	240–250° under nitrogen		135
VII	$C_6H_5C{\equiv}CC{\equiv}CC_6H_5$	Heat, 20–30 min.		240
III		β-Decalol, boil		240
III		β-Decalol, boil		240

TABLE XXXII (*continued*)

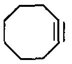
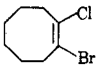
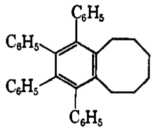
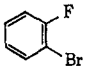
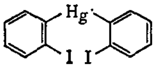
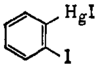
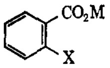
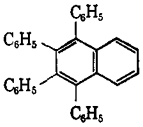
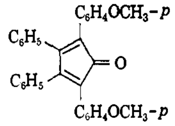
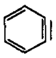
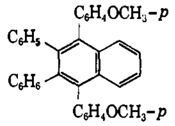
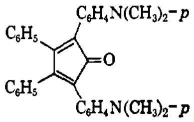
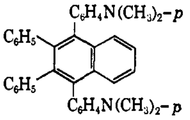
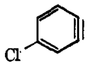
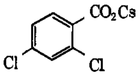
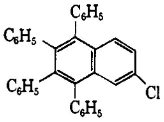
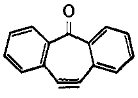
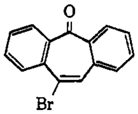
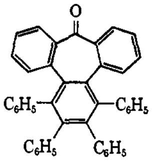
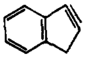
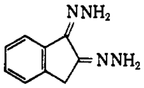
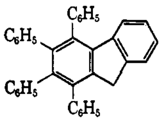
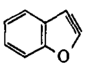
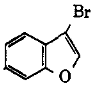
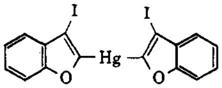
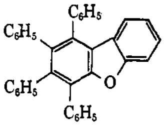
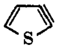
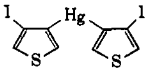
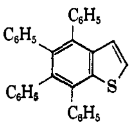
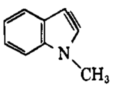
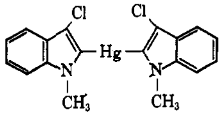
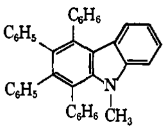
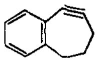
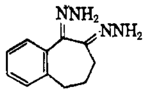
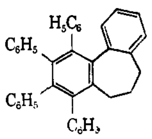
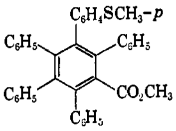
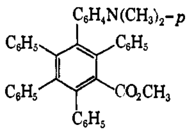
Cyclone	Acetylene	Conditions	Product	Ref.
III		 + Li(Hg)$_x$ $(C_2H_5)_2O$		282
III		 + Mg, THF (281)  (277, 280) , $h\nu$ (280)  (216) M = K, Ag, Cs, Na X = Br, Cl, I		69, 151, 153, 216, 277, 280, 281
				69
				69
III		Benzyne from 		216
III		 + KOC(CH$_3$)$_3$ + ether		272
III		 + oxidizing agent		277, 278, 279
III		 + alkoxide (278)  + heat (277,278,279)		277, 278, 279
III				277, 278, 279, 283
III		 + heat		279

Table XXXII (*continued*)

Cyclone	Acetylene	Conditions	Product	Ref.
III		 + oxidizing agent		279



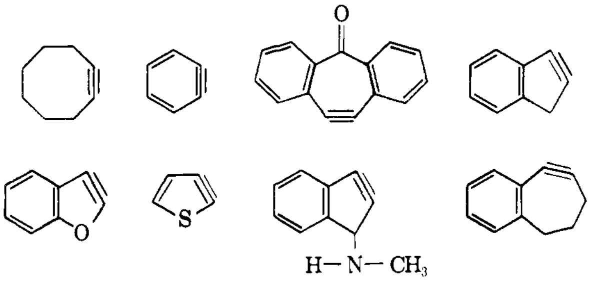
i



ii

[a] Authors uncertain if product is that listed, or i, or a mixture (m.p. 226.5–229.3°). [b] Authors uncertain if product is that listed, or ii, or a mixture (m.p. 235–239°).

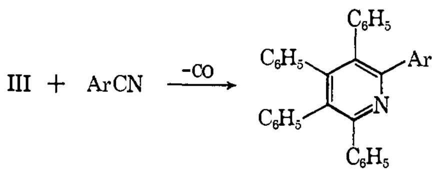
produced *in situ* (279, 282) and trapped with tetracyclone. Recently 1-aminobenzotriazole has been oxidized in benzene solution with lead tetraacetate to yield benzyne. The oxidation was run in the presence of tetracyclone, resulting in the formation of 1,2,3,4-tetraphenylnaphthalene (85a). Similarly the reaction using 1-amino-5-methylbenzotriazole gave 6-methyl-1,2,3,4-tetraphenylnaphthalene (85a).



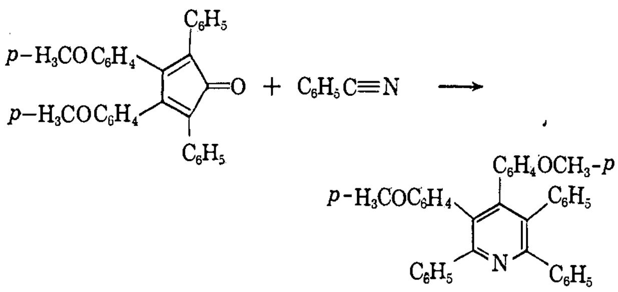
Kinetic studies of the reaction of tetracyclone with substituted methyl phenylpropiolates have shown that the reaction is accelerated by electron-withdrawing groups in the dienophile (61, 211).

c. Reaction with Nitriles

Tetracyclone has been treated with aromatic nitriles to yield tetraphenylarylpyridines (118, 135, 206, 235, 236).



In a similar manner, 3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopentadienone reacted with benzonitrile to yield 3,4-bis(4-methoxyphenyl)-2,5,6-triphenylpyridine (232).



When pyridinenitriles were used, bipyridines resulted (186), *e.g.*

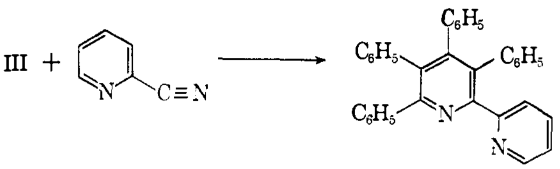
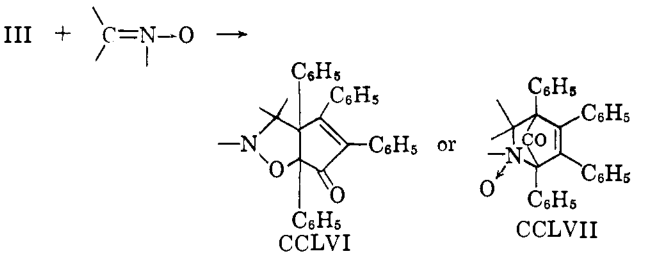


Table XXXIII summarizes these reactions. Kinetic studies have been run for the reaction between tetracyclone and benzonitrile, *o*-chlorobenzonitrile, and 2-cyanopyridine (187). Activation energies of 28.5, 26.9, and 24.4 kcal./mole, respectively, were obtained.

d. Reactions with Nitrones

Several nitrones have been allowed to react with tetracyclone (79, 80).

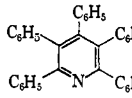
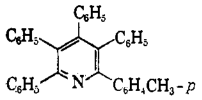
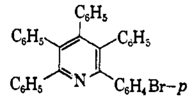
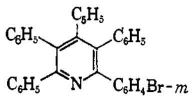
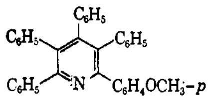
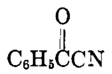
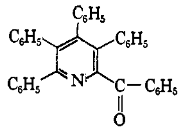
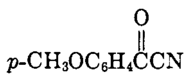
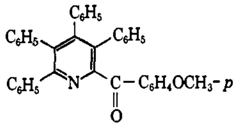
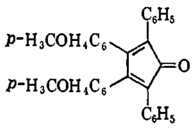
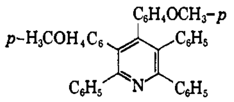
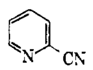
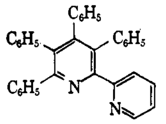
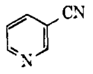
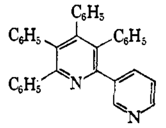
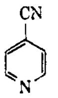
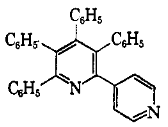


CCLVI CCLVII

Originally (80) no decision as to whether the product is CCLVI or CCLVII could be made. However, spectroscopic evidence favored CCLVII (79), and this re-

TABLE XXXIII

REACTIONS WITH NITRILES

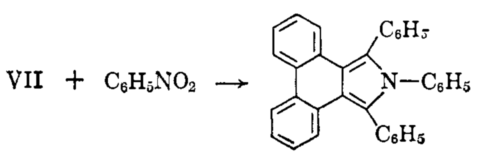
Cyclone	Nitrile	Conditions	Product	Ref.
III	$C_6H_5C{\equiv}N$	320–340° for 30–40 hr. or 275–300° for 6 hr. (135); 320–340° for 30–40 hr. (118); 200–312° for 60 hr. (236)		118,[a] 135,[b,c] 206, 236
III	p-$CH_3C_6H_4CN$	230–280° for 47 hr.		236
III	p-BrC_6H_4CN	230–260° for 34 hr.		236
III	m-BrC_6H_4CN	250–300° for 100 hr.		236
III	p-$CH_3OC_6H_4CN$	250–270° for 36 hr.		236
III	 $C_6H_5\overset{\overset{O}{\|}}{C}CN$	235° (235); 250–270° for 13 hr. (236)		235, 236
III	 p-$CH_3OC_6H_4\overset{\overset{O}{\|}}{C}CN$	235° for 50 min.		235
	C_6H_5—CN	270–300° for 10 hr. or 300–330°		232
III		215°		186
III		215°		186
III		215°		186

[a] CLXXVII may also be used. [b] Isolated as perchlorate salt. [c] Perchlorate salt converted to free base.

action was contrasted to that of cyclopentadiene with nitrones which yields adducts of type CCLVI (219). Table XXXIV lists the nitrones used.

e. Reactions with Nitro and Nitroso Compounds

Reactions with arylnitro and nitroso compounds lead to heterocyclic products whose structures would not be easily predicted. With nitrobenzene an N-phenylpyrrole is formed (117, 130).



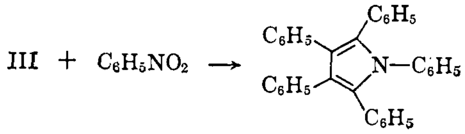


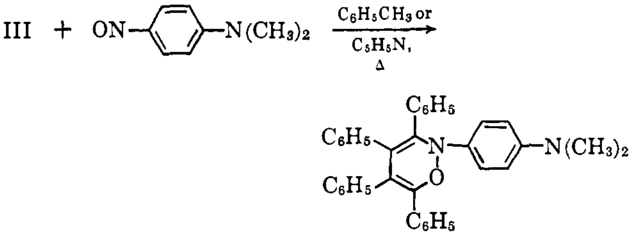
TABLE XXXIV

REACTIONS WITH NITRONES

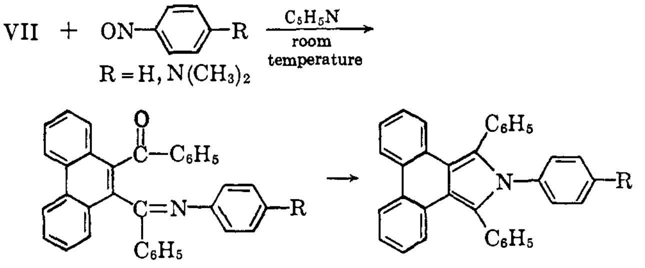
Nitrone	Conditions	Ref.
Dimer of 2,3,4,5-tetrahydropyridine	10 min. at 160–170° (80)	79,[a] 80
4,5,5-Trimethyl-Δ^1-pyrroline N-oxide	1 hr. at 100° (80)	79,[a] 80
β-Phenylisobenzaldoxime	5 hr. at 130°	79,[a] 80
β-Phenylisobenzaldoxime	24 hr. at 140°	79,[a] 80
β-Phenyliso-*p*-methoxybenzaldoxime	24 hr. at 140°	79,[a] 80
β-Phenyliso-*m*-nitrobenzaldoxime	24 hr. at 130°	79,[a] 80

[a] Structure CCLVII is the preferred structure.

A nitroso compound can yield either a 1,2-oxazine upon heating in pyridine or toluene (117, 130), *e.g.*



or a mono Schiff base of a diketone (130, 132) which could be converted to an N-phenylpyrrole.

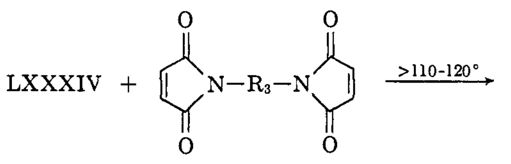


With butadiene and aromatic nitroso compounds, only 3,6-dihydro-1,2-oxazines resulted and kinetics of this reaction have been studied (170).

The mechanism of conversion of the Diels–Alder adducts to a pyrrole appears not to have been studied, although the course of the reaction appears challenging. Table XXXV summarizes these reactions.

f. Diels–Alder Polymers

Using 2,5-dialkyl-3,5-diphenylcyclopentadienones, several Diels–Alder polymers have been prepared by the use of bismaleimides (198). The reaction can be written as



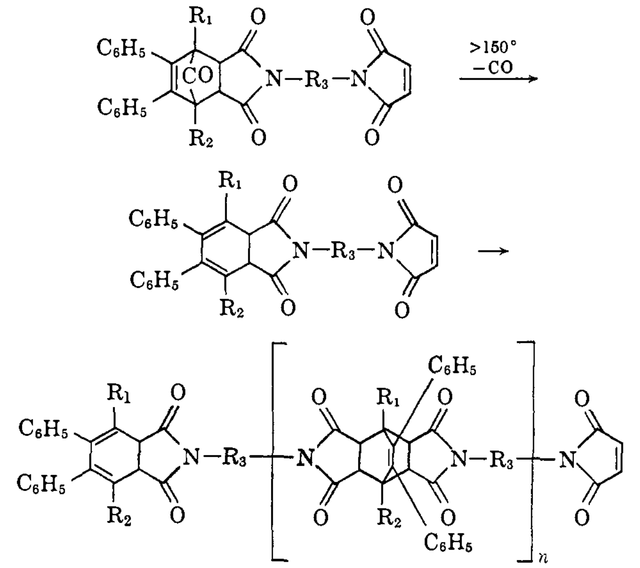
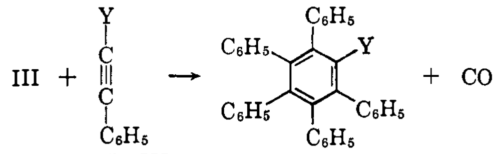


Table XXXVI lists the various polymers that have been prepared. The conditions used were either a reflux for 30 min. in α-chloronaphthalene or for 72 hr. in bromobenzene.

These polymers may prove to be quite useful since they are alleged to be thermoplastic with high softening points, high strengths, and good electrical properties (198).

g. Mechanism of the Diels–Alder Reaction of Cyclopentadienones

Several attempts have been made to elucidate the mechanism of the Diels–Alder reaction of cyclopentadienones by studying electronic effects. The relative rates of the reaction between tetracyclone (III) and substituted acetylenes (CCLVIII) were determined by observing the length of time required for cessation of the evolution of carbon monoxide (141). It was found



CCLVIII

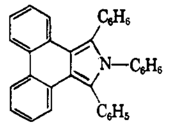
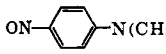
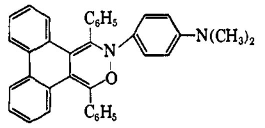
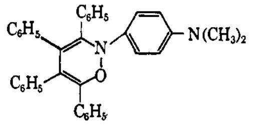
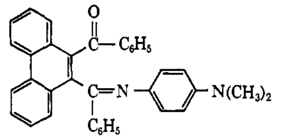
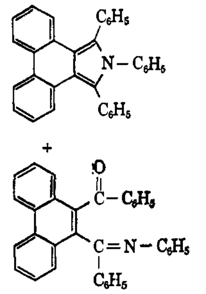
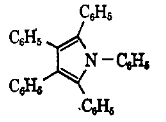
Y=H, CH_3, CH_2OH, CO_2H, CO_2CH_3, CHO

that the reaction times decreased in the order Y = CH_3, CH_2OH, CO_2CH_3, and CHO, which is the same order as increasing dipole moments in the series C_6H_5Y (141). The reactions with phenylacetylene and phenylpropiolic acid were felt to be complicated by the small size of the hydrogen atom in the former and by simultaneous decarboxylation of the latter. Thus, it was shown that electron-withdrawing substituents in the dienophile accelerate the reaction.

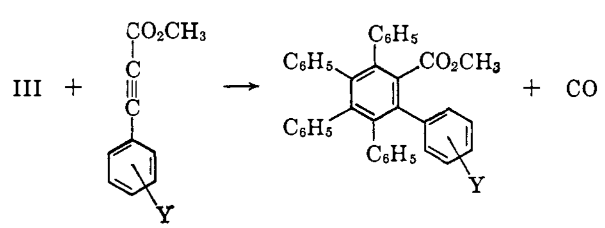
A more quantitative study put this hypothesis on a firmer foundation. The reaction between tetracyclone (III) and substituted methyl phenylpropiolates (CC-

TABLE XXXV

REACTIONS OF CYCLOPENTADIENONES WITH NITRO AND NITROSO COMPOUNDS

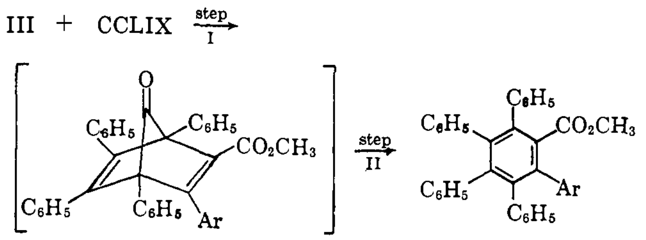
Cyclone	Nitro or nitroso	Conditions	Product	Ref.
VII	$C_6H_5NO_2$	Heat 1 hr. (117); heat 5–7 hr. (130)		117, 130
VII		C_5H_5N, heat		117
III	Same as above	$C_6H_5CH_3$, inert atm., heat 6–10 hr. (117); C_5H_5N, heat 6 hr. (130)		117, 130
VII	Same as above	C_5H_5N, nitrogen atm., room temp., 5–10 min.		132
VII	C_6H_5NO	C_5H_5N		130
III	$C_6H_5NO_2$	$C_6H_5NO_2$		130

LIX) was investigated and the reaction rates determined (61, 211). In the first investigation (61), it was demonstrated that the reaction possessed the characteristics of a Diels–Alder reaction. In particular the reaction was second order to 94% completion. It also exhibited typical energies of activation; namely, 18.2 and 18.9 kcal. mole^{-1} for methyl *o*-chlorophenylpropiolate and methyl *p*-chlorophenylpropiolate, respectively. It has been demonstrated that the rates are unaffected by increasing the surface area which rules out step II as the rate-determining step (211).



CCLIX

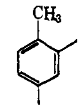
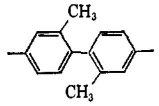
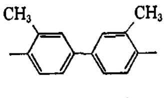
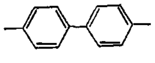
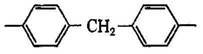
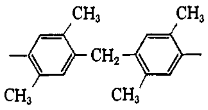
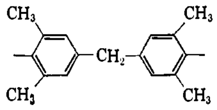
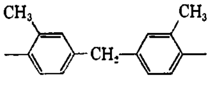
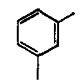
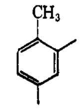
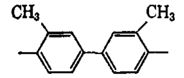
Y = *o*-CH_3, *m*-CH_3, *p*-CH_3, *o*-OCH_3, *m*-OCH_3, *p*-OCH_3, *o*-Cl, *m*-Cl, *p*-Cl, *o*-NO_2, *m*-NO_2, *p*-NO_2



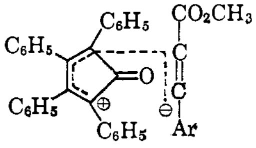
An analysis of the data obtained showed that a plot of log *k vs.* log K/K_0, where *k* is the rate constant for the reaction and K/K_0 the relative apparent ionization constant for the substituted phenylpropiolic acids in 50% aqueous ethanol, had a slope of +1.10 (61). Since a plot of log K/K_0 *vs.* Hammett's σ-values had a slope of +0.69, the data illustrated quantitatively the hypothesis that electron-withdrawing substituents in the dienophile accelerate the reaction while electron-donating substituents decelerate it.

Table XXXVI

Diels–Alder Polymers

R_1	R_2	R_3
CH_3	CH_3	$-(CH_2)_6-$
CH_3	CH_3	
CH_3	CH_3	
CH_3	CH_3	
CH_3	CH_3	
CH_3	CH_3	
CH_3	CH_3	
CH_3	CH_3	
CH_3	CH_3	
CH_3	$n-C_3H_7$	$-(CH_2)_6-$
CH_3	$n-C_3H_7$	
CH_3	$n-C_3H_7$	
CH_3	$n-C_3H_7$	

In an extended study (211) further activation energies were determined (Table XXXVII). In addition it was noted that the data have a better fit for a plot of log k *vs.* σ^- illustrating that the transition state has some ionic character about it, structure CCLX making some contribution to the over-all electronic character.



CCLX

An attempt was made to see if the inverse of the initial hypothesis was valid; that is, whether electron-withdrawing substituents in the diene would decelerate

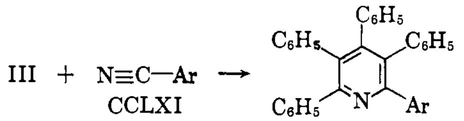
Table XXXVII

Activation Energies for the Reaction between III and CCLIX (211)

Y	E_a, kcal. mole^{-1}	Y	E_a, kcal. mole^{-1}
o-CH_3	19.0	H	20.0
p-CH_3	20.2	o-OCH_3	16.3
o-Cl	18.2	o-NO_2	19.0
p-Cl	18.9	p-NO_2	18.4

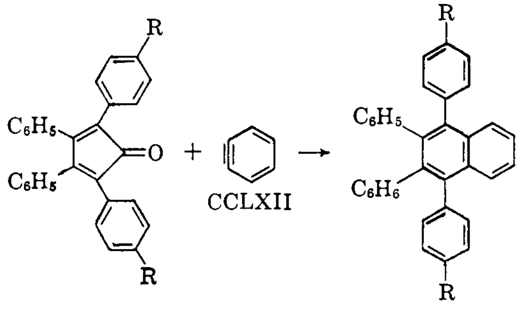
the reaction and electron-donating substituents accelerate it. The data illustrated that there exist subtleties in the electronic character of tetracyclone (III) which make such a simplification untenable (242).

The reaction between tetracyclone (III) and aromatic nitriles (CCLXI) has also been investigated as previously mentioned (187, 235, 236).



A detailed study in which kinetic rate constants were determined indicates that electron-withdrawing substituents in the nitrile accelerate the reaction (187). In addition, the energies of activation were evaluated as 28.5, 26.9, and 24.4 kcal. mole^{-1} for benzonitrile, o-chlorobenzonitrile, and 2-cyanopyridine, respectively (187). This led to the conclusion that the mechanism for the reaction is similar to that accepted for the Diels–Alder reaction (187). It is interesting to note the inherently higher activation energies for the carbon–nitrogen triple bond as compared to the carbon–carbon triple bond.

The reaction between benzyne (CCLXII) and substituted tetracyclones (CCLXIII) was investigated by determining the yields of the adducts CCLXIV (69). It was noted that CCLXIIIb was the best trapping agent, giving a 79% yield (69).



CCLXIIIa, R=H
b, $R=OCH_3$
c, $R=N(CH_3)_2$

CCLXIV

H. REACTIONS OF CYCLOPENTADIENONES WITH METAL CARBONYLS

Outlined in another section is the synthesis of cyclopentadienone adducts by the reaction between an

TABLE XXXVIII

ARYLATED CYCLOPENTADIENONE–METAL CARBONYL π-COMPLEXES

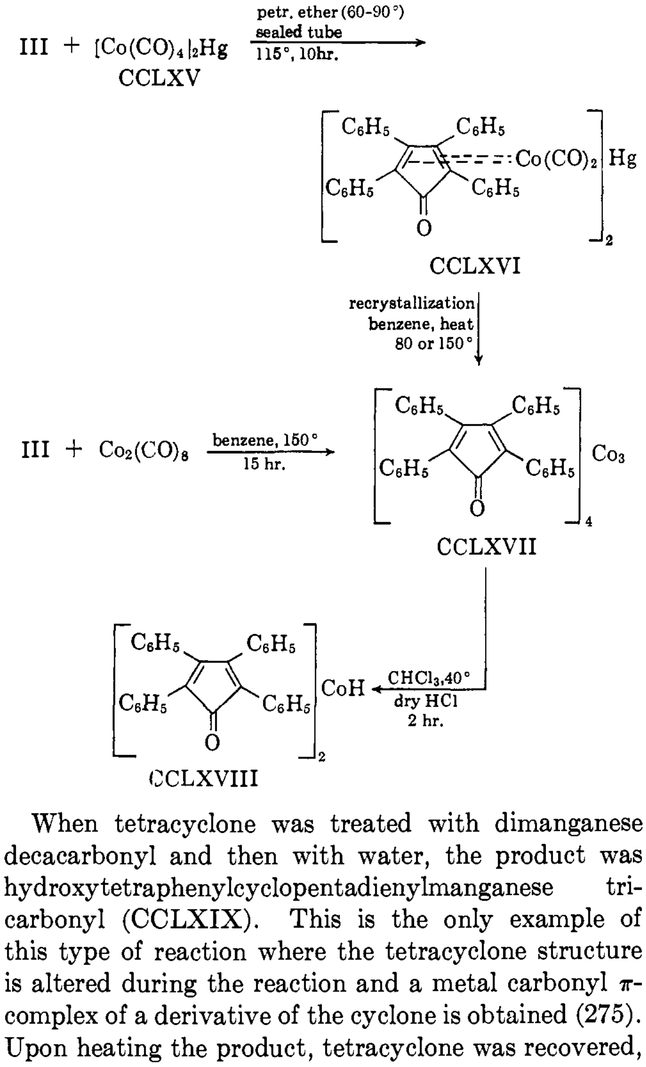
Cyclone							
R_1	R_2	R_3	R_4	Metal carbonyl	Conditions	Products	Ref.
CF_3	CF_3	CF_3	CF_3	$Fe(CO)_5$	[a]	$C_9F_{12}OFe(CO)_3$	108
CH_3	C_6H_5	C_6H_5	CH_3[b]	$Fe(CO)_5$	Benzene, autoclave, 190°, 20 hr. (275); benzene, autoclave, 185°, 15 hr. (262)	$C_{19}H_{16}OFe(CO)_3$	262, 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$[Fe(CO)_4]_3$	[a]	$C_{29}H_{20}OFe(CO)_3$	253
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$[Fe(CO)_4]_3$	Benzene, room temp., 3 hr., N_2; benzene, 1 hr., 40–50°	$C_{29}H_{20}OFe(CO)_3$	262
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$[Fe(CO)_4]_3$	Toluene, 1 hr., 90–100° (262); toluene, 1 hr., 95–100° (275)	$C_{29}H_{20}OFe(CO)_3$	262, 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Fe(CO)_5$	Benzene, reflux 2 hr., light	$C_{29}H_{20}OFe(CO)_3$	255
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Fe(CO)_5$	Sealed tube, xylene, 150°, 2 hr., N_2	$C_{29}H_{20}OFe(CO)_3$	262
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Fe(CO)_5$	Xylene or benzene, 150°, 3 hr., sealed tube	$C_{29}H_{20}OFe(CO)_3$	275
C_6H_5	*p*-Cl-C_5H_5	*p*-Cl-C_6H_5	C_6H_5	$Fe(CO)_5$	Petroleum ether (60–90°), sealed tube, 130–140°, 15 hr.	$C_{29}H_{18}Cl_2OFe(CO)_3$	262, 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Fe_2(CO)_9$	Benzene, 80°, 3 hr.	$C_{29}H_{16}Cl_4OFe(CO)_3$	262
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Fe_2(CO)_9$	Benzene, room temp., 5 hr., N_2; or 30–40° for 1 hr.	$C_{29}H_{20}OFe(CO)_3$	275
p-ClC_6H_5				$Fe_2(CO)_9$	Benzene, 75°	$C_{29}H_{16}Cl_4OFe(CO)_3$	275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Co_2(CO)_8$	Benzene, 15 hr., 150°, sealed tube (272); 17 hr., 160° (262)	$[C_{29}H_{20}O]_4Co_3$	262,[c] 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$[Co(CO)_4]_2Hg$	Petroleum ether, sealed tube, 10 hr., 115° (262,[c] 275); sealed tube, benzene, 160–170°, 17 hr. (262[c])	$[C_{29}H_{20}OCo(CO)_2]_2Hg$	262,[c] 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Cr(CO)_6$	Benzene, sealed tube, 175°, 60–70 hr.; benzene[a] (262[a])	$[C_{29}H_{20}O]_4Cr_3$	262
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Cr(CO)_6$	2,2,4-Trimethylpentane, reflux, N_2, 80 hr.	$C_{29}H_{20}OCr(CO)_3$	81
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Mn_2(CO)_{10}$	Benzene, sealed tube, 15 hr., 150° (275); ligroin, sealed tube, 150° (262[c])	$C_{29}H_{20}OHMn(CO)_3$	262,[c] 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$Mo(CO)_6$	Benzene, sealed tube, 3 days, 160–165° (275); benzene, sealed tube, 160–165°, 40 hr. (262)	$(C_{29}H_{20}O)_2Mo(CO)_2$	262, 275
C_6H_5	C_6H_5	C_6H_5	C_6H_5	$(C_6H_5)_3SnMn(CO)_5$	180–190°, 4 hr., N_2	$C_{29}H_{20}OMn(CO)_3Sn(C_6H_5)_3$	160
Phencyclone				$Fe_2(CO)_9$	Benzene, reflux, 1 hr.	$C_{29}H_{18}OFe(CO)_3$	275
Tetracyclone anil				$Fe(CO)_5$	Xylene, 170–180°, 16 hr., sealed tube (275); 15 hr. (262)	$C_{29}H_{20}NC_6H_4N(CH_3)_2Fe(CO)_3$ (CCLXXI)	262, 275
Phencyclone				$Fe(CO)_9$	Benzene, 80°, 3 hr.	$C_{29}H_{18}OFe(CO)_3$	262

[a] Conditions not given. [b] Cyclopentadienone is a dimer. [c] Structure of product not given.

acetylene and a metal carbonyl (177, 200). In this section the formation of these adducts by the reaction of a cyclopentadienone directly with a metal carbonyl is discussed. Indeed, the adducts prepared by the latter procedure have served as proofs of structure for the compounds prepared from the acetylenes.

The cyclopentadienones which have been subjected to the reaction with metal carbonyls are: tetrakis-(trifluoromethyl)-, 2,5-dimethyl-3,4-diphenyl-, tetraphenyl-, 2,5-diphenyl-3,4-bis(*p*-chlorophenyl)-, 2,3,4,5-tetrakis(*p*-chlorophenyl)cyclopentadienones, and phencyclone. The metal carbonyls which have been employed are: $Fe(CO)_5$, $[Fe(CO)_4]_3$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $[Co(CO)_4]_2Hg$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, and $[C_6H_5]_3SnMn(CO)_5$ (see Table XXXVIII for specific examples). Few generalizations are possible from the scanty data; however, it appears that the metal carbonyls may be divided into those requiring temperatures above 100° and those requiring temperatures below 100°. A tentative assumption that electron-withdrawing groups slow the reaction may be inferred from the experiments with dichloro- and tetrachlorotetracyclones whose syntheses were carried out at progressively higher temperatures.

Treatment of tetracyclone with bis(cobalt tetracarbonyl)mercury (CCLXV) afforded a nearly quantitative yield of the π-complex CCLXVI (262, 275), which upon recrystallization from benzene and heating at 80 or 150° produced (tetracyclone)$_4Co_3$ (CCLXVII) (275). This compound (CCLXVII) could be prepared directly by treatment of tetracyclone with dicobalt octacarbonyl (262, 275). When CCLXVII in chloroform was heated at 40° in the presence of dry hydrogen chloride for 2 hr. a new cobalt π-complex was formed, namely (tetracyclone)$_2$CoH (CCLXVIII) (275).



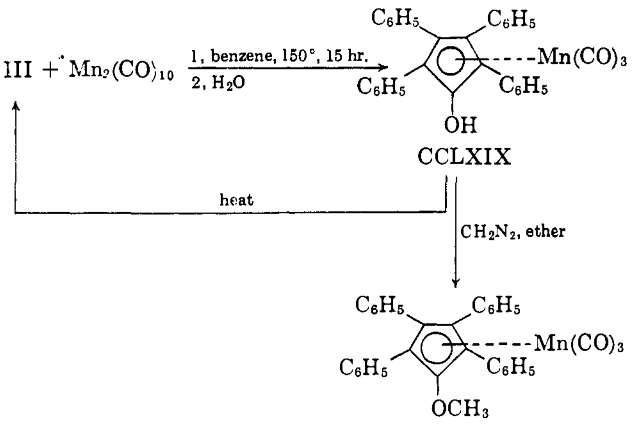
CCLXV

CCLXVI

CCLXVII

CCLXVIII

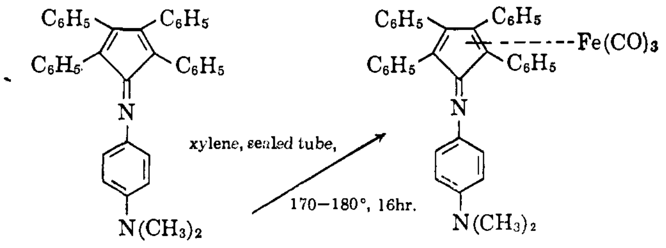
When tetracyclone was treated with dimanganese decacarbonyl and then with water, the product was hydroxytetraphenylcyclopentadienylmanganese tricarbonyl (CCLXIX). This is the only example of this type of reaction where the tetracyclone structure is altered during the reaction and a metal carbonyl π-complex of a derivative of the cyclone is obtained (275). Upon heating the product, tetracyclone was recovered, while treatment of the product with diazomethane in ether afforded methoxytetraphenylcyclopentadienylmanganese tricarbonyl (CCLXX).



CCLXIX

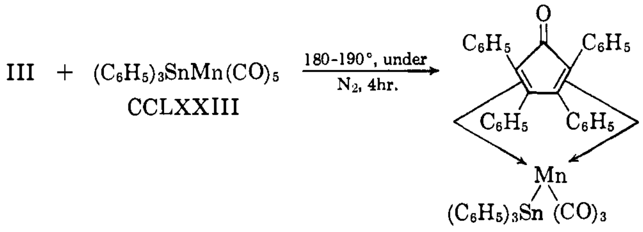
CCLXX

The anil of tetracyclone has also been subjected to reaction with iron pentacarbonyl and the product was the iron tricarbonyl π-complex (CCLXXI) (262, 275).



CCLXXI

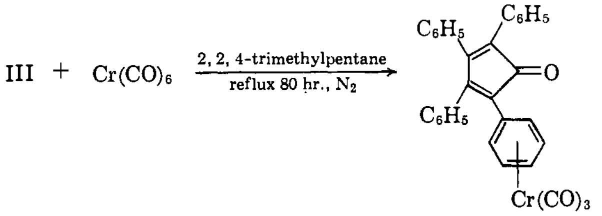
A unique reaction was observed when tetracyclone was treated with triphenyltinmanganese pentacarbonyl (CCLXXIII). In this case, both metal atoms were retained in the product, tetraphenylcyclopentadienone-triphenyltinmanganese tricarbonyl π-complex (CCLXXIV), with manganese being bonded to the cyclopentadienone ring. It is noteworthy that under somewhat milder conditions, mercury is eliminated from the tetracyclone adduct with bis(cobalt octacarbonyl)-mercury (CCLXVI).



CCLXXIII

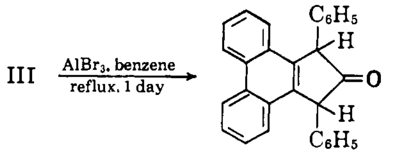
CCLXXIV

Treatment of tetracyclone with chromium hexacarbonyl in refluxing 2,2,4-trimethylpentane under nitrogen produces a chromium tricarbonyl π-complex with one of the four phenyl rings rather than a complex with the five-membered cyclopentadienone ring (81).



I. MISCELLANEOUS REACTIONS

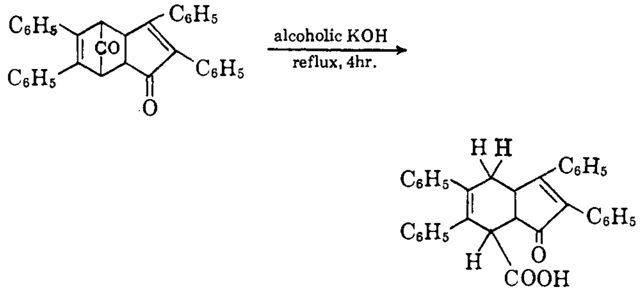
When tetracyclone is treated with aluminum halide in inert solvent a novel rearrangement occurs producing 1,3-dihydrophencyclone (CCXXVII) (197, 263). It was shown (177) that 1 plus moles of aluminum bromide are required for the rearrangement. Other conditions are cited in the equation. The product of this reaction has been mistakenly reported as tetrahydrotetracyclone



CCXXVII, yield 92.3%

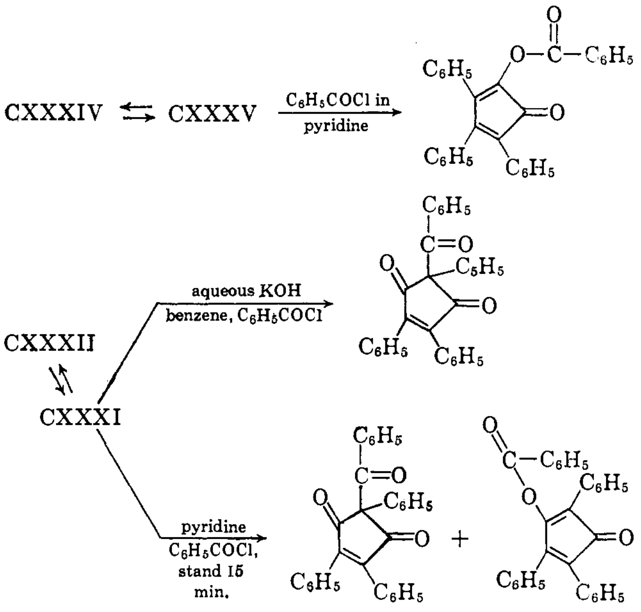
(36). The rearrangement reaction may be likened to an intramolecular Scholl cyclization (252, 271).

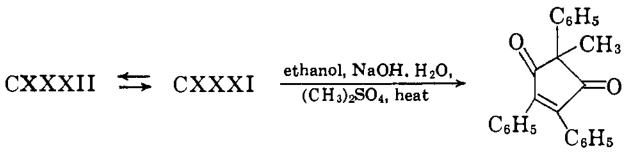
In the series of cyclopentadienones which exist as dimers, an unusual reaction is the cleavage of the bridge carbonyl with alkali to produce an acid (CCLXXV) (24). An extensive review of this reaction has been published (15).



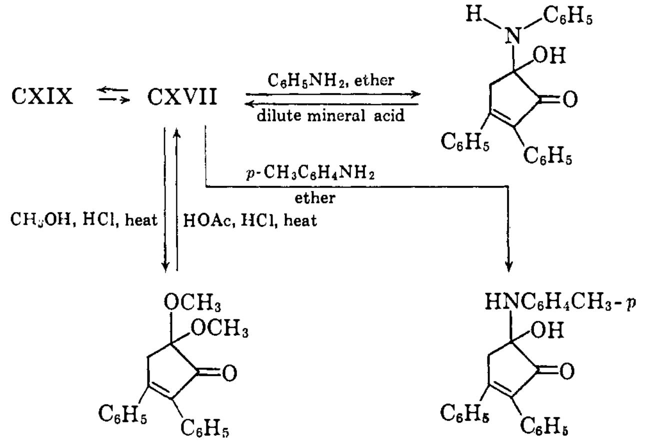
CCLXXV

The hydroxycyclopentadienones undergo reactions which are unique to the presence of the hydroxyl group. When 2-hydroxy-3,4,5-triphenylcyclopentadienone (CXXXIV stable as CXXXV) was treated with benzoyl chloride in pyridine, only O-benzoylation was obtained (194). However, when 3-hydroxy-2,4,5-triphenylcyclopentadienone (CXXXII stable as CXXXI) was treated with benzoyl chloride in benzene with aqueous alkali, C-benzoylation was observed; while treatment with benzoyl chloride in pyridine afforded both C-benzoylation and O-benzoylation (195). Compound CXXXII, stable as CXXXI, also gives C-methylation when treated with alkali and dimethyl sulfate (195).





2-Hydroxy-4,5-diphenylcyclopentadienone (CXIX stable as CXVII) formed a monoketal, of the nonconjugated carbonyl group, as expected, when treated with methanol and hydrogen chloride (158). Hydrolysis was effected in acetic acid solution with added hydrogen chloride. In ether, aniline and *p*-toluidine added to the same carbonyl group giving the arylated aldehyde-ammonia. Reversion to CXVII was effected for the aniline adduct with dilute mineral acid (158).

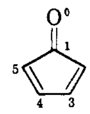


A recent article (146a), which was too late to be included in the original manuscript, reported the reaction of diazomethane with tetracyclone. In benzene solution containing methanol the product is 5,6-epoxy-1,2,3,4-tetraphenylfulvene which can be viewed as resulting from the addition of $-CH_2-$ across the carbonyl group. When the reaction is run in benzene solution in the dark, the product is 6-oxo-3a,4,5,6a-tetraphenyl-3a,6a-dihydro-3H-cyclopentapyrazol resulting from the addition of diazomethane across one of the double bonds of tetracyclone. In benzene with ultraviolet irradiation, the product is 4-oxo-3a,5,6,6a-tetraphenyl-3a,6a-dihydrocyclopentapyrazol, again resulting from the addition of diazomethane across one of the double bonds but in a reverse sense to that previously mentioned. Some 6-oxo-3a,4,5,6a-tetraphenyl-3a,6a-dihydro-3H-cyclopentapyrazol is also formed along with a tautomeric product.

IV. PHYSICAL PROPERTIES

A. MOLECULAR ORBITAL CALCULATIONS

The calculations of bond orders, electron densities, free valences, and localization energies of cyclopentadienone (X) have been performed (82, 106, 107). Table XXXIX lists the bond orders and Table XL lists the electron densities. It was concluded that the



X

Table XXXIX

Bond Orders for Cyclopentadienone

Bond	Bond order	Ref.
0:1	0.742	82
	0.911	107
	0.911	106
1:2	0.289	82
	0.177	107
2:3	0.880	82
	0.886	107
3:4	0.306	82
	0.423	107

Table XL

Electron Densities for Cyclopentadienone

Position	Density	Ref.
0	1.558	82
	1.313	107
1	0.560	82
	0.684	107
2	1.082	82
	1.025	107
3	0.859	82
	0.976	107

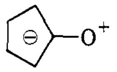
calculations showed a high reactivity for the 2:3 bond, that the most important resonance structure is X, that the electron densities require an appreciable polarization of the carbonyl bond, and that cyclopentadienone has a greater dienic ability in a Diels–Alder reaction than fulvenes (82). It was further noted that cyclopentadienone itself would therefore dimerize upon formation (82, 107) in the same manner as the simple cyclopentadienones.

The carbonyl absorption frequency was calculated as 1730 cm.$^{-1}$. This value has not been corroborated since cyclopentadienone dimerizes upon formation.

The calculation of an "excitation energy" indicates that this value for cyclopentadienone may reach a low value that is characteristic for biradicals (144). Therefore it seems that the ground state for cyclopentadienone may contain a contribution from a biradical form.

B. INFRARED ABSORPTION

Cyclopentadienones show a characteristic absorption peak in the infrared for the carbonyl group. Since infrared absorption is actually a measure of the force constant existing between atoms, then any significant shift in the absorption band of a carbonyl group is indicative of a change occurring in the force constant which is directly related to the bonding between the atoms. If an ionic form such as CCLXXVI makes a significant contribution to the ground state of cyclopentadienones, then a significant shift in the carbonyl absorption bands from that of other ketones would be expected.



CCLXXVI

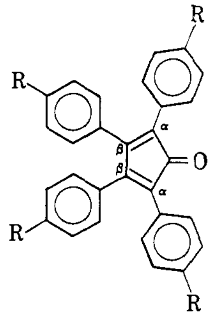
In the arylated cyclopentadienone series infrared data for only five representative members have been reported; these values appear in Table XLI along with the carbonyl absorption band for cyclopentanone for comparison. From the values it has been claimed that the arylated cyclopentadienones contain a "true double bonded carbonyl" in that the ionic structure does not contribute appreciably to the real state of the molecule (64). It has further been postulated, on the basis of the carbonyl absorption of tetracyclone (5.87 μ) *vs.* phencyclone (5.93 μ), that the former exists as a nonplanar structure whereas the latter exists as a planar structure (17).

Table XLI

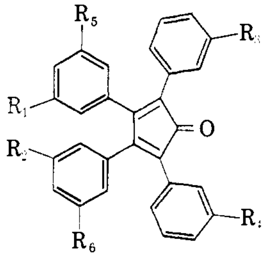
Infrared Absorption of Carbonyl in Arylated Cyclopentadienones

Cyclopentadienone	CO absorption, μ	Ref.
Cyclopentanone	5.78	67
2,3,4-Triphenylcyclopentadienone	5.95	229
2-Methyl-3,4,5-triphenylcyclopentadienone	5.88	229
Tetracyclone	5.78	263
	5.87	17
	5.85	64, 67, 190
Phencyclone	5.93	17
15,16-Diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one	5.88	22

A study (189) of a series of *para*-substituted tetracyclones has shown that the carbonyl absorption is not influenced by substituents in both *para* positions on the α-phenyl groups but that substituents on both β-phenyl groups modify the infrared spectra owing to a weak conjugation effect.



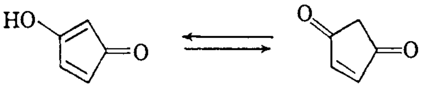
An examination (54) of a series of *meta*-methyl substituted tetracyclones indicates that no change occurs in the position of the carbonyl frequency from that observed for tetracyclones. This may be explained by assuming that the extent of hindrance is too small to be observed. The substituted tetracyclones show a prominent carbonyl band at 5.85 μ, characteristic also of tetracyclone. The fundamental difference normally



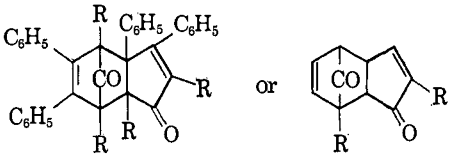
R_1	R_2	R_3	R_4	R_5	R_6	Carbonyl absorption, μ	C-H absorption, μ
H	H	H	H	H	H	5.85	
CH_3	CH_3	H	H	H	H	5.82	3.42, 7.23
H	H	CH_3	CH_3	H	H	5.82	3.42, 7.23
CH_3	CH_3	CH_3	CH_3	H	H	5.84	3.39, 7.25
CH_3	CH_3	H	H	CH_3	CH_3	5.85	3.41, 7.24

expected for the C–H absorption shows up in all cases at 3.42 and 7.23 μ. However, in the tetrasubstituted cyclone, the intensities of these two bands are approximately double those in the disubstituted analogs.

The only other infrared data available for a monomeric cyclopentadienone are those for 3-hydroxycyclopentadienone, stable as the 1,3-cyclopentanedione (104, 105); when these data are compared with carbonyl absorption (5.83 μ strong peak and at 5.73 μ medium peak, the theoretically calculated value of the carbonyl absorption in cyclopentadienone, 5.88 μ (70)), only a slight deviation is observed.



Dimeric cyclopentadienones have also been examined in the infrared. This type of cyclopentadienone contains two carbonyls, one forming the bridge and an additional conjugated ketonic carbonyl group.



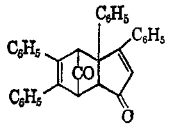
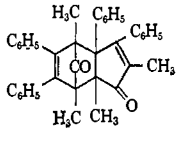
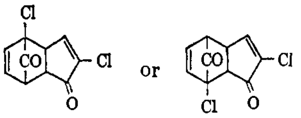
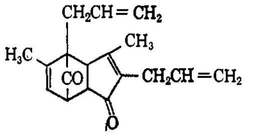
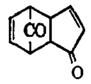
As expected, two bands attributable to carbonyl absorption can be found in the infrared spectra of these compounds. The band appearing at 5.64 μ is characteristic of a *para*-carbonyl bridge in a six-membered ring and the band appearing at 5.99 μ characteristic for the additional ketonic carbonyl peak (22). Table XLII records the available data.

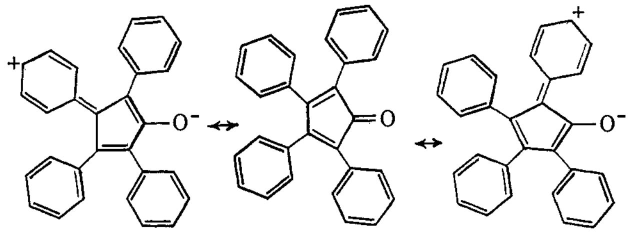
C. ULTRAVIOLET ABSORPTION

The electronic spectrum of tetracyclone in benzene shows two absorption maxima, one at 342 mμ with a molar absorption of 6760 and one at 512 mμ with a molar absorption of 1320 (87, 260, 269). In isooctane the 342-mμ peak is shifted to 333 mμ and the molar absorption is increased to 7200 (88), while in a 1:1 mixture of methanol and dioxane, a peak at 330 mμ appears with a molar absorption of 6850 and one at 510 mμ with a molar absorption of 1340 (88). In benzene, the absorption maximum at 342 mμ was attributed to an excited state of type IIIa and that at 512 mμ to an excited state of type IIIb (54, 87, 88, 91, 197, 260).

TABLE XLII

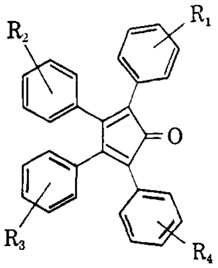
INFRARED ABSORPTION VALUES FOR DIMERIC CYCLOPENTADIENONES

Compound	Bridge carbonyl absorption, μ	Conjugated carbonyl absorption, μ	Ref.
	5.64	5.99	22
	5.64	5.99	22
	5.54		97
	5.64	5.92	47
	5.67	5.86	167



IIIa III IIIb

This was determined by examination of the electronic spectra of substituted tetracyclones (IIIc) (54, 87, 88, 91, 197, 260, 269).



IIIc

Table XLIII

Spectra of IIIc (R_1 = Y, R_2 = R_3 = R_4 = H)

R_1	R_2	R_3	R_4	Solvent[a]	λ_1[b]	α_{m1}[c]	λ_2[b]	α_{m2}[c]	Ref.
H	H	H	H	B	342	6.76	512	1.32	87, 260, 269
o-Cl	H	H	H	B	334.5	7.98	464	0.850	269
o-F	H	H	H	B	335	7.70	490	1.04	91
p-SO_2CH_3	H	H	H	B	345	7.11	505	1.60	88
p-Cl	H	H	H	B	340	7.02	510	1.46	87
p-Cl	H	H	H	B	340	7.10	510	1.46	88
p-Br	H	H	H	B	340	6.78	510	1.46	87
p-Br	H	H	H	B	340	6.88	510	1.46	88
p-F	H	H	H	B	340	7.06	510	1.52	87
p-F	H	H	H	B	340	7.10	510	1.53	88
p-CH_3	H	H	H	B	340	6.30	515	1.51	87
p-CH_3	H	H	H	B	341	6.31	515	1.51	88
p-OC_6H_5	H	H	H	B	330	6.68	524	1.81	88
p-OCH_3	H	H	H	B	342	6.10	525	1.87	87
p-OCH_3	H	H	H	B	343	6.10	525	1.88	88
p-SCH_3	H	H	H	B			530	2.16	88
p-SC_6H_5	H	H	H	B			532	2.18	91

[a] B is benzene. [b] λ in mμ. [c] $\alpha_m \times 10^{-3}$ listed.

Table XLIV

Spectra of IIIc (R_1 = R_4 = Y, R_2 = R_3 = H)

R_1	R_2	R_3	R_4	Solvent[a]	λ_1[b]	α_{m1}[c]	λ_2[b]	α_{m2}[c]	Ref.
H	H	H	H	B	342	6.76	512	1.32	87, 260, 269
o-Cl	H	H	o-Cl	B	332	8.85	436.5	0.610	260
o-F	H	H	o-F	B	335	8.40	460	0.860	91
p-Cl	H	H	p-Cl	B	341	7.08	512	1.75	269
p-Br	H	H	p-Br	B	336	7.32	515	1.91	88
p-CH_3	H	H	p-CH_3	B	341	7.20	518	2.26	88
p-OC_6H_5	H	H	p-OC_6H_5	B	330	7.72	538	2.33	91
p-SC_6H_5	H	H	p-SC_6H_5	B	340	7.72	542	3.24	91
p-OCH_3	H	H	p-OCH_3	B	340	6.66	545	2.26	88
m-CH_3	H	H	m-CH_3	CH	342.5	6.00	510–515	1.48	54

[a] B is benzene; CH is cyclohexane. [b] λ in mμ. [c] $\alpha_m \times 10^{-3}$ listed.

Table XLV

Spectra of IIIc (R_2 = Y, R_1 = R_3 = R_4 = H)

R_1	R_2	R_3	R_4	Solvent[a]	λ_1[b]	α_{m1}[c]	λ_2[b]	α_{m2}[c]	Ref.
H	H	H	H	B	342	6.76	512	1.32	87, 260, 269
H	$\overset{+}{N}(CH_3)_3\overset{-}{X}$	H	H	MD	330	6.17	510	1.26	88
H	o-Cl	H	H	B	332	6.00	492.5	1.59	260
H	p-SO_2CH_3	H	H	B	342	6.12	510	1.37	88
H	p-Br	H	H	B	342	7.70	510	1.26	87
H	p-Br	H	H	B	342	7.57	510	1.26	88
H	p-Cl	H	H	B	345	7.74	510	1.36	87
H	p-CH_3	H	H	B	350	7.50	510	1.07	88
H	p-OC_6H_5	H	H	B	358	8.48	509	1.22	91
H	p-OCH_3	H	H	B	370	8.95	510	0.87	88
H	p-OCH_3	H	H	B	370	9.04	512	1.21	87
H	p-SC_6H_5	H	H	B	378	9.305	516	1.736	91
H	p-SCH_3	H	H	B	388	9.20	510	1.29	88
H	p-$N(CH_3)_2$	H	H	B	428	9.61			87

[a] B is benzene; MD is 1:1 mixture of methanol and dioxane. [b] λ in mμ. [c] $\alpha_m \times 10^{-3}$ listed.

With R_1 = Y and R_2 = R_3 = R_4 = H, Table XLIII, the peak that is affected the most is the one at 512 mμ. This effect is also clear in the case of R_1 = R_4 = Y and R_2 = R_3 = H, Table XLIV. The 342-mμ peak is affected the most when R_2 = Y and R_1 = R_4 = R_3 = H, Table XLV, while the 512-mμ peak is slightly affected. This is also evident in the case of R_2 = R_3 = Y and R_1 = R_4 = H, Table XLVI. Table XLVII lists

TABLE XLVI

SPECTRA OF IIIc ($R_2 = R_3 = Y$, $R_1 = R_4 = H$)

R_1	R_2	R_3	R_4	Solvent^a	$\lambda_1{}^b$	$\alpha_{m1}{}^c$	$\lambda_2{}^b$	$\alpha_{m2}{}^c$	Ref.
H	H	H	H	B	342	6.76	512	1.32	87, 260, 269
H	*o*-Cl	*o*-Cl	H	B	325	4.75	500	2.11	260
H	*p*-Cl	*p*-Cl	H	B	340	7.88	514	1.22	269
H	*p*-Br	*p*-Br	H	B	343	8.55	511	1.21	88
H	*p*-CH_3	*p*-CH_3	H	B	354	8.95	510	1.25	88
H	*p*-OC_6H_5	*p*-OC_6H_5	H	B	363	11.59	515	1.59	91
H	*p*-OCH_3	*p*-OCH_3	H	B	375	10.4	510	0.87	88
H	*p*-SC_6H_5	*p*-SC_6H_5	H	B	380	13.36	525	1.717	91
H	*m*-CH_3	*m*-CH_3	H	CH	340–345	7.62	512	1.53	54
H	3,5-di-CH_3	3,5-di-CH_3	H	CH	346	7.70	507	1.32	54

^{a} B is benzene; CH is cyclohexane. ^{b} λ in mμ. ^{c} $\alpha_m \times 10^{-3}$ listed.

TABLE XLVII

SPECTRA OF IIIc ($R_1 = R_2 = R_3 = R_4 = Y$)

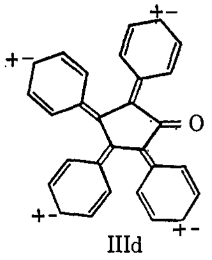
R_1	R_2	R_3	R_4	Solvent^a	$\lambda_1{}^b$	$\alpha_{m1}{}^c$	$\lambda_2{}^b$	$\alpha_{m2}{}^c$	Ref.
H	H	H	H	B	342	6.76	512	1.32	87, 260, 269
o-F	*o*-F	*o*-F	H	B	325	8.15	485	1.70	91
o-F	*o*-F	*o*-F	*o*-F	B	325	8.24	460	1.18	91
p-Cl	*p*-Cl	*p*-Cl	*p*-Cl	B	341	8.60	514	1.58	269
p-Br	*p*-Br	*p*-Br	*p*-Br	B	342	9.42	518	1.74	88
p-CH_3	*p*-CH_3	*p*-CH_3	*p*-CH_3	B	343	6.60	525	1.88	88
p-OCH_3	*p*-OCH_3	*p*-OCH_3	*p*-OCH_3	B	385	9.60	560	1.46	88

^{a} B is benzene. ^{b} λ in mμ. ^{c} $\alpha_m \times 10^{-3}$ listed.

the spectrum of tetrasubstituted tetracyclones. The large effects of the *ortho* substituents are explained as caused by their steric interaction with the *o*-hydrogens on the adjacent phenyl ring, which causes the phenyl ring on which they are bound to twist further out of the plane of the five-membered ring (91, 260).

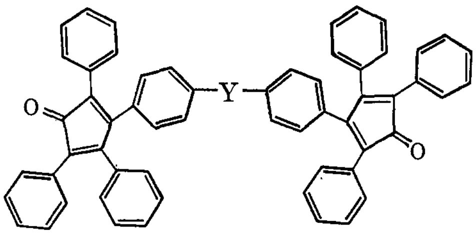
The absorption maximum between 250 and 350 mμ has been attributed to C=C absorption and that at 510 mμ to C=O absorption (66), or to an n → π transition in a molecular orbital involving oxygen (189).

In isooctane, tetracyclone (III) shows an absorption maximum at 262 mμ with a molar absorption of 27,800 (88). By studying the spectra of substituted tetracyclones (IIIc) it was concluded that this peak represents a *cis*-stilbene absorption such as IIId in which the carbonyl group is not involved (54, 88, 197).



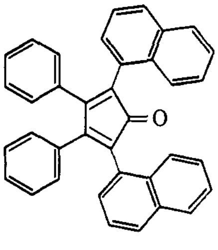
IIId

The ultraviolet absorption spectra of "bis-tetracyclones," IX, have also been examined (225). For IXb, IXc, and IXd, the spectra are largely similar to that for tetracyclone, the shift that occurs being similar to that for the phenoxy- and phenylthiocyclones in Table XLV.



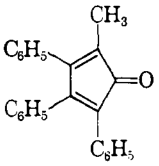
IXa, Y = nil
b, Y = CH_2
c, Y = O
d, Y = S

The absorption spectra of 2,5-bis(1-naphthyl)-3,4-diphenylcyclopentadienone (CLI) shows a maximum at 287 mμ (α_m 21,200) and one at 485 mμ (α_m 1000) (178). Since CLI may be viewed as tetracyclone in which a benzene ring has been fused on both the 2- and 5-phenyls, it would be expected that the 512-mμ peak should be shifted the most. Since both peaks are vastly affected, then some form of steric interaction may be present (178).



CLI

The ultraviolet absorption spectrum of 2-methyl-3,4,5-triphenylcyclopentadienone (CXXVII) shows maxima at 270 and 322 mμ with a log ϵ of 4.32 and 3.93, respectively (229). The 270-mμ band could possibly correspond to the 262-mμ band observed in tetracyclone while the 322-mμ peak could possibly be the shifted 342-mμ band, although this is not stated.


CXXVII

The absorption spectrum of 2,3,4-triphenylcyclopentadienone (CXXV) shows maxima at 266, 276, 306, 606, and 940 mμ, with log ϵ 4.17, 4.17, 4.28, 3.28, and 3.01, respectively (229). It is possible that the peaks at 276, 306, and 606 mμ correspond to the 262, 342, and 512 mμ peaks of tetracyclone, although no such statement is made.

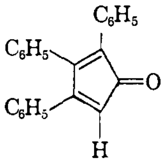

CXXV

Table XLVIII lists the characteristics of the ultraviolet spectra of several other cyclopentadienones that have been determined.

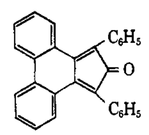
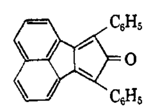
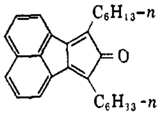
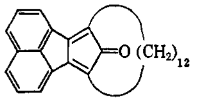
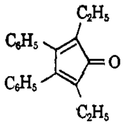
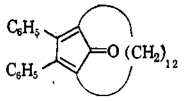
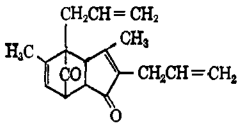
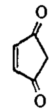
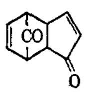
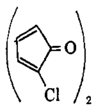
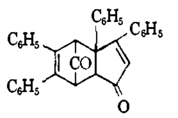
When the absorption maxima for the 3rd, 4th, and 5th compounds in Table XLVIII are compared with those of the arylated analogs, it appears that the "342-bands" have shifted significantly to shorter wave length regions. This suggests that there is a significant interaction between the 2- and 5-aryl rings and the C_5-ring. Further work to elaborate this correlation would be desirable.

Parenthetically, it is interesting to point out that the cyclones provide a good example of the fact that minor structural changes affect the electronic spectrum of a compound grossly while the infrared spectrum of the same material is affected to only a small degree. The addition of two hydrogens to the ring changes tetracyclone to colorless cyclopentenone with the 512-mμ peak completely absent. Two more hydrogens remove the ultraviolet band at 340 mμ. During these drastic shifts the CO frequency changes in a minor way from 5.85 μ for tetracyclone and 2,3-dihydrotetracyclone to 5.78 μ for tetrahydrotetracyclone (263).

	Tetracyclone	2,3-Dihydrotetracyclone	Tetrahydrotetracyclone	Ref.
Ultraviolet-visible (λ)	252 349	300	260	263
CO band in infrared (μ)	5.85	5.85	5.78	263

Table XLVIII

Ultraviolet Spectra of Miscellaneous Cyclopentadienones

Cyclopentadienone	Solvent[a]	λ, mμ	log α_m[b]	Ref.
	B	301 520	(2590) (773)	60
	B	333 575	(16800) (1510)	60
	I	278 365 278 350	4.58 3.87 4.19 3.86	44
	I	278 265	4.90 3.87	44
	I	255 295	4.33 3.96	44
	I	254 297	4.38 4.00	44
	M	239 310	3.97 2.14	47
	E	239 320	(9110) (110)	202
		222 322 367	4.16 1.30 1.30	104, 105
		338 323 354	1.75 1.68 1.62	167
		239.2	(9200)	97
		Graph		23

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[a] B is benzene; I is isooctane; M is methanol; E is ethanol.

[b] Values in parentheses are α_m values.

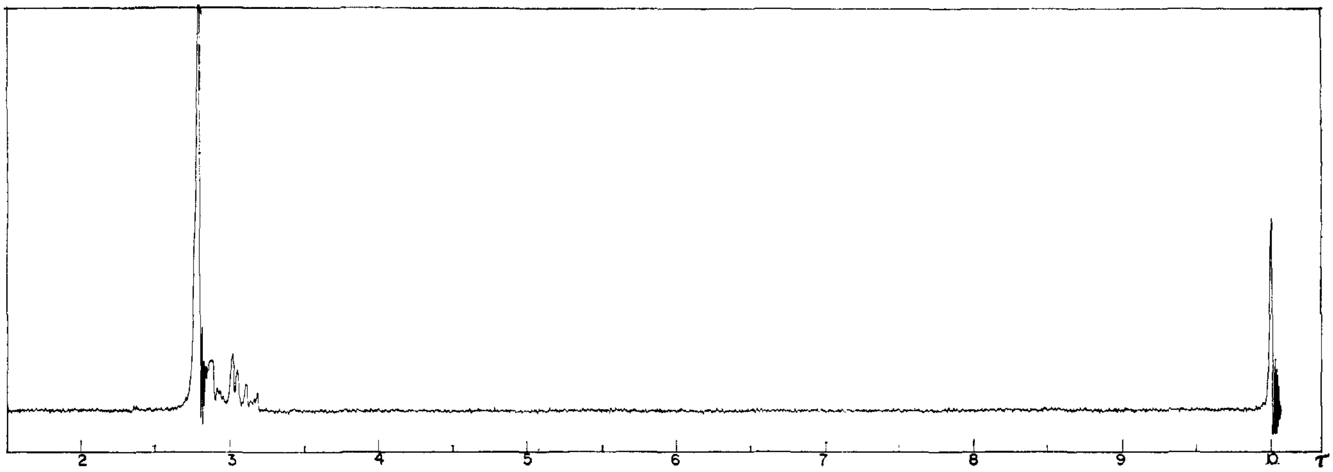


Figure 1.—Nuclear magnetic resonance spectrum of tetracyclone.

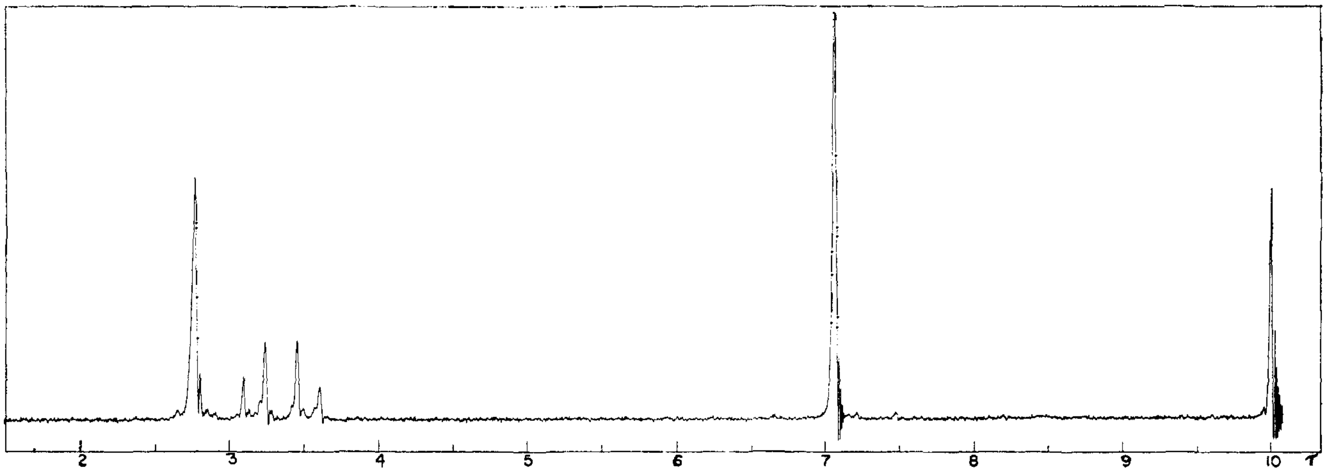


Figure 2.—Nuclear magnetic resonance spectrum of 3,4-bis-*p*-dimethylaminophenyl-2,5-diphenylcyclopentadienone.

D. NUCLEAR MAGNETIC RESONANCE

The nuclear magnetic resonance spectra of a number of cyclones have recently been investigated with the aim of learning of new correlations in this cross-conjugated system (55). The 60-Mc. nuclear magnetic resonance spectrum of tetracyclone (Figure 1) in chloroform is composed of a sharp singlet at 2.76 τ and two groups of partially resolved multiplets centered at approximately 2.8 and 3.1 τ. Comparison with the spectra of the 3,4-bis-*p*-dimethylaminophenyl-2,5-diphenylcyclopentadienone (Figure 2) and the 2,5-bis-*p*-dimethylaminophenyl-3,4-diphenylcyclopentadienone (Figure 3) has established that the singlet arises from the protons on the 2,5-rings and the multiplets from the $C_{3,4,5}$ (low-field group) and the $C_{2,6}$ (high-field group) protons on the 3,4-rings, respectively. At the present time, the spectra of more than 50 cyclones have been obtained bearing a variety of substituents at different sites, and, while several important structural types remain to be included, the available data have already revealed the following, apparently general relationships.

Protons in unsubstituted 2,5-rings normally occur as a singlet at 2.76 τ. Both the position and singlet character are virtually independent of the nature and location of substituents in the 3,4-rings. In 3-*para*-substituted derivatives and in "biscyclones" (section IIF2) bridged by O and CH_2CH_2, the 2- and 5-ring protons appear as two discrete singlets near 2.76 τ separated by 0.02–0.07 τ. The peak separation and chemical shifts are functions of the substituent. Fusion of the 3,4-rings deshields the 2,5-ring protons to 2.60 τ (singlet) in phencyclone and to 1.6–2.6 τ (series of multiplets) in acecyclone. A reasonable explanation is that the angular strain imposed on the C_3- and C_4-carbon atoms in the dienone ring is partially relieved by an increased double bond character of the C_3–C_4 bond. Conceivably, then, the nuclear magnetic resonance spectra of these fused ring analogs reveal the electron depletion in the 2,5-rings consequent to enhanced "hairpin" resonance. The smaller perturbation in phencyclone is consistent with the reduced strain at the C_3–C_4 bond. Also compatible with this hypothe-

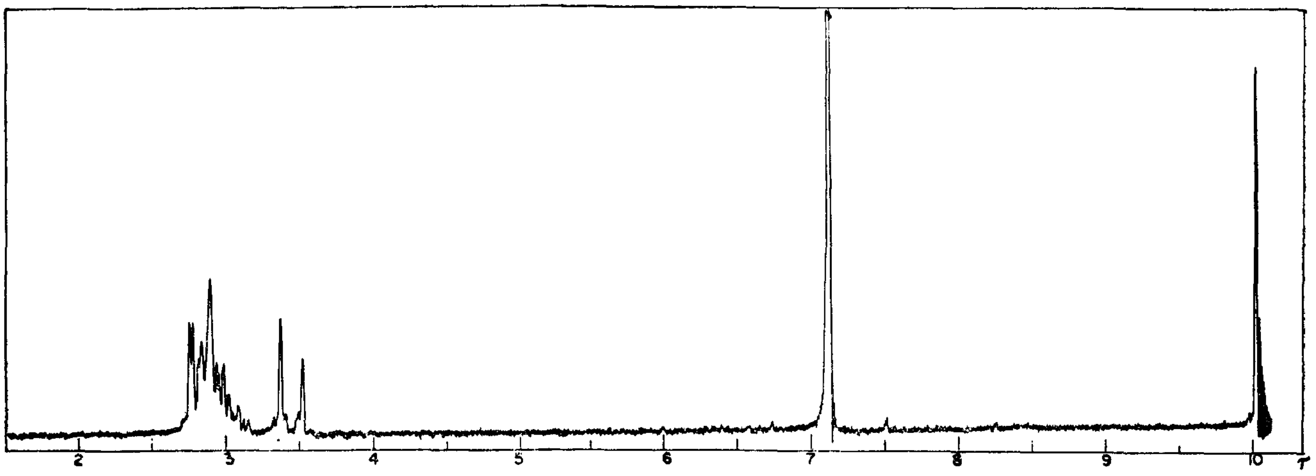


Figure 3.—Nuclear magnetic resonance spectrum of 2,5-bis-*p*-dimethylaminophenyl-3,4-diphenylcyclopentadienone.

sis is the bathochromic shift of the visible and carbonyl absorption bands relative to tetracyclone.

Similar to the findings for the 2,5-ring protons, the signals of the unsubstituted 3,4-ring protons are virtually independent of the nature and location of the 2,5-ring substituents. It is a direct consequence of this "bilateral" independence that the nuclear magnetic resonance spectra of 2,3,4,5-tetrakis(substituted phenyl)-cyclopentadienones are essentially composites of the substituted ring peaks of the 2,5- and 3,4-disubstituted analogs.

Although the influence of substituents on ring proton positions has not been fully explored, the data on *para*-substituted derivatives are in basic agreement with published findings (89a, 210a, 251a). As seen in Table XLIX, the effects are felt primarily by the protons *ortho* to the substituent.

Table XLIX

Influence of *para* Substituents on the Chemical Shift of Ring Protons

	3,4-Ar rings		2,5-Ar rings	
Substituent	$H_{2,6}$	$H_{3,5}$	$H_{2,6}$	$H_{3,5}$
H	3.1(m)[a]	2.8(m)	2.76(s)[a]	2.76(s)
CH_3	3.22(d)[a]	3.02(d)	2.90(s)	2.90(s)
OCH_3	3.15(d)	3.37(d)	2.81(d)	3.26(d)
$N(CH_3)_2$	3.18(d)	3.54(d)	2.80(d)	3.48(d)
Cl	3.18(d)	2.81(d)	2.82(s)	2.82(s)
Br	3.25(d)	2.68(d)	2.92(d)	2.63(d)
I	3.33(d)	2.44(d)	3.04(d)	2.42(d)
SCH_3	3.18(d)	2.95(d)	2.87(s)	2.87(s)

[a] s = singlet, d = doublet, m = multiplet.

Although the generality has yet to be established, evidence obtained on the methyl and methoxyl groups indicates that the shielding of substituent protons increases in the order: *para*, 2,5-*meta*, and 3,4-*meta*. The data are presented in Table L.

Further increases in shielding values are anticipated in the *ortho* series.

Table L

Chemical Shift of Substituent Protons as a Function of Ring Position

Substituent	3,4-Ring	2,5-Ring
p-CH_3	7.70	7.71
m-CH_3	7.90 7.92[a]	7.76
p-OCH_3	6.23	6.25
m-OCH_3	6.50	

[a] 3,4-Bis-3,5-dimethylphenyl analog.

A study of solvent effects has shown that in pyridine and benzene the unsubstituted 2,5-ring protons appear as two groups of well-resolved multiplets, while the protons on unsubstituted 3,4-rings are observed as a singlet in nearly all cases. It is noteworthy that this represents an almost complete reversal of the characteristic line shapes in chloroform. The average positions are listed in Table LI.

Table LI

Chemical Shift of Unsubstituted Ring Protons in Pyridine-d_5 and Benzene-d_6

	2,5-Ar rings		3,4-Ar rings
Solvent	$H_{2,6}$	$H_{3,4,5}$	
Pyridine-d_5	2.5 ± 0.1 (m)	2.7 ± 0.1 (m)	2.8 ± 0.1 (s)
Benzene-d_6	2.5 ± 0.1 (m)	2.9 ± 0.1 (m)	3.1 ± 0.1 (s)

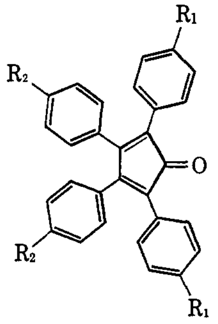
A comparison with the corresponding figures in chloroform indicates that the shielding effect of the aromatic solvents increases from a minimum at the molecular center to a maximum at the periphery of the cyclone molecule. This trend is also observed for the substituent protons.

The nuclear magnetic resonance spectra of the related diene and fulvene derivatives have turned up several important relationships which bear on some unresolved problems in cyclone spectra. One such problem is the nonequivalence of the 3,4-ring protons and unusually high-field position of the $C_{2,6}$-protons. These related effects may be due to long-range shielding from neighboring rings or to an electron drift from the dienone ring. Dipole moment measurements and evidence suggesting a "propellor type" arrangement of the four aromatic rings favor the former explanation. The collapse of the 3,4-ring proton signals to a singlet in the tetraphenylcyclopentadiene derivatives is more satisfactorily explained in terms of an electronic effect and clearly indicates the need for additional data before a solution to the problem can be reached.

Cyclopentene-3,5-dione, its mono-*d*-substitution product, and 1-methylcyclopentene-4,5-dione have been examined by means of nuclear magnetic resonance spectroscopy (99, 165). Although these compounds may be considered to be hydroxycyclopentadienones (section IIA3) their nuclear magnetic resonance spectra are consistent with ene-diones and a discussion will be omitted here.

E. DIPOLE MOMENTS OF TETRAPHENYLCYCLOPENTADIENONES

The dipole moments of three tetracyclones (III, CCLXXVII, and CCLXXVIII) have been determined, Table LII (65, 85, 110).



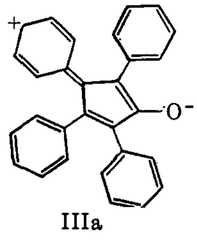
III, $R_1 = R_2 = H$
CCLXXVII, $R_1 = Cl$, $R_2 = H$
CCLXXVIII, $R_1 = R_2 = Cl$

TABLE LII

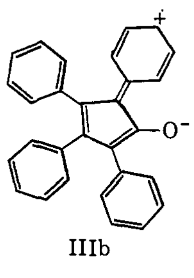
DIPOLE MOMENTS OF TETRACYCLONES

R_1	R_2	μ, D.	Ref.
H	H	3.43 ± 0.1	110
H	H	3.61 ± 0.04	65
H	H	3.52	85
Cl	H	4.61 ± 0.1	110
Cl	Cl	2.26 ± 0.1	110

The moment for tetracyclone is about 0.5×10^{-18} e.s.u.-cm. higher than expected (110), which could be due to resonance contributions from structures such as IIIb and IIIa. Structures such as IIIa and IIIb represent two of twelve such possible structures. A very small resonance contribution to the ground state of tetracyclone from structures such as IIIa and IIIb would result in a large change in the dipole moment since these structures have large moments. Since the dipole moment is enhanced by only 0.5×10^{-18} e.s.u.-cm. these structures must indeed make a small contribution (110). This is probably due to the fact that steric interaction between the phenyl rings inhibits coplanarity which is necessary for resonance. Furthermore, this rationalizes the fact that the dipole moment of tetracyclone is smaller than that for aliphatic ketones.



IIIa



IIIb

Using 1.58×10^{-18} e.s.u.-cm., the moment for chlorobenzene, as the contribution from a *p*-chlorophenyl group, and a symmetrical pentagon for the five-membered ring, then the calculated moment for CCLXXVII is 4.4 D. and that for CCLXXVIII is 1.8 D. If, on the other hand, the angles for cyclopentadiene are used, then the calculated moments are 5.04 D. for CCLXXVII and 2.07 D. for CCLXXVIII (110). Thus, it is seen that in tetracyclone the single bonds in the five-membered ring possess some double bond character since this would give a better agreement with the observed dipole moments by expanding the angles at the 2- and 5-carbon atoms (110).

V. USES

The most important uses of cyclopentadienones are as synthetic intermediates. These reactions have been covered in the reaction section, the most noteworthy being the Diels–Alder reaction. This reaction provides an elegant synthesis for many aromatic compounds which would be difficult to prepare by other methods. Cyclopentadienones also offer a starting material for the preparation of heterocyclic compounds such as thiophenes, furans, pyridazines, and pyridines. Diels–Alder polymers which were already mentioned may prove to be interesting plastics. Patents also describe the preparation of certain vat dyes.

ACKNOWLEDGMENT.—The authors sincerely acknowledge a debt to Mr. Byron H. Arison for the section on nuclear magnetic resonance.

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