CARBONYL BRIDGE COMPOUNDS AND RELATED SUBSTANCES[1]

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Received May 1, 1945

CONTENTS

I. INTRODUCTION

Alicyclic compounds containing a group of atoms not connected to adjacent atoms in a carbon ring have long been known to organic chemists, but until the advent of the diene synthesis the available varieties were limited almost entirely to the terpenes and their derivatives. During the last decade there has been considerable interest in such bridged compounds, especially in those in which a carbonyl group serves as the bridge; for convenience, these compounds have been called "carbonyl bridge compounds." They have all contained at least one ethylenic linkage and have been polyarylated. Their most characteristic behavior has been the elimination of the bridge when heated. The known carbonyl bridge compounds of this type and related substances, as well as a few molecules containing carbinol, lactone, and anhydride bridges, which show a similar behavior in certain reactions, will be described in this paper. The terpene ketones, which can be visualized (formula A) as containing a —CH_2CO— bridge, will not be considered, since none of their properties appear to be connected with the presence of the bridge.

II. NOMENCLATURE

To the organic chemist, the term "bridged" implies a condensed cyclic system having three or more atoms (usually carbon) common to two rings. Bridged

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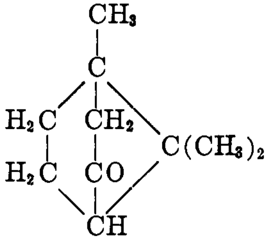
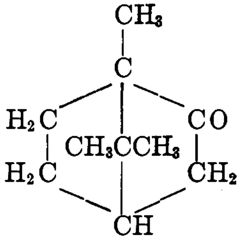
[1] Communication No. 1033 from the Kodak Research Laboratories.

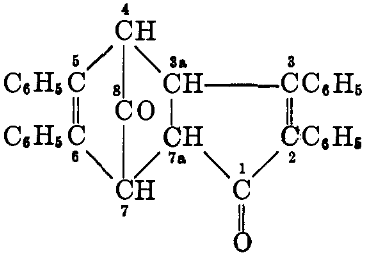
rings have long been known in considerable variety, and are commonly associated with terpene derivatives in the camphor series and with the tropine alkaloids, though many other systems are recorded in the literature. There is nothing in this nomenclature to suggest anything in regard to the nature of the bridge, and examples are known in which the atoms forming the bridge are carbon, nitrogen, oxygen, etc., alone or in combination. The term "bridged," therefore, is used for convenience. Through continued usage, this term has come to mean any group of atoms in a cyclic substance connecting two other atoms that are not in adjacent positions, and by convention the shortest chain is considered to be the bridge. Thus, camphor is ordinarily written as B rather than A. In modern nomenclature, the bridge is indicated by placing numerals in brackets. The numerals indicate the number of atoms in the chains between the bridgeheads; in *Chemical Abstracts* usage, the bridge is the last of the bracketed numerals. Thus, camphor is 1,7,7-trimethylbicyclo[2.2.1]-2-heptanone. In polycyclic ring systems having more than two rings, the bridge is inserted in the name, as methano, ethano, etc. Thus, the substance shown in formula I is named 2,3,5,6-tetraphenyl-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione.



A



B



I

When one examines three-dimensional models, a better idea of the spatial positions of the atoms comprising the ring structures is obtained. If the observer looks directly down upon the molecule, at the point of union of the bridge and ring, i.e., along the 1,4-axis, he sees three bonds radiating outwards (figure 1) at equal angles; if viewed from the side, the molecule resembles a cage (figure 2). There is no great difference in linking or spatial characteristics between the bridge and other parts of the ring. This lack of difference emphasizes the danger of distinguishing between the behavior of the bridge and that of any other portion of the molecule. Chemical behavior, then, must be associated with the nature and type of linkage of the groups present, rather than with a peculiarity of the bridge. With this concept in mind, plane bridged formulas are used in the examples given in this paper.

III. Types of Bridged Compounds

The bridged compounds to be described comprise those in which the ring is numerically saturated and those having an ethylenic linkage. They are further subdivided according to the size of the ring.

A. SATURATED RINGS

There are recorded in the literature two substances with the molecular formula $C_7H_{10}O$ which the respective authors represented as having a saturated six-membered carbon ring and a carbonyl bridge.

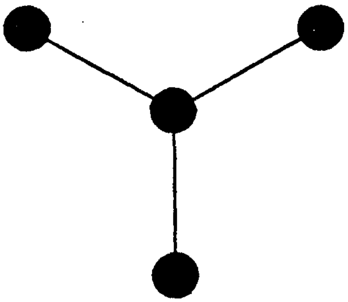


Fig. 1

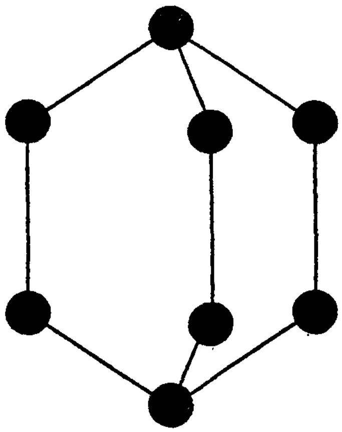
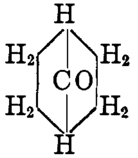


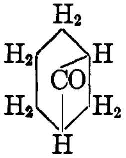
Fig. 2

Zelinski (86) hoped to prepare norcamphane by the reduction of the ketone II, which he expected to secure by distillation of the alkaline earth salts of *trans*-hexahydroterephthalic acid. He obtained along with a small amount of benzene a much smaller fraction (b.p. 150–180°C.); from the latter fraction he prepared a semicarbazone which, he wrote, "must correspond to the ketone" (II). It was not investigated further and its existence should be considered doubtful.

By a similar procedure, Stark (75) attempted to secure the ketone III from



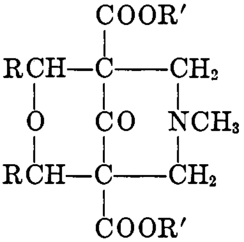
II



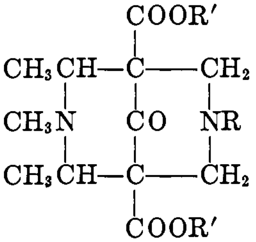
III

hexahydroisophthalic acid. He obtained a small fraction, from which was prepared a semicarbazone, m.p. 179–180°C. This ketone is referred to by Böeseken and Peek (29), who wrote, "....the ketone of Stark has the properties of an unsaturated substance which could be a cyclobutanone. It is very probable that it is, in fact, a derivative of cyclobutanone, stabilized by the other ring, placed ...." However, Ruzicka and Trebler (73) pointed out that Stark could not have had the compound claimed, for its refractive index is much too high and its behavior towards bromine is like that of other unsaturated ketones. The melting point of the semicarbazone is the same as that of the semicarbazone of 1-methyl-3-cyclohexen-2-one. Thus, it appears that there is a reasonable doubt as to the correctness of the structures of both II and III.

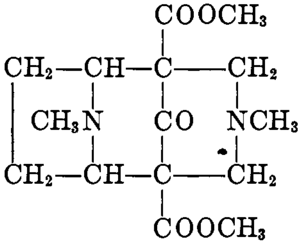
Mannich (67–69) has described two bicyclic eight-membered heterocyclic ring systems "Pydin" (IV) and "Bispidin" (V), and the tricyclic "Bispidone" (VI). From the method of preparation they were expected to contain a carbonyl group but its presence could not be demonstrated directly; upon degradation of one of the compounds, the formation of a known pyrrolidone was taken as evidence that the carbonyl group was present as such in the bicyclic substance.



IV
"Pydin"



V
"Bispidin"



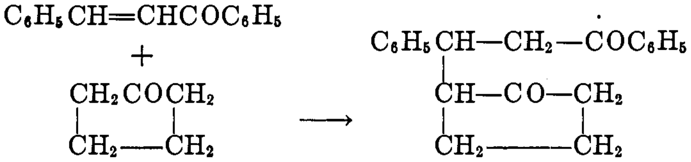
VI
"Bispidone"

An instance of a saturated eight-membered carbon ring having a carbonyl bridge (IX) is described later because of its relation to certain unsaturated systems.

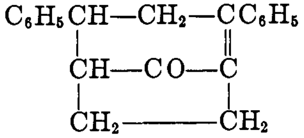
B. UNSATURATED RINGS

1. *Rings having more than six carbon atoms*

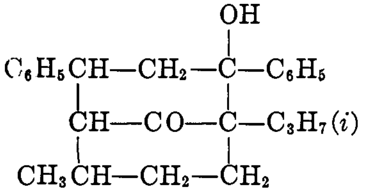
There are only a few bicyclic ring systems known having more than six atoms in the ring and containing both a carbonyl bridge and an ethylenic linkage. Half of these were prepared by Stobbe (77–83) during his investigations on semicyclic ketones, and the rest by Allen and Sallans (14). For example, cyclopentanone was added to benzalacetophenone, and the intermediate ketone (VII) thus formed was cyclized by the action of hydrogen chloride in warm alcohol to give the unsaturated bridged substance VIII, m.p. 122°C. (79).



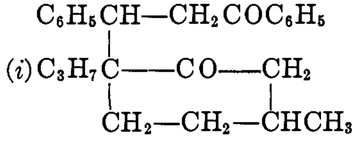
VII



VIII



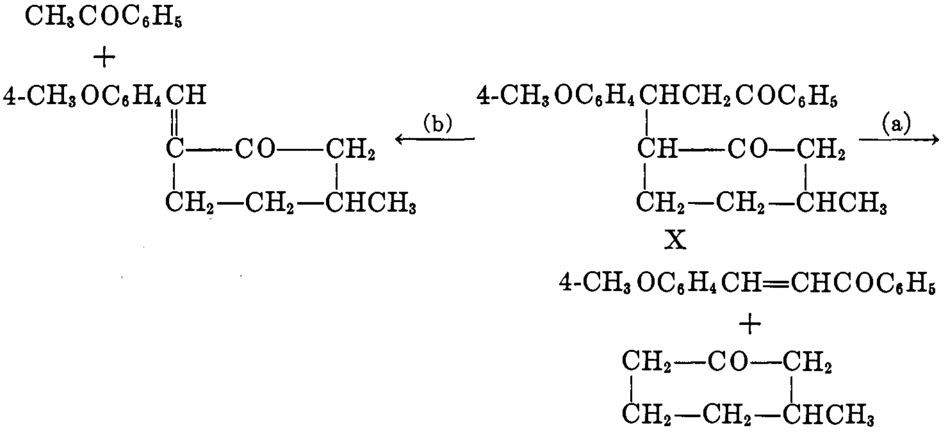
IX



IXa

A cyclic keto alcohol (IX) could be isolated only when menthone was selected as the addend (82). Such keto alcohols are isomeric with the corresponding addition products, and are probably intermediate products in the formation of the bicyclic ring systems. Accordingly, Stobbe took great care in establishing the open structures.

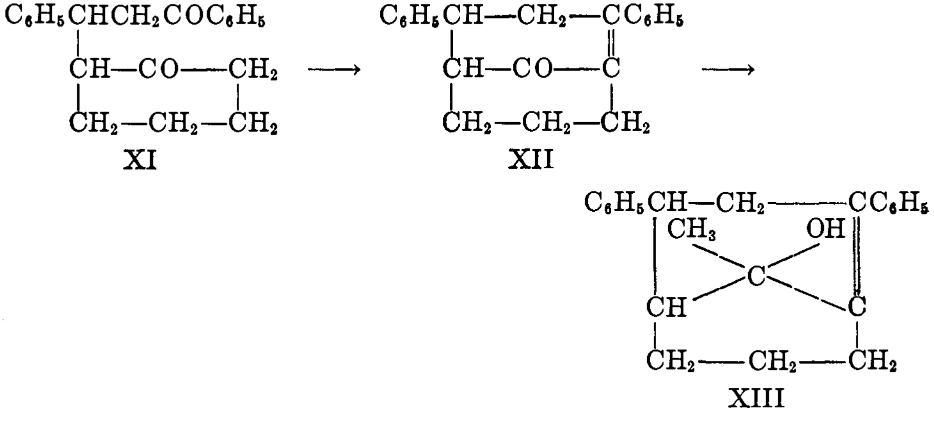
These intermediate ketones (called semicyclic ketones by Stobbe, for convenience) dissociate into their components on distillation. This cleavage may take place in two ways: for example, 2-phenacylobenzylcyclopentanone (VII) re-forms cyclopentanone and benzalacetophenone, while with 2-phenacyloanisyl-5-methylcyclohexanone (X)· the products are (*a*) anisalacetophenone and 3-methylcyclohexanone, and (*b*) acetophenone and anisal-3-methylcyclohexanone (77).



These intermediate ketones form mono- and di-oximes, oxime-semicarbazones, and disemicarbazones. The ketones can be regenerated from the disemicarbazones. The monoximes can be cyclized into heterocyclic bases, tetrahydroquinolines, or pyrhydrindenes (81). These ketones can be converted into pyrylium salts (14). They add quantitatively two equivalents of methylmagnesium iodide without evolution of gas (14).[2] They react with aromatic aldehydes, indicating the presence of a methylene group adjacent to the carbonyl group, although a dibenzal type never results (77). The location of the methyl group in X was shown by the formation of β-methyladipic acid upon oxidation (77).

The keto alcohol IX (82), however, forms only a monoxime, which does not give a heterocyclic base, and a monosemicarbazone. It can be distilled unchanged, it does not give pyrylium salts, and it does not react with aromatic aldehydes. When treated quantitatively with methylmagnesium iodide, it reacts with two equivalents, forming one equivalent of methane, a reaction which indicates one active hydrogen atom (hydroxyl). This last reaction also affords confirmation of the structure IX, for Stobbe was unable to prove the presence of the hydroxyl group. If the menthone had added to the benzalacetophenone in the opposite possible manner (IXa), an open-chain ketone would have resulted or, if a keto alcohol had been formed, it would have lost a molecule of water, as occurs with the other 1,5-diketones when they are treated with hydrogen chloride.

The bicyclic bridged ketones are obtained by warming absolute alcoholic solutions of the open-chain ketones and hydrogen chloride; a molecule of water is eliminated. Although two stereoisomers are produced, only one is obtained in quantity. The new ketones can be distilled without decomposition. They form monoximes and monosemicarbazones. They react with one equivalent of methylmagnesium iodide, forming carbinols (14). They do not cyclize to heterocyclic bases. In illustration, 2-phenacylobenzylcyclohexanone (XI) gives two stereoisomeric bicyclo[3.3.1]-2,4-diphenyl-9-keto-4-nonenes (XII) (m.p. 143°C., 151°C.), and, after treatment with methylmagnesium iodide, bicyclo[3.3.1]-2,4-diphenyl-9-methyl-9-hydroxy-4-nonene (XIII). The cyclic


XI XII XIII

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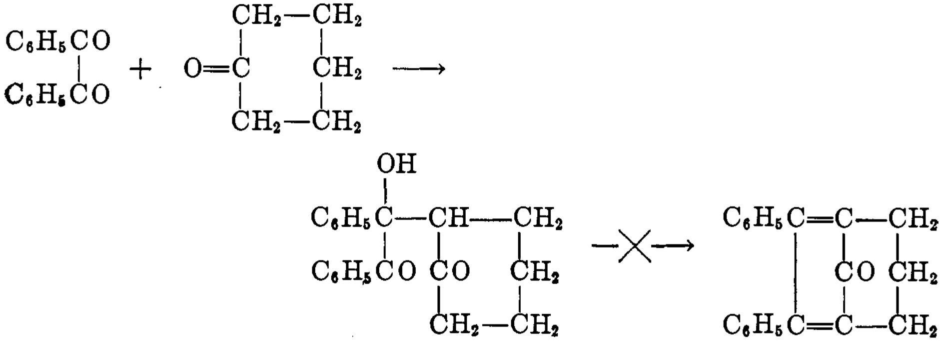
[2] One of the modern methods of establishing the presence of a carbonyl group is to examine its behavior in the Kohler–Richtmyer apparatus (devised to measure quantitatively the amount of methylmagnesium iodide consumed and gas evolved) (66). The reagent used up, but not accounted for by the gas formed, is interpreted as having reacted by addition.

ketone XII does not decolorize permanganate or bromine, whereas the lower homolog VIII "easily adds bromine" (77) but, since bromine evolves hydrogen bromide and forms tars with all these substances containing a reduced ring, it is not a useful reagent. The arylhydrazines likewise form tars with these intermediate ketones.

The location of the double bond has not been absolutely proved. As always written by Stobbe, it is at a bridgehead and so contrary to Bredt's rule (28). The available evidence rests (*a*) on the method of formation (position of groups for an aldol-type reaction), (*b*) on the fact that the keto alcohol IX, obtained from menthone, does not lose water, and (*c*) on the observation that the ketone from cyclohexanone does not decolorize permanganate or bromine, as would be anticipated if the double bond were in any other position. At the moment, these substances constitute exceptions to Bredt's rule.

At this point it may be mentioned that attempts to prepare the doubly unsaturated carbonyl bridge compound XIV were unsuccessful (4). Only the first step of the reaction, analogous to the one found applicable by Japp to many aliphatic ketones (60, 61), took place to give XV. Efforts to push the reaction led mainly to the formation of resinous materials.


XV XIV

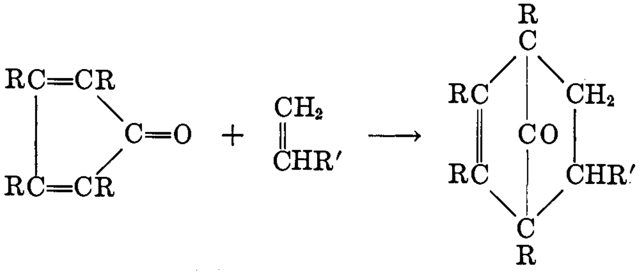
In summary, the few known seven- and eight-membered unsaturated bicyclic ring systems having a carbonyl bridge do not exhibit any unusual properties and they are not altered by being heated.

2. Six-membered rings

(a) Methods of preparation

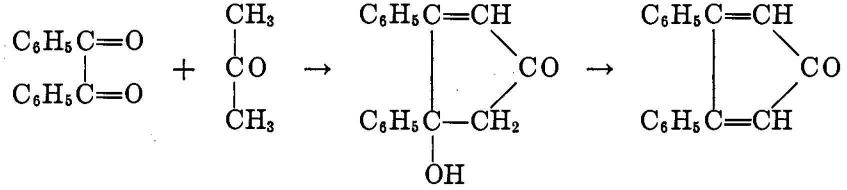
There are a large number of six-membered multicyclic ring-systems having a carbonyl bridge. Nearly all have been made available by the diene synthesis (70). A few, although long known by empirical formulas, have had their structures elucidated only during the last decade. The reaction consists of the 1,4-addition of a substance having a sufficiently active ethylenic linkage to the ends of the carbon–carbon conjugated system of double bonds in a cyclopentadienone.

Examples will be given later to illustrate the use of acetylenic addends, as well as the reversibility of the reaction. The variety of products is limited by (*1*) the available cyclopentadienones and (*2*) the unsaturated addends; the former is the more important factor.



Relatively few cyclopentadienones are known (because they add to themselves, as will shortly become evident), and they are all polyarylated. They are obtained from 1,2-diketones and dibenzyl ketones, a reaction of aldol condensation investigated by Japp (60, 62, 63) (who, however, never isolated any of the cyclopentadienones) and by Dilthey (37–51). The most useful has been tetraphenylcyclopentadienone (47, 55); the name has been abbreviated to "tetracyclone" and the class as a whole is sometimes termed "cyclones."

A potential source of cyclopentadienones that has been very useful is the group of substances known from the first of the series as anhydroacetonebenzils. These were first prepared by Japp (60, 62, 63) and his students, and unexpectedly found to be cyclic. With acidic dehydrating agents, two molecules of anhydroacetonebenzil (XVI) and its homologs lost two molecules of water and gave a complex molecule double the size of the starting material; for convenience, these have been termed "bimolecular products." The structure of these complex substances was determined about a decade ago (17, 18), and led to the recognition of the existence of carbonyl bridge compounds. The expected cyclopentadienone (XVII) could not be isolated because of its tendency to add to itself, but its presence as an intermediate has been shown (15), as will be described later. In a few instances, these bimolecular products dissociate in solution, so that reactions of the monomeric form can be observed (19, 22).



XVI XVII

Anhydroacetonebenzil

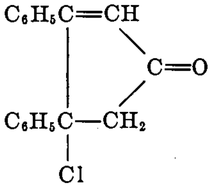
Some of these bimolecular products have also resulted from the action of alkaline reagents on various diphenylchlorocyclopentenones (13, 16);[3] the latter can be conveniently considered as related to anhydroacetonebenzil by the replacement of a hydroxyl group by a chlorine atom, so that removal of hydrogen and chlorine leaves diphenylcyclopentadienone (XVII), which at once dimerizes.

(b) Properties of six-membered unsaturated rings

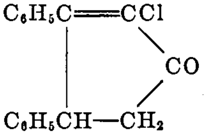
The most conspicuous property of the carbonyl bridge compounds having a six-membered ring and one ethylenic linkage is their behavior when heated—*the bridge is split out as carbon monoxide.* This "decarbonylation," which is usually quantitative, is rapid at 200–220°C., and in favorable instances can be detected at 75–80°C. The other product of the reaction is usually a dihydrobenzene derivative, but occasionally this is dehydrogenated to the corresponding aromatic compound; these reactions are used as a part of the proof of structure. Aromatic compounds are produced directly when acetylenic addends are used; this variation will be considered separately.

(*i*) *Bicyclic carbonyl bridge compounds:* Styrene adds readily to tetracyclone in boiling benzene to give the carbonyl bridge compound XXII (20). The presence of the carbonyl group is shown by the formation of carbinols when the substance is treated with Grignard reagents. When the product is heated to 200°C., carbon monoxide is rapidly given off, and the dihydrobenzene XXIII is formed;

[3] With many acid chlorides, anhydroacetonebenzil gives the chloride XVIII (16), for which the structure has been established to the satisfaction of those interested in the field, but with hydrogen chloride under certain conditions, both this chloride and anhydroacetonebenzil give the same isomeric chloride (16, 60), the structure of which is not yet agreed upon. The English investigators (30, 31, 32) prefer the structure XIX for this isomer.

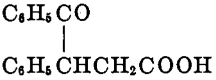


XVIII



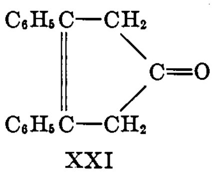
XIX

Neither group has been able to repeat the other's work *in toto*. It is the author's opinion that the assignment of any structures in such a system where anionotropic and prototropic shifts are possible should be considered as tentative and subject to revision. Ozone does not appear to be a reliable reagent, for the reference compound desylacetic acid (XX) can be obtained from 3,4-diphenyl-3-cyclopenten-1-one (XXI) where it would be least expected (31).



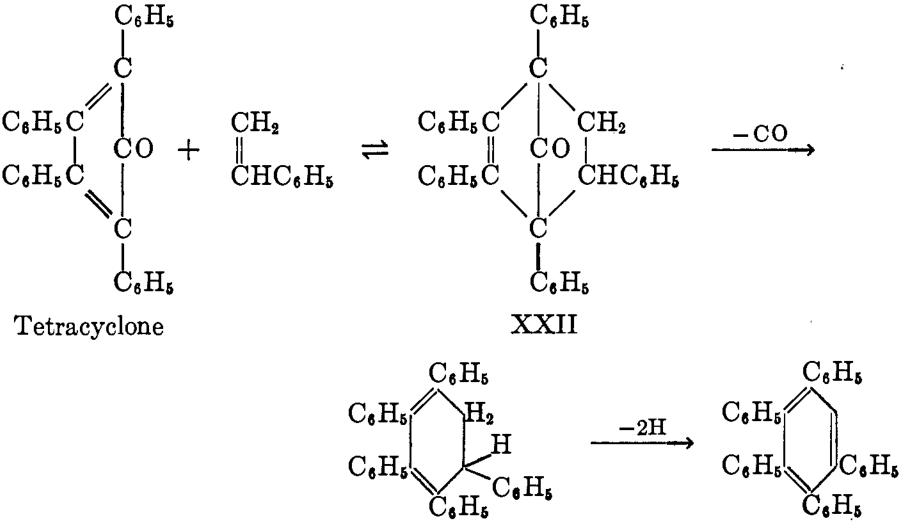
$$\begin{array}{l}C_6H_5CO\\ \;|\\ C_6H_5CHCH_2COOH\end{array}$$

XX
Desylacetic acid



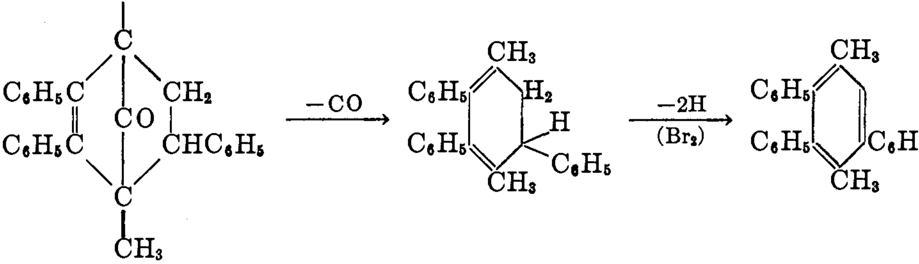
XXI

this same product is also obtained (1) when styrene and tetracyclone are refluxed together in the absence of a solvent—that is, the temperature of reaction is above that at which the bridged ketone is stable. The dihydrobenzene XXIII can be dehydrogenated to pentaphenylbenzene (XXIV) by heating with sulfur (20) or with selenium at 180–200°C. (1). It may be concluded, therefore, that the addition product XXII contained a six-membered carbon ring. A parallel proof of structure has been used in many other instances; for example, the dimethyl analog (XXV) exhibits the same behavior, being decarbonylated to the dihydrobenzene (XXVI) and the latter being dehydrogenated by bromine to the aromatic hydrocarbon (XXVII). With this bridged ketone, the presence of the carbonyl group was detected by the formation of a 2,4-dinitrophenylhydrazone, as well as through use of the Grignard reagent (19). In all cases, the structures of the aromatic compounds have been proved by independent syntheses.



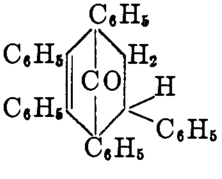
XXIII

XXIV
Pentaphenylbenzene

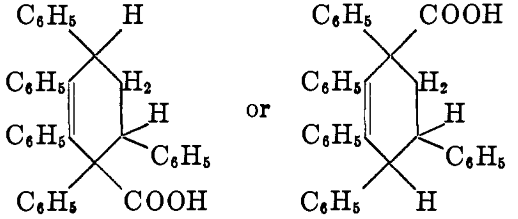


XXV XXVI XXVII

Another type of reaction, the limits of which are not yet known, is cleavage of the bridge at one end only by means of alcoholic alkaline solutions (9, 22, 23). Upon analysis of the product of the reaction, it is found that a molecule of water has been added. The new substance is a carboxylic acid, i.e., the carbonyl group of the ketone has become converted to a carboxyl group. Since the bridge may open at either end, isomeric acids are possible (the structures due to stereoisomerism are disregarded); one usually predominates.[4] In the case of the pentaphenylated ketone XXII, the acids would be those shown in XXVIII. It is not possible to assign more definite configurations from the available facts.



XXII

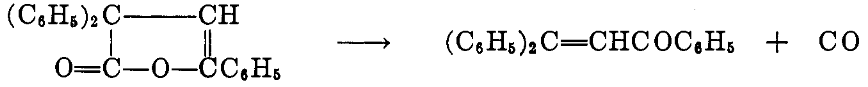


XXVIII

Upon aromatization of the acid by prolonged boiling with permanganate, pentaphenylbenzene (XXIV) is produced, but when the acid XXVIII is decarboxylated by heating at 300°C., the dihydropentaphenylbenzene XXIII is obtained (23). Thus, the presence of a six-membered ring in the addition product has again been demonstrated.

It is not possible to state whether the acid loses carbon dioxide as the result of a decarboxylation during the permanganate treatment, or whether the carboxyl group comes off as formic acid, which is then oxidized; the nature of the products obtained with more complicated substances (see pages 234, 240) indicates that the second possibility merits serious consideration.

The loss of carbon monoxide, resulting from the heating of organic compounds, is not too common a reaction, especially when it takes place at moderate temperatures, and is not a pyrolysis. The carbonyl bridge compounds evolve gas most rapidly at 180–220°C., but the same process takes place very slowly at 130°C. (15) or at even lower temperatures, in very favorable instances. In most of the other instances recorded, the substance heated contains more than one oxygen atom, and the products are carbon monoxide and an aldehyde or ketone (25, 26). For example, triphenylcrotolactones lose carbon monoxide and form α,β-unsaturated ketones (27, 61), as is illustrated by the formation of β-phenylbenzalacetophenone.[5]



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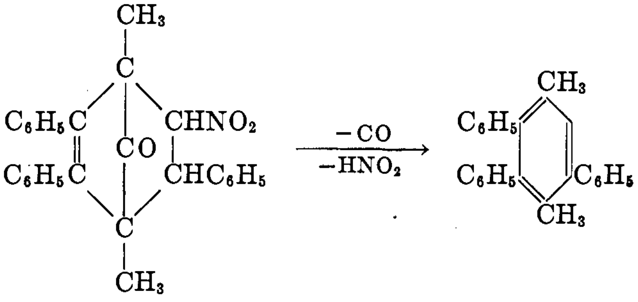
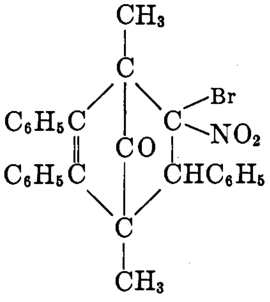
[4] The action of alkaline reagents on carbonyl bridge compounds has not been completely investigated. Although acidic substances appear to predominate, there are usually neutral products, the nature of which has not yet been determined (23). The latter are more numerous when the carbonyl bridge compound contains other functional groups.

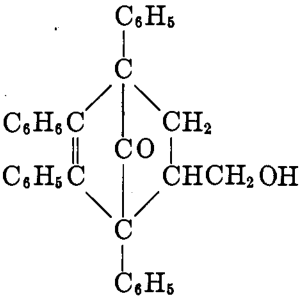
[5] Beilstein, *Handbuch der organischen Chemie*, 4th Edition, Vol. VII: in footnote 2, page 836, it is recorded that the substance $C_{21}H_{16}O$ "could be identical with β-phenylchalcone."

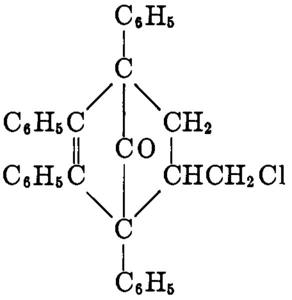
The bicyclic ketones XXII and XXV are the simplest of these carbonyl bridge compounds. There is a considerable variety of bicyclic polyfunctional substances prepared by the same general reaction. The substitution of β-nitrostyrene for styrene gives a nitro derivative (XXIX); this loses nitrous acid during decarbonylation to give the aromatic hydrocarbon. Like other aliphatic nitro compounds, it can be brominated in the form of its sodium derivative. The bromonitro derivative (XXX) decomposes violently when heated; the nature of the reaction has not been determined (19).

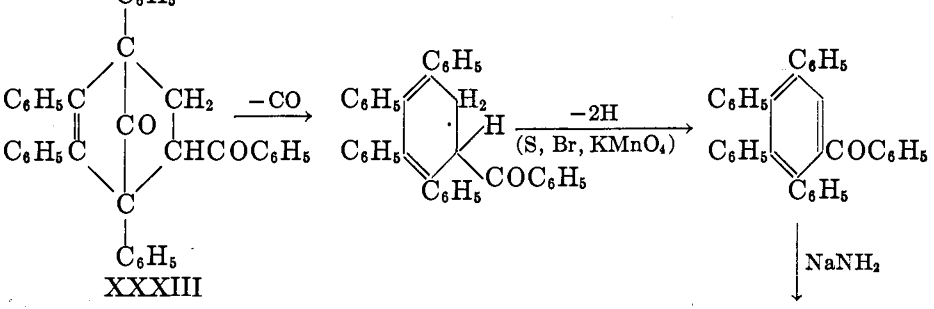

XXIX XXVII

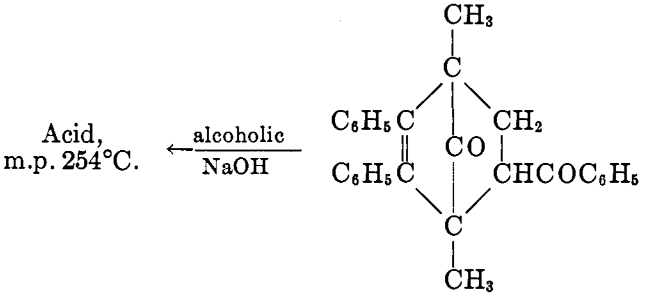

XXX

Allyl alcohol and allyl chloride have been added to tetracyclone, yielding the alcohol XXXI and chloride XXXII, respectively (1), while phenyl vinyl ketone gives the ketone XXXIII (5); the dimethyl analog XXXIV is also known

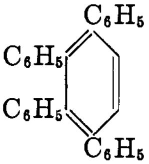

XXXI


XXXII


XXXIII

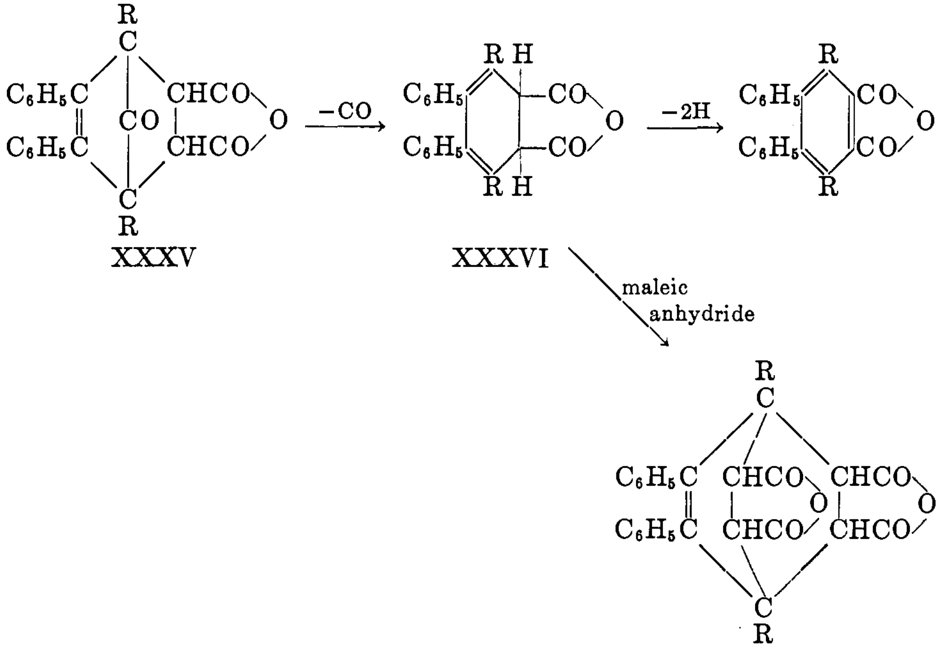


XXXIV



(19). Both ketones have been degraded stepwise to the corresponding benzophenones, which, in turn, were cleaved by means of sodium amide to the known hydrocarbons. The ketone XXXIV gives among other products an acid of undetermined structure upon treatment with alcoholic alkali (23) (*cf.* page 219).

The use of unsaturated anhydrides, acids, and esters gives rise to a considerable variety of polyfunctional carbonyl bridge compounds. The chemical behavior of these depends, in part, upon the substituent groups, as will be seen by the description of several individual instances. Tetracyclone and maleic anhydride readily give the bridged compound XXXV (R = C_6H_5) (15, 50, 51), which easily loses carbon monoxide to form the dihydrobenzene XXXVI. The latter loses the two hydrogen atoms to form the aromatic anhydride very easily; as



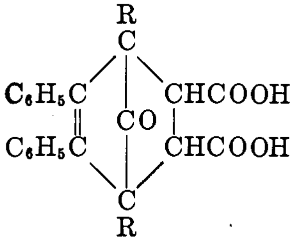
XXXV

XXXVI

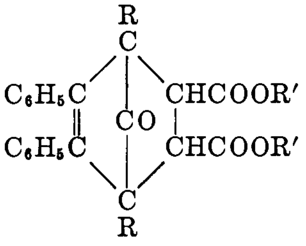
XXXVII

is often true in this work, if proper precautions are not observed, the intermediate products cannot always be isolated before they react to form substances other than those desired. The anhydrides can usually be converted into acids and esters.

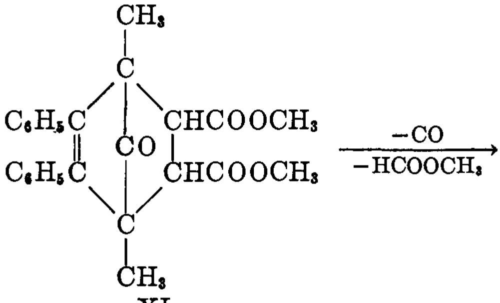
The two conspicuous properties of the bridged anhydride are that (*a*) in the Grignard machine it shows one active hydrogen and two additions (15), and (*b*) if it is heated with maleic anhydride above the temperature of decarbonylation, a dianhydride (XXXVII) is obtained—its formation results from the addition of maleic anhydride to the dihydrobenzene derivative. The dianhydride is often secured during the initial addition reaction of maleic anhydride if suitable precautions are not observed. In order to get the relatively simple anhydride (XXXV; R = H), anhydroacetonebenzil is dehydrated by maleic anhydride at the boiling point of ethylene bromide (15), but the monomethyl homolog can be obtained by the general procedure (22). To secure the optimum yields, a trace of mineral acid is essential. The acids (XXXVIII) are usually secured from the anhydrides but in some instances can be formed directly from the components. The esters (XXXIX) are usually prepared by the addition of maleic, fumaric, or other unsaturated esters to the cyclopentadienones. The use of maleic and fumaric esters often gives rise to stereoisomers, which can be converted into the same aromatic ester. Like the previous bridge compounds, these lose carbon monoxide to give dihydrobenzene derivatives. An unusual reaction was encountered with the *cis*-form of the ester XL, which lost methyl



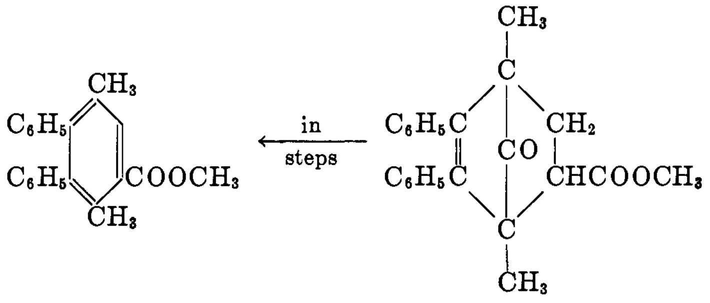
XXXVIII



XXXIX



XL



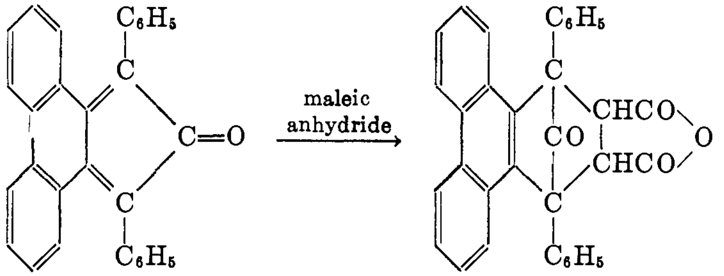
XLI XLII

formate during decarbonylation, to give the aromatic monoester XLI (also prepared (19) by the addition of methyl acrylate to the corresponding cyclopentadienone, followed by decarbonylation and dehydrogenation of the addition product XLII). The presence of the carbonyl group in the acids, anhydrides, and esters is inferred from their analogous behavior with other carbonyl bridge compounds. An oxime has been prepared in one instance (XXXVIII; R = H) (14).

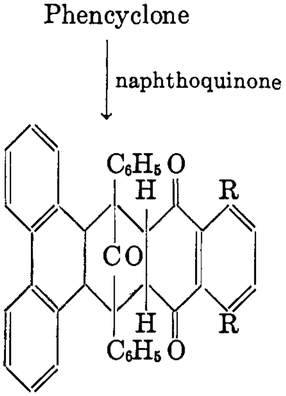
The bicyclic carbonyl bridge compounds are summarized in table 1.

(*ii*) *Multicyclic carbonyl bridge compounds:* For convenience in consideration, the multicyclic series of compounds can be divided into (*a*) the polynuclear series and (*b*) the indenes and related substances.

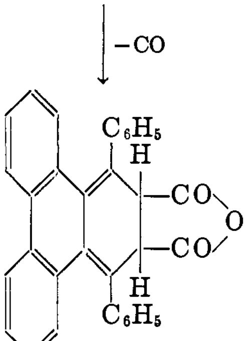
(*a*) The polynuclear series: The members of this group resemble in most respects the various compounds already described. Thus, they are prepared from polynuclear cyclopentadienones, such as phencyclone (XLIII), by similar procedures. In most instances, the bridged compound has been isolated, decarbonylated, and dehydrogenated to an aromatic structure. In illustration, maleic anhydride in benzene or chlorobenzene adds to phencyclone; the addition product (XLIV) loses carbon monoxide and hydrogen, so that the dihydroanhydride (XLV) is never obtained completely pure. The aromatic derivative (XLVI), however, is easily prepared (41).



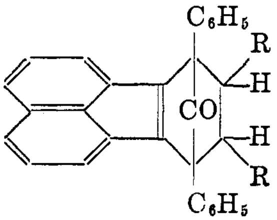
XLIII XLIV



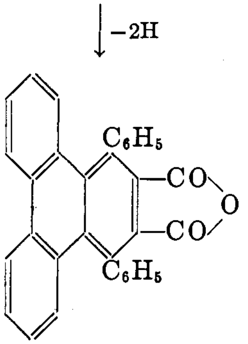
XLVII



XLV



XLVIII



XLVI

Quinones have been added in similar fashion (XLVII) (24, 45); decarbonylation was carried out in boiling nitrobenzene, probably because it resulted in a cleaner product.[6] Acecyclone gives carbonyl bridge compounds (XLVIII) less frequently, for the temperature of decarbonylation is often below that at which they are formed; consequently, the polynuclear dihydro and aromatic fluoranthene derivatives are obtained directly (5, 39).

The multicyclic polynuclear carbonyl bridge compounds are summarized in table 2.

(*b*) The indenes and related substances: Historically, these comprise the earliest known carbonyl bridge compounds, and were the first to have their structures elucidated.

Cyclopentadiene adds to tetracyclone; although the addition product (XLIX) regenerates the components when warmed, it gives a dibromide, and is reducible to a cyclopentane derivative (L). The latter can no longer reverse on warming, so that it loses carbon monoxide in boiling cymene solution (56). The presence of the six-membered carbon ring was shown by degradation after aromatization

---

[6] Since nitrobenzene serves as a dehydrogenating agent, it is frequently used in diene syntheses which cannot otherwise be realized. The aromatization of the dihydro addition products removes them from the equilibrium and the reaction runs to completion.

TABLE 1

Unsaturated bicyclic compounds having a carbonyl bridge

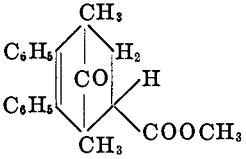
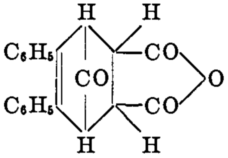
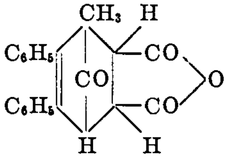
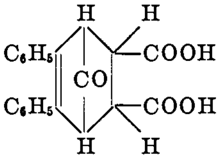
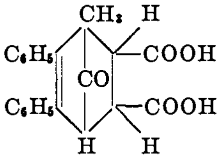
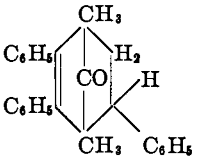
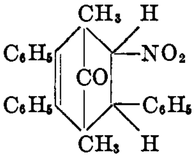
NO.	SUBSTANCE	REFERENCE
XLII		(19)
XXXV; R = H		(15)
		(22)
		(15)
		(22)
XXV		(19)
XXIX		(19)

TABLE 1—*Continued*

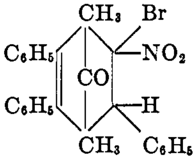
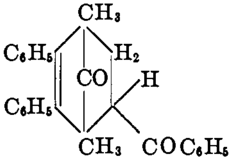
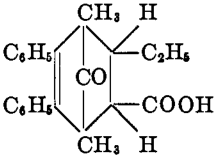
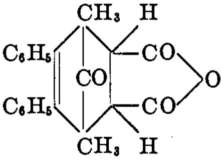
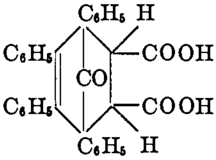
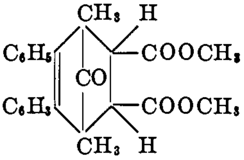
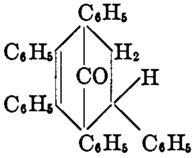
NO.	SUBSTANCE	REFERENCE
XXX		(19)
XXXIV		(19)
		(19)
XXXV; R = CH_3		(19)
XXXVIII; R = C_6H_5		(15)
XL		(19)
XXII		(20)

TABLE 1—*Continued*

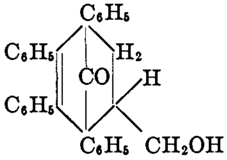
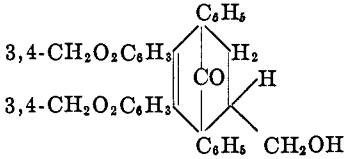
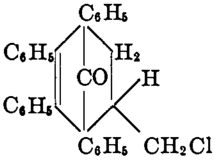
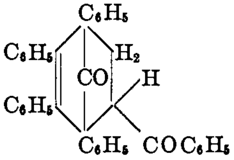
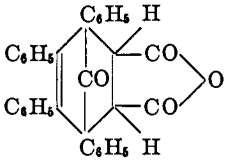
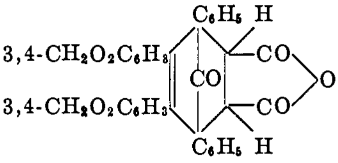
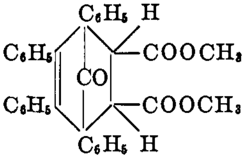
NO.	SUBSTANCE	REFERENCE
XXXI		(1)
		(96)
XXXII		(1)
XXXIII		(5)
XXXV; R = C_6H_5		(15)
		(96)
XXXIX; R = C_6H_5 R′ = CH_3		(15)

TABLE 2

Multicyclic compounds (polynuclear series)

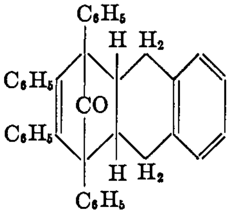
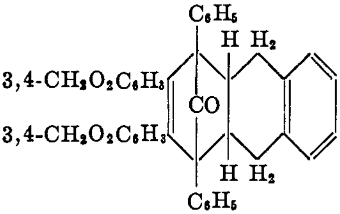
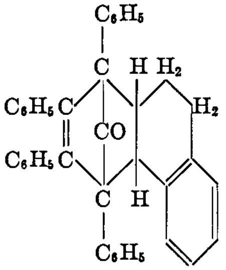
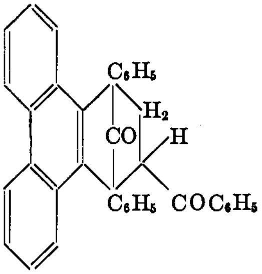
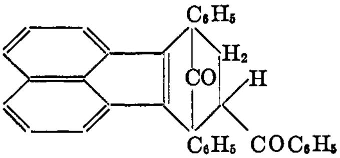
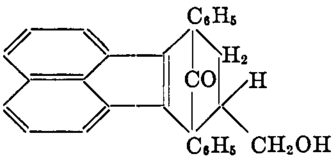
NO.	SUBSTANCE	REFERENCE
		(97)
		(97)
		(97)
		(5)
		(5)
		(1a)

TABLE 2—*Continued*

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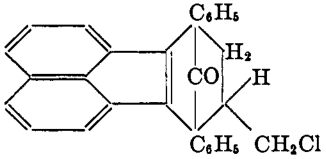
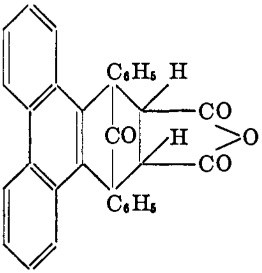
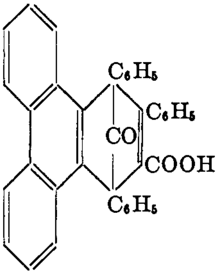
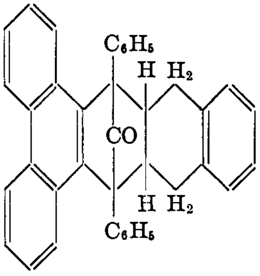
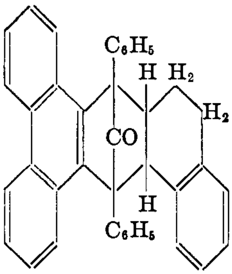
		(1a)
XLIV		(41)
LXXXV		(40)
		(97)
		(97)

TABLE 2—*Continued*

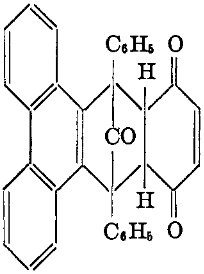
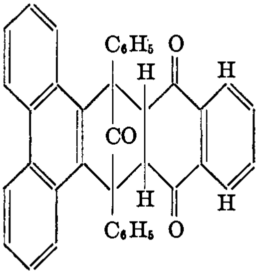
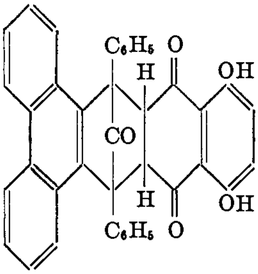
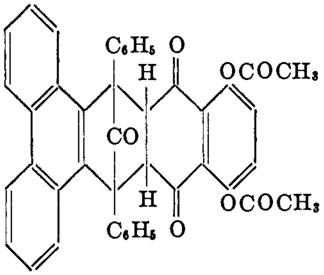
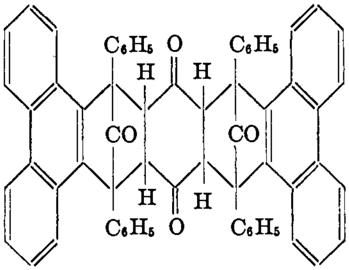
NO.	SUBSTANCE	REFERENCE
		(24, 25)
XLVII; R = H		(24, 45)
XLVII; R = OH		(45)
XLVII; R = $OCOCH_3$		(45)
		(24)

TABLE 2—*Concluded*

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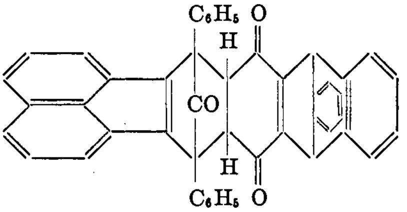
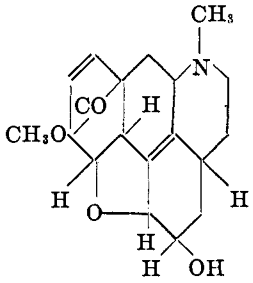
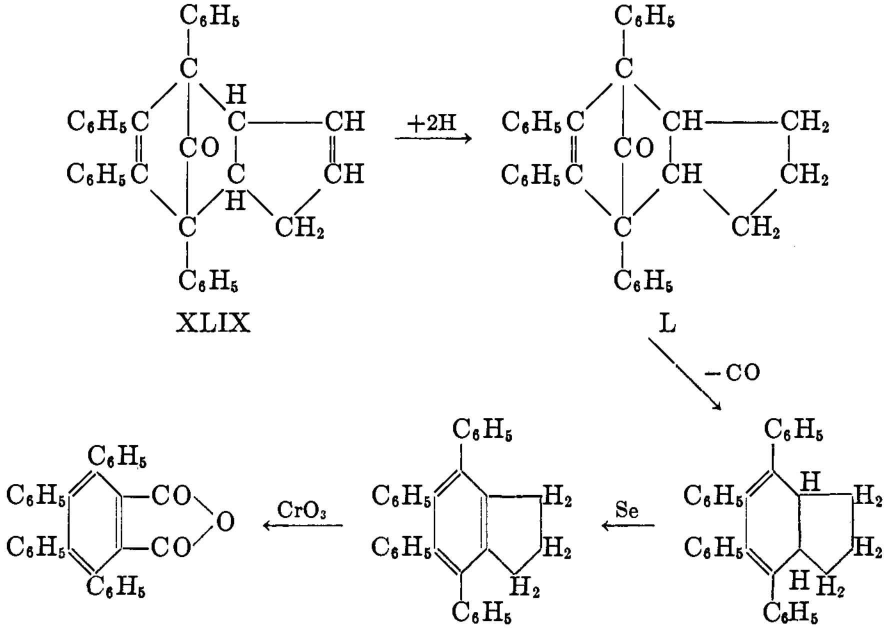
		(1a)
LX		(71)

in the usual way. The presence of the carbonyl group in both XLIX and L was detected in the Grignard machine; each substance consumed one equivalent of reagent without evolution of gas, i.e., underwent one addition (23).



As was mentioned earlier, Japp's anhydroacetonebenzil (XVI) gave a bimolecular product with acidic dehydrating agents, according to the equation:

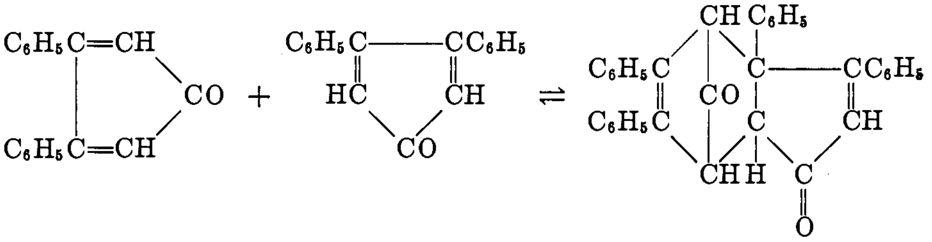
$$2C_{17}H_{14}O_2 \longrightarrow C_{34}H_{24}O_2 + 2H_2O$$

The doubled formula was originally adopted because the substance, when heated, evolved one equivalent of carbon monoxide and gave a product that formed a phenylhydrazone (60), thus:

$$C_{34}H_{24}O_2 \longrightarrow C_{33}H_{24}O + CO$$

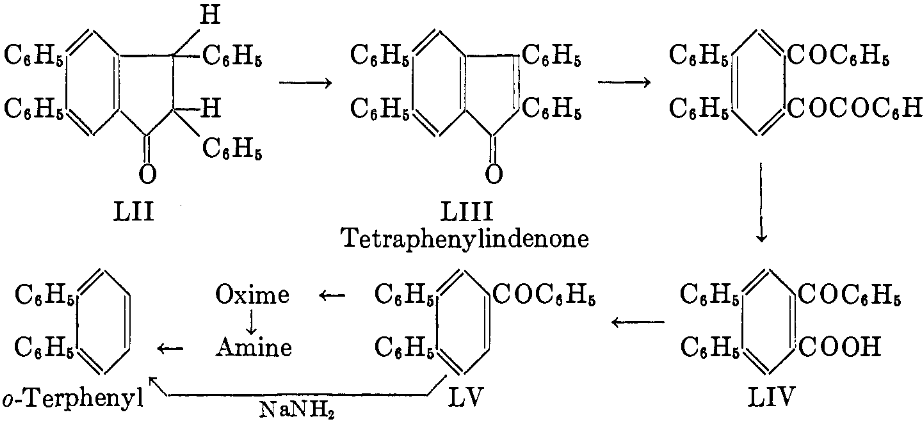
Subsequent cryoscopic molecular-weight determinations in benzene gave values of 463 and 473, whereas the calculated value is 464 (62). The dimeric substance did not give a derivative with phenylhydrazine. Homologous bimolecular products were later obtained with α- and β-methylanhydroacetonebenzils (63), α,β-dimethylanhydroacetonebenzils (54), and amylanhydroacetonebenzil (22). It is important to have a trace of mineral acid present to effect dehydration, for *pure* anhydroacetonebenzil can be distilled unchanged (84). No structures were suggested for the bimolecular product.

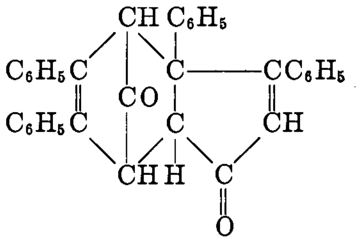
In 1933, Allen and Spanagel proposed a structure for the bimolecular product, as a result of their investigation of anhydroacetonebenzil and related compounds. Noting that diphenylcyclopentadienone (XVII), the dehydration product of anhydroacetonebenzil, was both a diene and a substance containing an ethylenic linkage, they suggested that a diene synthesis occurred (17, 18). The new structure (LI) contains a six-membered carbon ring having a carbonyl bridge and an angular phenyl group, and can be considered to be an indenone. The essential correctness of this structure was shown through a long degradation that terminated in the known *o*-terphenyl; this degradation will be given in detail, since it illustrates the difficulties inherent in dealing with such multicyclic systems.

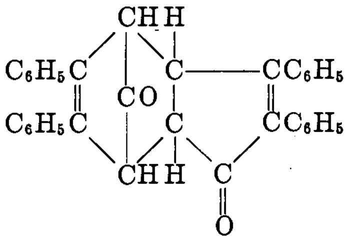

XVII LI

In the first place, the structure LI represents the molecule as having two carbonyl groups, which are linked differently and hence would be unlike in behavior. The bimolecular product loses carbon monoxide, a reaction which indicates dissimilar linkings, and it is a diketone for it forms a dioxime, which exists in stereoisomeric forms. As Japp found, the decarbonylated product is a ketone, for it forms a phenylhydrazone. Allen and Spanagel made the assumption that this ketone was the indanone LII, and this was later found to be correct. To account for its formation from the bimolecular product, it was proposed that there had been a 1,3-rearrangement of a phenyl group. Although the reaction was unrecognized at that time, other instances have since been discovered (11, 20, 21).

The degradation of the indanone proceeded as follows (18): It was first dehydrogenated by the use of sulfur to the red tetraphenylindenone (LIII), and the latter was then oxidized to a triketone in which two carbonyl groups are adjacent. This was cleaved by alkaline hydrogen peroxide to the keto acid LIV, which was then decarboxylated. The oxime of the resulting ketone (LV) was submitted to a Beckmann rearrangement, and the aminoterphenyl produced deaminated through the diazo reaction to *o*-terphenyl; the latter was identical with an authentic specimen. Later on, the ketone was cleaved directly to *o*-terphenyl by means of sodium amide (5), thus avoiding the troublesome manipulations previously encountered. Subsequently, all these degradation products were synthesized by independent reactions (5, 10). The formation of *o*-terphenyl proves the presence of a six-membered ring with two phenyl groups in the ortho-position to each other. The location of the side chain is clear from the keto acid LIV, and the other two phenyl groups are located in the 2- and 3-positions in the indenone LIII. It must be concluded, therefore, that during either the formation of the bimolecular product or the decarbonylation, there has been a 1,3-shift of the phenyl group; the first alternative appears to be more probable. The structure for the bimolecular product shown in LI was accepted by others interested in the field (30, 38), but the stage at which the phenyl shift occurred was not determined. Allen and Gates (8) continued the experimental work and



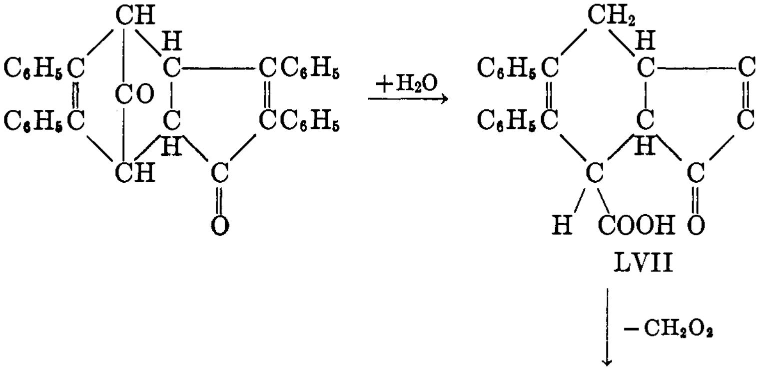

LI


LVI

from the results concluded that the correct structure was that shown in formula LVI.

In the first place, the bimolecular product has the expected molecular weight (62). Second, the phenyl groups are, beyond any reasonable doubt, in the 2- and 3-positions in the indenones. Third,[7] although the bimolecular product was formed at a relatively low temperature, an independent check was considered desirable—this was found in its behavior with alkaline reagents (9), a type of reaction already described (page 219). In the present instance, it is of special interest to note that although there are two carbonyl groups in the bimolecular product, the reaction takes place only with the carbonyl bridge.

The bimolecular product, after treatment with methyl alcoholic potassium hydroxide, gives an acid (sodium alkoxides give the corresponding esters), the analysis of which shows the addition of a molecule of water. Since the acid can no longer be decarbonylated, it is the carbonyl bridge that has become converted to a carboxyl group. Oxidation of the acid (as the sodium salt) results in the loss of CH_2O_2 (formic acid?) and formation of a dienone (LIX). The dienone is an α,β-unsaturated ketone, for it gives a ketone (LVIII) when treated with the Grignard reagent; the formation of a ketone indicates the presence of an ethylenic linkage in the position alpha to the carbonyl group. From these facts it is inferred that the acid is correctly represented by structure LVII. (Although there is, to be sure, another α,β-unsaturated system involving the indene ring, the possibility of 1,4-addition to this is excluded because of the observation that other indenones containing the same system give only carbinols, formed by 1,2-addition.) The oxidation results are accounted for by a retrograde Michael reaction, in which formic acid is split off and destroyed by the oxidizing agent. An additional instance of this reaction is given on page 240.



LVII

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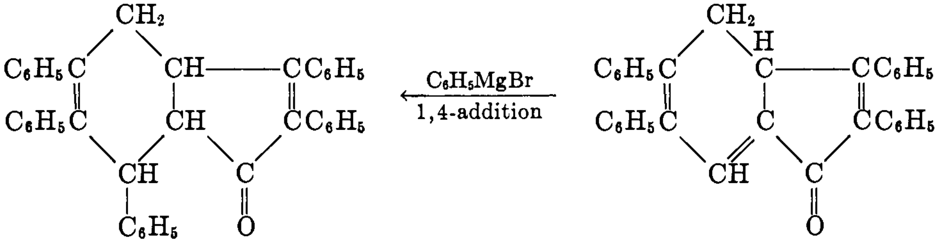
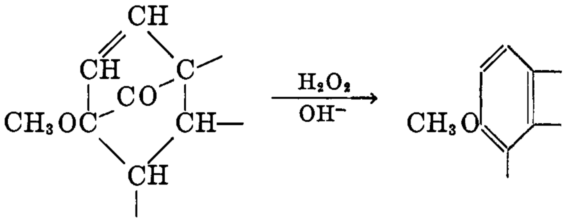
[7] At the time the structure LI was proposed, one of the arguments that appeared to be in its favor was the formation of thiophenol when the substance was heated with sulfur; by analogy with Ruzicka's terpene work (72), the assumption was made that sulfur would remove the angular group as thiophenol. This argument lost its force when it was found that thiophenol was obtained in other sulfur dehydrogenation reactions where there was no reasonable doubt as to the absence of an angular phenyl group (8).



LVIII LIX

This sort of cleavage has an analogy in morphine chemistry; Rakshit (71) found that porphyroxin (LX), upon treatment with sodium hydroxide and hydrogen peroxide, lost CH_2O_2 and gave codeine (LXI) (only partial formulas are used for convenience).



LX LXI

Porphyroxin is an unsaturated carbonyl bridge compound of exactly the same type as those under discussion; unfortunately, the author did not examine its behavior on heating. It does give the usual carbonyl derivatives (oxime, phenylhydrazone, semicarbazone). It is of particular interest to note that the double bond of porphyroxin methyl ether can be reduced, and that the saturated ketone can no longer be cleaved by the alkaline oxidizing agent.[8]

The bimolecular product, then, is represented by the structure LVI. Any open-chain structures for dimers of the diphenylcyclopentadienones are excluded by most of the reactions that have been described, as well as by the fact that α,β-dimethylanhydroacetonebenzil, which forms a dimer, could not give rise to any of the possible open-chain structures. It does not seem likely that the bimolecular product is a mixture, even though it forms two dioximes, because it is regenerated from both of these with the same melting point as the original dimer.

Owing to its many functional groups, the bimolecular product undergoes other reactions. There are three hydrogen atoms in the position alpha to carbonyl groups, all of which can be replaced by bromine (8). The tribromoketone formed gives a dicarbinol with methylmagnesium iodide, showing that it still has two carbonyl groups. When treated quantitatively with methylmagnesium iodide in the Grignard machine, the bimolecular product gives anomalous results, one active hydrogen and one addition (18); the methane is evolved only

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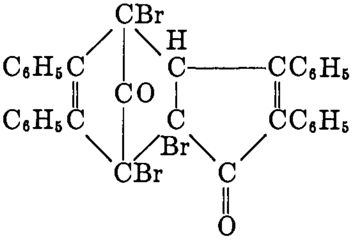
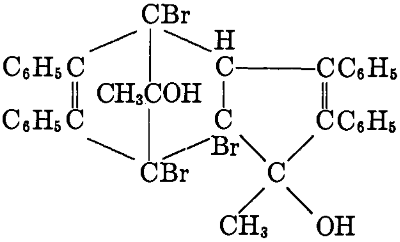
[8] Some doubt has been expressed recently as to the existence of porphyroxin as a definite chemical entity (93).

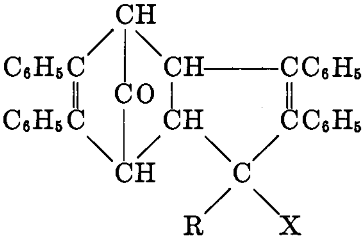


LXII



LXIII

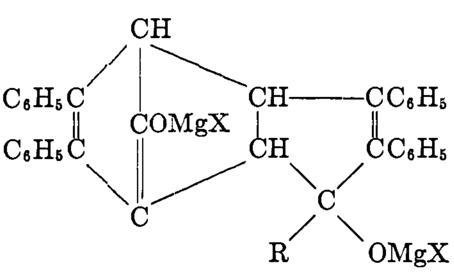
during the heating period, a reaction which indicates that enolization is taking place but that the enol is not already existent. The bimolecular product is not regenerated upon acidification; instead there is formed a carbinol (LXIV), which



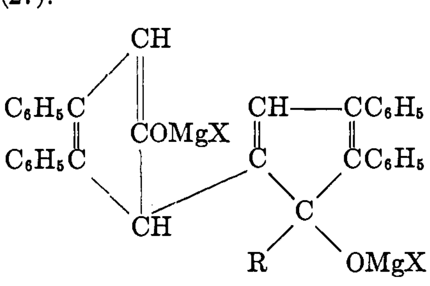
LXIV

still has the carbonyl bridge, for it can be decarbonylated and dehydrated to a hydrocarbon of known structure (when R = C_6H_5 and X = OH, a polyphenylindene results) (11). This indicates that addition has taken place with the indenone carbonyl group. Whether the complex is a real enolate or not, the carbonyl group is obviously covered in some way, for any exposed group would never survive the huge excess of Grignard reagent used.

A bimolecular product which has no available hydrogen does not give off gas with methylmagnesium iodide (19). Thus, it appears that the carbonyl bridge and one of the hydrogen atoms in the position alpha to it are involved. The structure of the magnesium complex is uncertain; as first proposed (8) (LXV), all the facts are accounted for, but the presence of a double bond at the bridgehead is at variance with Bredt's rule (27).[9]



LXV



LXVa

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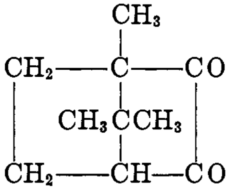
[9] Carvopinone is generally believed to have a double bond at the bridgehead (94).

An alternate possibility is shown in formula LXVa, in which it must be assumed that one ring has been opened under the influence of the Grignard reagent. Upon acidification, recyclization must take place, for the product can be decarbonylated easily. Evidence in its favor is the behavior of camphorquinone (LXXX). This substance has a carbonyl group and adjacent alpha hydrogen, and if its behavior paralleled that of known hindered 1,2-diketones (25a, 25b), it would be expected to be practically completely enolized. Its enol would have to have a double bond at a bridgehead. With methylmagnesium iodide, camphorquinone evolves no gas but shows two additions (23); this indicates that enolization is not likely to occur, if it involves the formation of a double bond at a bridgehead. This analogy was suggested by Woodward (85a), who also favors a structure of the type of LXVa for the magnesium enolate.

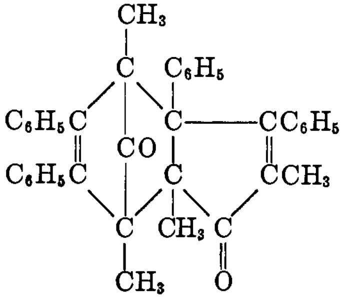


LXXX
Camphorquinone

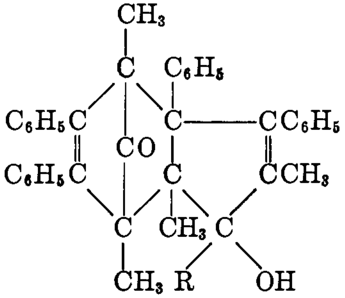
The open-chain structure for the bimolecular product, corresponding to the enolate LXVa and analogous to that of dipyrroles (11a), was considered previously and discarded because (*a*) no such structure is possible in the case of the dimer obtainable from α,β-dimethylanhydroacetonebenzil, (*b*) the bimolecular product does not react with aromatic aldehydes, and (*c*) the easy decarbonylation can be accounted for only by assuming a prior cyclization.

Other bimolecular products, formed by dimerization of cyclopentadienones, are known, but they must have structures corresponding to LI, because they all dissociate to varying degrees in solution or when heated; hence, there have been no rearrangements. For example, Dilthey (44) observed that 2,3,5-triphenylcyclopentadienone was colorless in the solid state, but turned red at the melting point; the values (601, 575, 439, 394, 349) found for the molecular weight were between those for the dimeric (616) and the monomeric (308) formulas. He concluded that this was an intermediate case between the colorless dimeric 3,4-diphenylcyclopentadienone (the bimolecular product described) and the deep red monomeric tetraphenylcyclopentadienone; in considering structures, the possibility of the occurrence of a diene synthesis was mentioned.

Allen and VanAllan (19) found that the dimeric 2,5-dimethyl-3,4-diphenylcyclopentadienone (LXVI) gave products the nature of which indicated that it had partially dissociated to the monomeric form. It gave abnormal values for molecular weight (table 3, page 245), which were taken to indicate about 20 per cent dissociation. The observation that the boiling benzene solution was highly colored, although the solid was white, was interpreted as a confirmation of the assumption that dissociation had occurred, for the known monomeric tetraphenylcyclopentadienone is deep red. The dimethylated dimer forms a hexabromide, the structure of which is unknown, with evolution of hydrogen bromide, and it gives indenols (LXVII) which still have the carbonyl bridge, for they can be decarbonylated; thus, it does not dissociate in all its reactions.

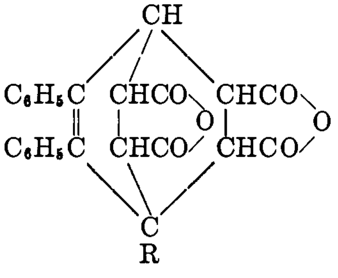


LXVI

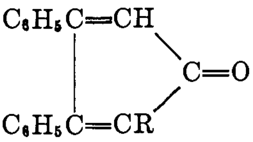


LXVII

Bimolecular products are obtained from monomethyl- and *n*-amyl-anhydroacetonebenzils (22). They appear to be intermediate in properties between the unassociated tetracyclone and the dimerized dimethyl analog (LXVI). The benzene solutions are colorless and there is no addition of maleic anhydride in this solvent, but in boiling trichlorobenzene some carbon monoxide is evolved and a mixture of two anhydrides is obtained. One of these is a dianhydride (LXVIII), which corresponds to the one obtained from the other anhydroacetonebenzils, and which can only have been obtained by a dissociation of the bimolecular product into the monomer LXIX, prior to the addition. The other is a monoanhydride derived from the decarbonylated indenone which has lost both carbon monoxide and a molecule of benzene.



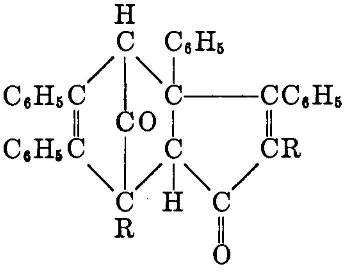
LXVIII



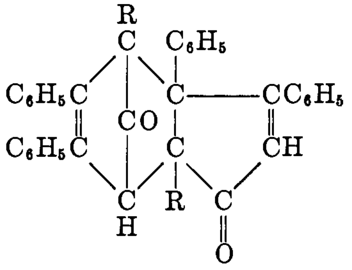
LXIX

Since all these substituted dimers dissociate to give products identical with those derived from the corresponding monomeric anhydroacetonebenzil, it is clear that there has been no rearrangement of a phenyl group; the original bimolecular product, therefore, is an exception. Thus, the difference in the dissociation of the dimers derived from unsubstituted, monosubstituted, and disubstituted anhydroacetonebenzils is one of degree only.

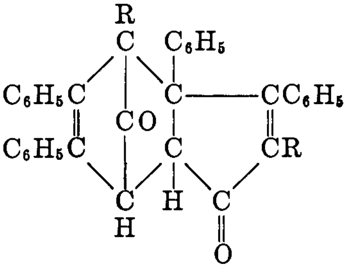
Without regard to the possible existence of stereoisomers, the dialkylated bimolecular products obtained from the monoalkylated anhydroacetonebenzils can have four structures, LXX–LXXIII, depending upon which side of the addend molecule LXIX is used. In order to decide upon one structure among them it is necessary to compare the chemical properties with those of the analogous bimolecular products.



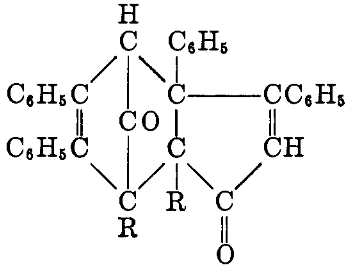
LXX



LXXII



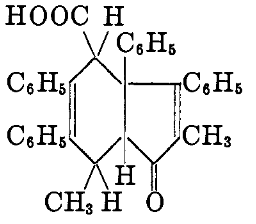
LXXI



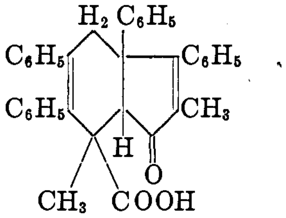
LXXIII

The fact that the bimolecular product dissociates so that a derivative of the monomolecular dienone can be obtained indicates that there has been no rearrangement; that is, it resembles the bimolecular product (LXVI) of dimethylanhydroacetonebenzil. The bimolecular product (LVI) from anhydroacetonebenzil, however, has been shown to differ from the anticipated structure (LI) in the location of a phenyl group, which migrated from the angular position to the 2-position, as discussed previously. Such a rearrangement is possible because of the presence of the hydrogen atom at this point on the indenone ring—with which the phenyl group appears to interchange. The available evidence on angular phenyl groups indicates that they show a great tendency to migrate when this is possible, but there is, as yet, no single instance of a shift involving a displacement of any atom or group other than hydrogen. It may, therefore, be concluded that if there is no rearrangement, there is no hydrogen atom in the 2-position of the indenone ring. Hence, structures LXXII and LXXIII can be excluded. Since all dimerized cyclopentadienones have been formed from anhydroacetonebenzils having phenyl groups in the 2- and 3-positions, it follows that in those bimolecular products that show dissociation there must be an angular phenyl group. The proof of the presence of such a group is secured in the same degradation reactions used to distinguish between the structures LXX and LXXI.

When the dimethylated bimolecular product from α-methylanhydroacetonebenzil is treated with alcoholic sodium hydroxide, a reaction that has been shown to cleave the carbonyl bridge at one end (7), two isomeric acids are obtained (22). The formation of these two acids may be taken to indicate that cleavage has taken place on both sides of the bridge. If structure LXX is arbitrarily selected for the bimolecular product (though this might be considered to have a preference over LXI because its formation would be less sterically hindered), the two acids may be represented by LXXIV and LXXV.



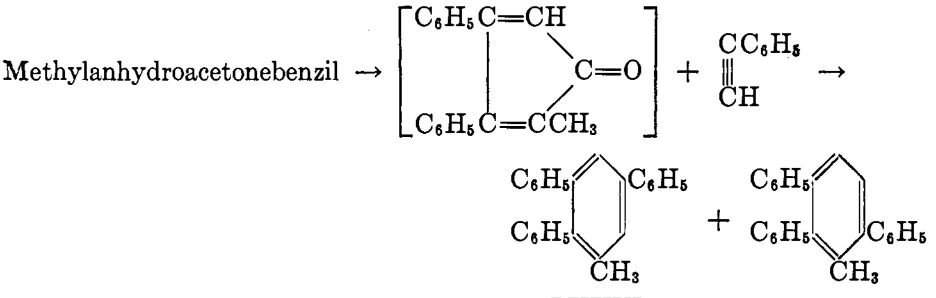
LXXIV



LXXV

It has previously been shown (7) that a γ-carboxylic ketone of the type of LXXV loses CH_2O_2 upon treatment with potassium permanganate. One of these acids exhibits this behavior, and gives a ketone; consequently, to this acid is assigned the structure LXXV.

The second acid, upon similar treatment with permanganate, loses $C_{10}H_{10}O$ and gives an aromatic acid, $C_{26}H_{20}O_2$; this reaction strongly indicates that the methyl and carboxyl groups are not attached to the same carbon atom, so the structure LXXIV is assigned to this acid. Upon decarboxylation, the aromatic acid gives a hydrocarbon, $C_{25}H_{20}$. This hydrocarbon is 2,3,5-triphenyltoluene, which can be synthesized easily from methylanhydroacetonebenzil and phenylacetylene. The synthesis is ambiguous, in that two isomeric hydrocarbons could be formed, owing to the unsymmetrical nature of the components. However, only one product is obtained, and it is identical with the triphenyltoluene formed from the degradation of the dimer. This identity, moreover, definitely eliminates structures LXXII and LXXIII. It also proves the existence of a six-membered ring in the bimolecular product.



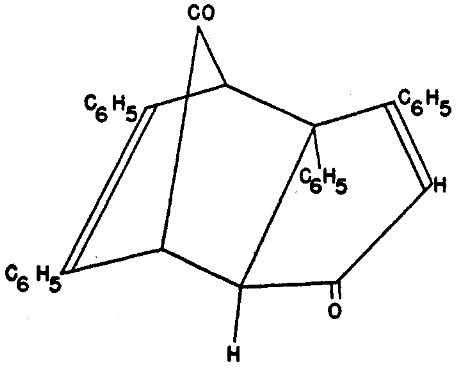
LXXVI

The presence of the third phenyl group, the location of which with respect to the other two is established by the synthesis, is very significant. It furnishes unequivocal proof that there is an angular phenyl group in the acid formed by cleavage of the bridge, and thus in the bimolecular product itself. The presence of this angular phenyl group has previously been inferred from a wealth of evidence, but this is the first time it has been clearly demonstrated.

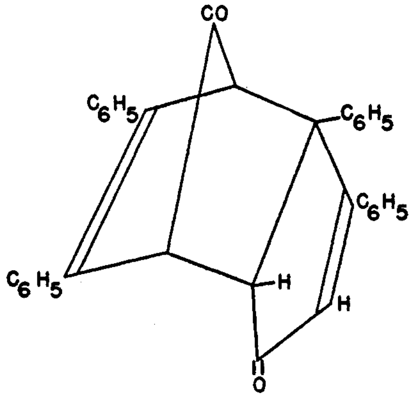
As the two acids that could be derived from LXXI by a similar cleavage of the carbonyl bridge would not be expected to give both these reactions just described (barring a transannular elimination which seems to us extremely unlikely), that structure is eliminated from consideration; the preferred structure for the dimer is that shown in LXX.

Since all the known dimerized cyclopentadienones have been formed from anhydroacetonebenzils having phenyl groups in the 2- and 3-positions, it follows that in those bimolecular products that show dissociation there must be an angular phenyl group.

From an inspection of the structural formula assigned to the bimolecular product, as it appears written in the plane of the paper, it is obvious that stereoisomeric forms are possible. When one views the three-dimensional multicyclic system, the position of the ring planes in space gives rise to a variety of stereoisomers that have been called endo and exo (70d). Practically always only one form is produced in a reaction, and when its configuration has been determined, it has been endo. Such forms are shown in formulas LXXVII and LXXVIII. By analogy with the behavior of cyclopentadiene, the bimolecular products from the cyclopentadienones are assumed to be endo, with the reservation that such a generalization is not absolute. A stereoisomeric substance, which may have the exo configuration, was obtained from the endo form by the action of certain oxidizing agents.

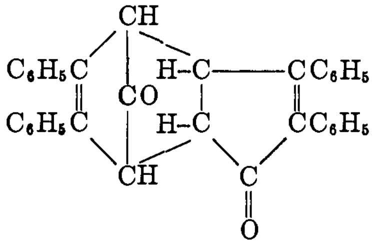


LXXVII
exo

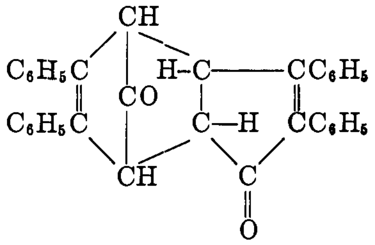


LXXVIII
endo

Stereoisomeric forms are also possible in which the rings are joined in *cis* and *trans* positions. Interconversion of the two forms could be visualized as possible through a process of enolization, as Hückel was able to realize quantita-



LVIa



LVIb

tively in the conversion of *cis*-decalone to the *trans*-form (57).[10] The bimolecular product obtained from anhydroacetonebenzil was assigned the *cis* structure (LVIa) on the inconclusive evidence that the product formed on decarbonylation readily added maleic anhydride; such an addition is in accordance with the *cis* principle. From an examination of models it was observed that this particular bicyclic ring system linked in the *trans* positions could not add maleic anhydride without a distortion which is so great that it practically rules out such a possibility.

When the bimolecular product is stirred at room temperature with cold alkaline hydrogen peroxide, it gives a "peroxide" containing four extra atoms of oxygen; while the product seems stable at room temperature, it decomposes violently when heated. This new peroxide liberates iodine from potassium iodide in acetic acid, and bromine from hydrobromic acid, the starting material being regenerated. However, when it is dissolved in acetic acid, oxygen is liberated, and an isomer of the starting material results (9).

This isomer still contains a carbonyl bridge, for it evolves carbon monoxide when heated; the other product is an indanone (LXXIX) isomeric with LII (13). All other reactions are the same as that of the starting material: e.g., it gives the same acid with alcoholic potassium hydroxide, shows one active hydrogen and one addition, and gives the same carbinol with phenylmagnesium bromide. That is, reactions used to prove structure indicate that the groups are linked alike in both substances; the difference between the two, therefore, must be of a spatial nature. The fact that both give the same derivatives can be accounted for by interconversion catalyzed by acidic or basic substances present in all reactions. The only reaction carried out in the absence of catalysts is the pyrolysis; in each case, this leads quantitatively to a different substance.

When the original bimolecular product (LVI) was treated with chromium trioxide in acetic acid, varying but poor yields of oxygen-containing substances were obtained (13); the latter were not of constant composition, never containing as much as four atoms of oxygen, but all showed the same behavior in reactions, as described in the preceding paragraph. It appears that oxidation of this type

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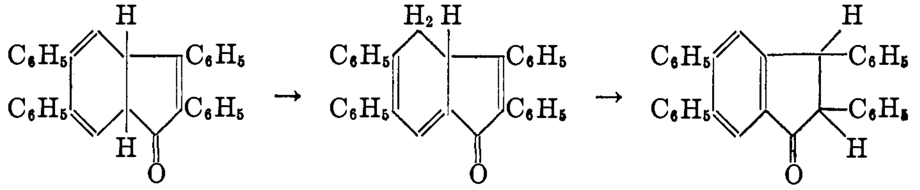
[10] This easy interconversion was explained as proceeding through the enol (which would have a double bond at a bridgehead and not be in accord with Bredt's rule). Whether a parallel reaction would take place in the hydrindone series is unknown, since only the β-ketone has been examined (58).

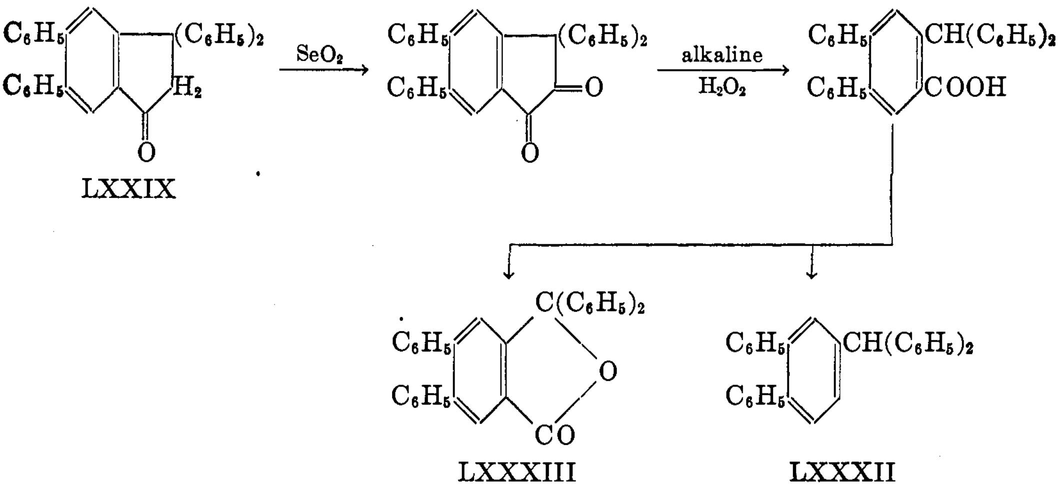
of carbonyl bridge compound yields some sort of peroxide, and is thus unsuitable for proving structure in the ordinary way. It will be recalled that the results of the Grignard machine examination indicated one enolizable hydrogen, and that enolic forms (LXV and LXVa) were suggested. Now, since Kohler has shown (65) that enols of unsaturated ketones easily form peroxides, the instances just cited find some support. These two anomalous properties, enolization and peroxide formation, must be connected in some way with the presence of the carbonyl bridge and an adjacent hydrogen atom, as well as space relations, for the new isomer which is formed from decomposition of the peroxide does not itself form a peroxide. At the present time, the structure of these oxygen-containing substances is left in abeyance, but, presumably, one oxygen atom has added to each ethylenic linkage to give a multicyclic polyoxido system. Whether the bimolecular product and its isomer are of the exo,endo or *cis,trans* types is unsettled.

The products of decarbonylation of both isomers must next be described. Although, as outlined, Japp (60) obtained the dihydroindanone LII directly, Allen and Spanagel (18) were able to isolate an isomeric indenone which was easily rearranged to Japp's substance. Furthermore, Allen and Gates (7) obtained an additional indenone (LXXXII) and showed that it was an intermediate between the two, LXXXI and LII. The only difference in the three isomers is in the location of double bonds and hydrogen atoms. The first dienone was assigned the structure LXXXI, for it added maleic anhydride; the evidence for the others has already been given. The sequence terminating in Japp's indanone is accomplished in the laboratory by heat and/or acidic catalysts. Probably it goes in the direction indicated, because each form has an increased stability; the isolated double bonds (one pair conjugated) first become a long conjugated system (LXXXI) and then aromatize.



LXXXI LXXXII LII

The isomeric indanone formed on decarbonylation of the *trans*-isomer has the structure LXXIX. This was shown by degradation to the known substances LXXXII and LXXXIII, which were synthesized independently (9). Analogous reactions of indanones lacking the *Ar*-phenyl groups were exactly parallel. In the structure thus established, there are now two phenyl groups on one carbon atom. It must be concluded, therefore, that in this instance there has been a 1,2-shift of a phenyl group;



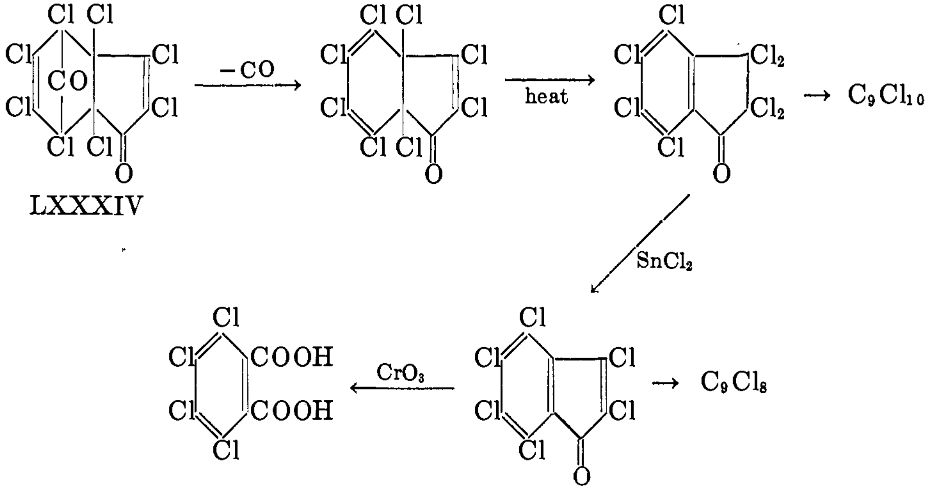
LXXIX

LXXXIII

LXXXII

apparently, configuration can be a determining factor in the nature of rearrangements.

A completely chlorinated carbonyl bridge compound in the indenone series, LXXXIV, was discovered by Zincke many years ago (89). Its structure was established by a stepwise degradation, eventually producing tetrachlorophthalic acid. The carbonyl group in the indane-indenes was detected by means of phosphorus pentachloride (88, 90). The similarity between this series and the bimolecular product LVI should be noted, in particular that here there is a 1,3-shift of chlorine, comparable to the 1,3-phenyl rearrangement.



LXXXIV

An as yet unexplained feature is the observation that molecular-weight determinations of the bimolecular products, while satisfactory in benzene and other solvents, are unreliable in boiling carbon tetrachloride. The values are given in table 3.

Another noteworthy feature encountered in the work with carbonyl bridge compounds is the frequency with which they retain solvent of crystallization. The most conspicuous examples of solvents are benzene and acetic acid. Prolonged drying *in vacuo* is required to obtain good analytical figures from substances that exhibit this behavior.

(c) Other types of addends

(*i*) *Acetylenic compounds:* Earlier in this article it was pointed out that substances containing an acetylenic linkage would add to cyclopentadienones. With this class of addends, the carbonyl bridge is usually eliminated during the reaction, and the substance formed is a dihydrobenzene that is easily dehydrogenated to give an aromatic structure. In this way a large number of polyarylated benzene derivatives has been secured (15, 19, 22, 37, 40, 42, 43, 49, 50, 51).

There is no doubt that a carbonyl bridge compound is an intermediate, but the temperature of reaction is above that of decarbonylation. An explanation of the easy cleavage will be discussed later. In one instance, the carbonyl bridge compound was isolated—when phenylpropiolic acid added to phencyclone (LXXXV) (40) (see page 257).

TABLE 3

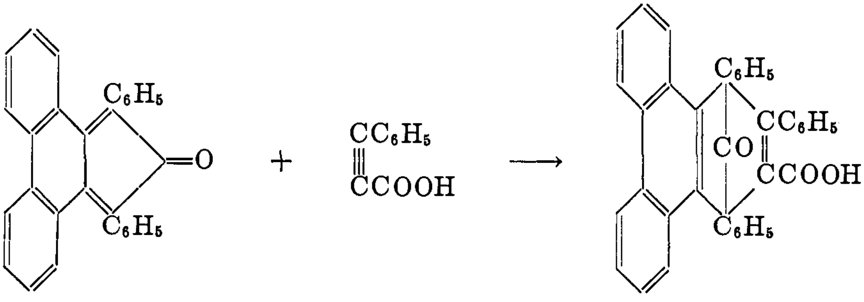
Molecular-weight determinations of bimolecular products

	MELTING POINT	MOLECULAR WEIGHT		
		Calculated	Found	
			In C_6H_6	In CCl_4
	°C.			
Unsubstituted; LI	206	464	463* 463, 473†	388, 385
Dimethyl	230	492	461*	400
Di-*n*-amyl	154	604	578*‡	491
Tetramethyl; LXVI (19)	181	520	414, 417*	470, 380

* Ebullioscopic (22).

† Cryoscopic (62).

‡ In ethanol*, 635; in chloroform*, 594, 587; in methylene chloride*, 590 (22).



LXXXV

TABLE 4

Multicylic compounds (indene series)

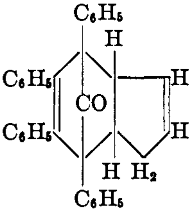
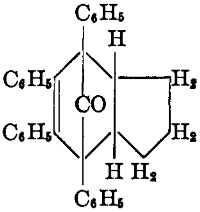
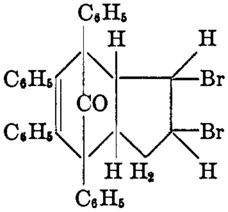
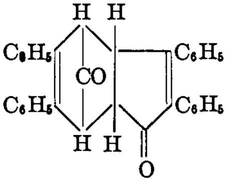
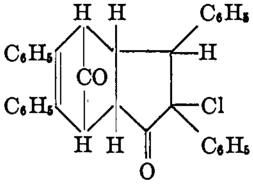
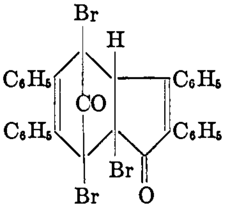
NO.	SUBSTANCE	REFERENCE
XLIX		(56)
L		(56)
		(56)
LVI		(7, 13, 18, 60)
		(13, 30)
LXII		(8)

TABLE 4—*Continued*

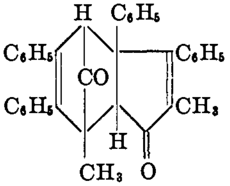
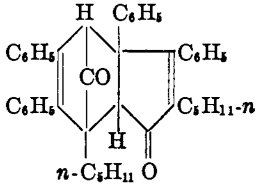
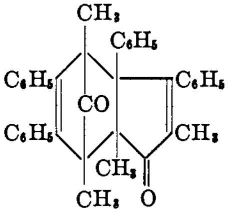
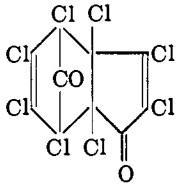
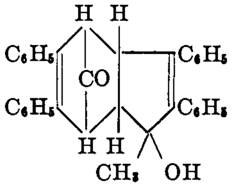
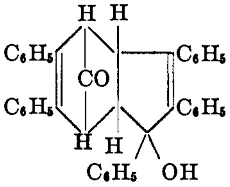
NO.	SUBSTANCE	REFERENCE
LXX; R = CH_3		(63)
LXXI; R = n-C_5H_{11}		(22)
LXVI		(54)
LXXXIV		(88)
LXV; R = CH_3 X = OH		(8)
LXV; R = C_6H_5 X = OH		(8)

TABLE 4—*Continued*

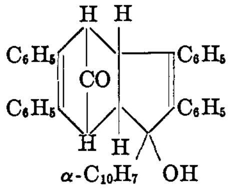
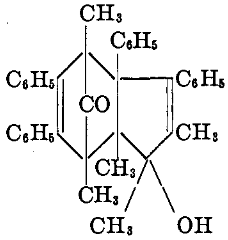
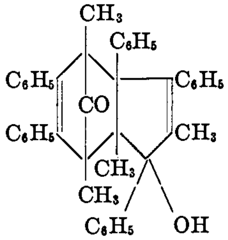
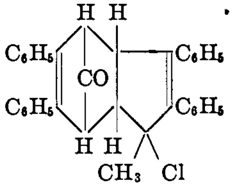
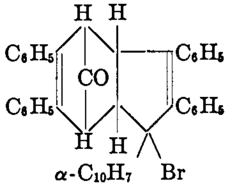
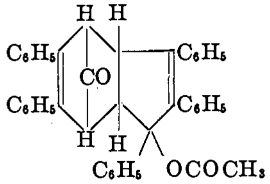
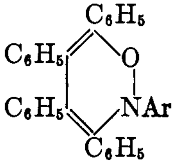
NO.	SUBSTANCE	REFERENCE
LXV; R = α-$C_{10}H_7$ X = OH		(8)
LXVII; R = CH_3		(19)
LXVII; R = C_6H_5		(19)
LXV; R = CH_3 X = Cl		(8)
LXV; R = α-$C_{10}H_7$ X = Br		(8)
LXV; R = C_6H_5 X = $OCOCH_3$		(8)

TABLE 4—*Continued*

NO.	SUBSTANCE	REFERENCE
LXXX	Structures not yet determined	
	B.P. Peroxide	(9)
	$C_{35}H_{28}O_3$	(13)
	$C_{34}H_{23}O_2Cl$	(8)
	$C_{34}H_{22}O_2Cl_2$	(16)
	$C_{34}H_{22}O_2Br_2$	(16)
	$C_{38}H_{32}O_2Br_6$	(19)

A few points of particular interest may be mentioned: 1,2,4,5-tetraphenylbenzene has been obtained from (*a*) anhydroacetonebenzil and tolane and (*b*) the dimer of 2,3,5-triphenylcyclopentadienone (which is another of the carbonyl bridge bimolecular products that dissociates) and phenylacetylene; this tetraphenylbenzene proved to be identical with the one formed by the action of phenylmagnesium bromide on hexabromobenzene (43). While the phenylacetylene might have added in two ways to give isomers, only the one hydrocarbon was produced. Dilthey also prepared 1,2,3,4-tetraphenyl-, hexaphenyl- and pentaphenyl-benzenes. The last-named hydrocarbon has also been obtained from tetracyclone and β-nitrostyrene; the addition product was not isolated since it lost carbon monoxide and nitrous acid so easily (6).

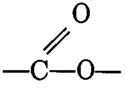
(*ii*) *Nitroso compounds:* A few aromatic nitroso compounds have been added to tetracyclone and phencyclone (44, 46), the —N=O double bond resembling a C=C linkage. No intermediate carbonyl bridge compound could be isolated, for decarbonylation occurred too easily, but there seems to be little doubt that it was an intermediate. The similarity in structure of the final product, the oxazine LXXXVI, to other decarbonylated dihydroaromatics is noteworthy.



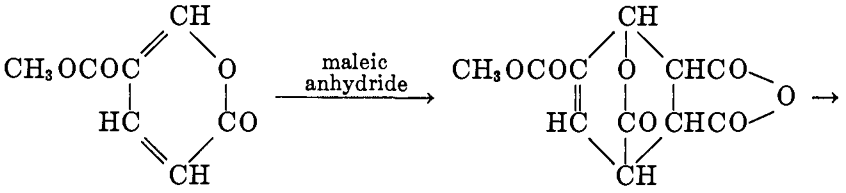
LXXXVI

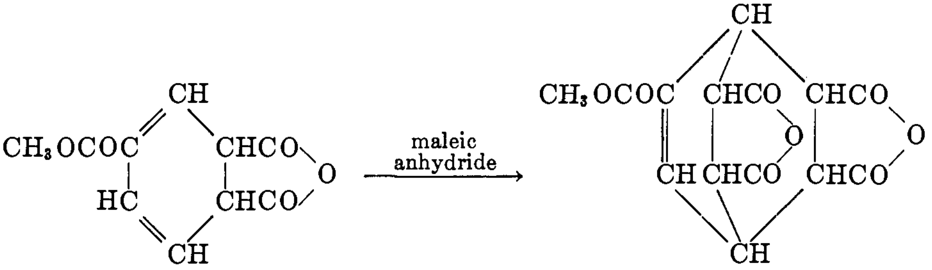
(d) Unsaturated six-membered rings having lactone and anhydride bridges

Two other types of bridged six-membered rings are related in their behavior to the carbonyl bridge compounds; they are lactones and anhydrides.



The lactones, which have a $-\overset{O}{\overset{\|}{C}}-O-$ bridge between the 1- and 4-positions, are obtained by the application of the diene synthesis to pyrones (2, 36). If the synthesis is carried out at a moderate temperature, the desired addition product LXXXVII is formed, but at higher temperatures the bridge is lost as carbon dioxide; the expected dihydroaromatic substance (LXXXVIII) at once adds a second molecule of maleic anhydride to give LXXXIX. The bridge can be eliminated from the addition product by moderate heating, and the dihydro compound (not isolated) aromatized.

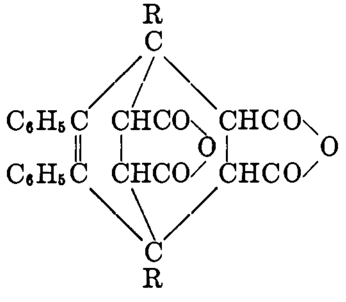

LXXXVII

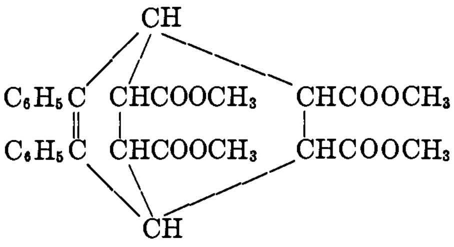

LXXXVIII LXXXIX

If an acetylenic addend is used, the addition product cannot be isolated, for it immediately loses carbon dioxide (2). The behavior of these lactone bridged compounds is thus completely parallel to that of those having a carbonyl bridge.

The various cantharic acids are written (87) as having a lactone bridge between the 1- and 3-positions without any rigorous proof of structure, or comment on behavior towards heat (whether they are saturated or unsaturated), except that while pseudocantharic acid is stated to decompose on distillation, it can be sublimed, with melting point dropping from 187° to 174°C. ("unwesentlich")! The known substances having a lactone bridge are summarized in table 5.

Several of the anhydride bridge compounds (XXXVII, LXVII, LXXXIX) have already been mentioned; they were obtained as end products in reactions


XXXVII


XC

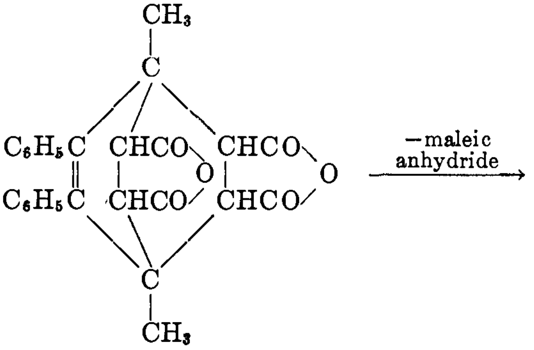
carried out at elevated temperatures with maleic anhydride as a solvent, the primary addition product losing carbon monoxide or dioxide during the reaction.

All compounds formed by addition of maleic anhydride to the terpenes and polynuclear aromatic hydrocarbons will be omitted, since these have been summarized elsewhere (70). Those related to this work are collected in table 6.

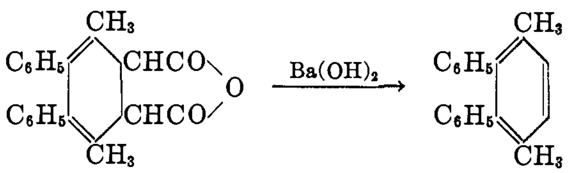
The chemical reactions of the dianhydrides are those expected from their structures; they may be restricted somewhat on account of steric influences. The dianhydride XXXVII (R = H) can be esterified completely to give the fully alkylated ester (XC) of the tetracarboxylic acid (18).

The substituted dianhydride XXXVII (R = CH_3) titrates as a dibasic acid in the cold, the second ring opening only on warming (19).

When heated to elevated temperatures, the dianhydrides lose one equivalent of maleic anhydride; this is separable by distillation, but the residue, which is a dihydroaromatic (XCII), is often difficult to manipulate because of decomposition brought about by the heat. If barium hydroxide is previously mixed intimately with the dianhydride XCI, decarboxylation takes place in addition to the loss of the maleic anhydride, and an aromatic hydrocarbon is formed (12). This affords a source of certain highly arylated hydrocarbons not readily obtainable in other ways; e.g., 2,3-diphenyltoluene (22); 2,3-diphenyl-*p*-xylene (19); 2,3-diphenyl-*n*-amylbenzene (22).



XCI



XCII

IV. Loss of the Bridge and its Relation to the Double-bond Rule

In the previous pages, a summary of the behavior of a variety of closely related bridged compounds has been given. All these had as common features of structure (*a*) a six-membered ring containing an ethylenic linkage, (*b*) a bridge, and (*c*) a particular relation between the unsaturation and the bridge. As a common property, they all lost the bridge when heated, giving rise to a dihydroaromatic compound; the bridge appeared as a small molecule. While

TABLE 5

Unsaturated six-membered ring compounds with a lactone bridge

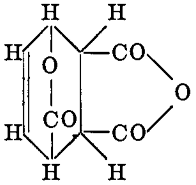
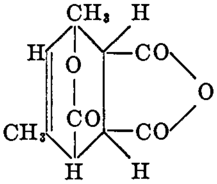
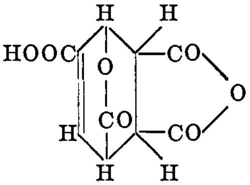
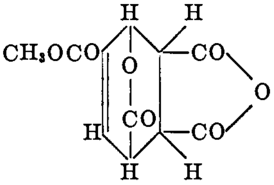
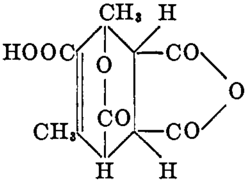
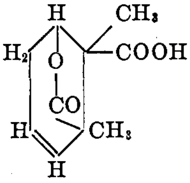
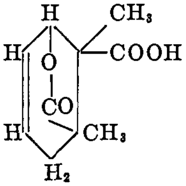
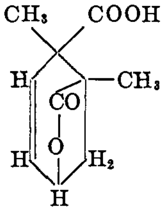
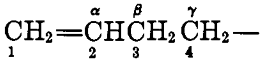
NO.	SUBSTANCE	REFERENCE
		(35)
		(35)
		(35)
LXXXVII		(35)
		(35)
		(83)

TABLE 5—*Continued*

NO.	SUBSTANCE	REFERENCE
		(83)
		(83)

this behavior was at first incorrectly associated with the nature of the bridge, it has become obvious with the accumulation of a large number of instances, that it is not a property of the bridge as such, but it is its relation to the unsaturated linkage that is responsible for this cleavage.

Staudinger (76) was the first to point out that in an unsaturated bond system, such as



$$\underset{1}{CH_2}{=}\overset{\alpha}{\underset{2}{C}}H\overset{\beta}{\underset{3}{C}}H_2\overset{\gamma}{\underset{4}{C}}H_2—$$

the strength of the bonds between carbon atoms 3 and 4 (or β to the double bond) is less than that between 2 and 3, so that should scission occur, it would take place preferably at that point. This was independently enunciated by Hurd (59). In a paper on the dissociation of carbon bonds, Schmidt (74) drew attention to the double-bond rule—"the double bond between two carbon atoms strengthens the following single carbon bond and weakens the next following"—and cited seven instances. This statement is conveniently known as Schmidt's double-bond rule (52).

Using the ketone XXII in illustration, it will be noted that in the structural formula there are two sets of single bonds which are beta to the ethylenic linkage. Either of these would be likely to cleave according to the double-bond rule. If cleavage occurs in the direction indicated by the dashes, the result is tetracyclone and styrene—that is, the components have been regenerated, and the diene synthesis has been reversed. However, if the molecules break as indicated by the dots, carbon monoxide is split out, and pentaphenyldihydrobenzene is formed. Since the diene synthesis is reversible, while the loss of carbon monoxide is irreversible, the reaction will run to completion in this direction (namely, elimination of the bridge). (See page 257.)

TABLE 6

Six-membered ring compounds with an anhydride bridge

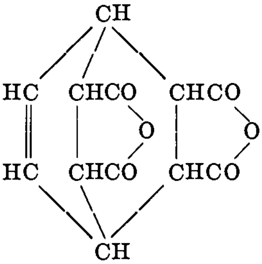
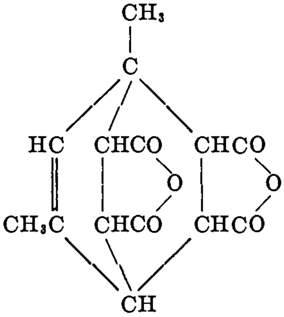
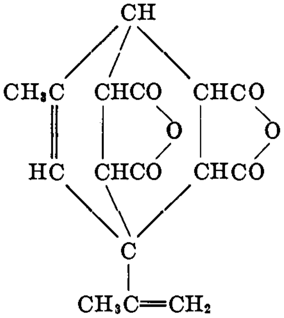
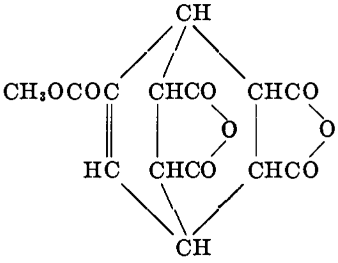
NO.	SUBSTANCE	REFERENCE
		(36)
		(36)
		(33)
LXXXIX		(36)

TABLE 6—*Continued*

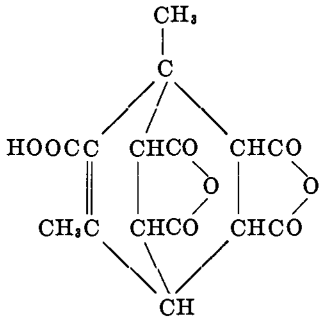
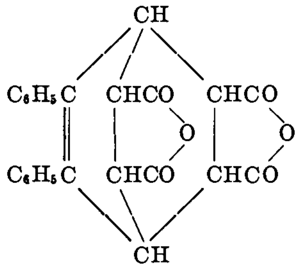
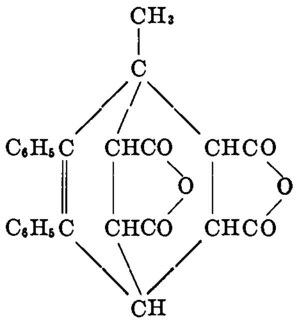
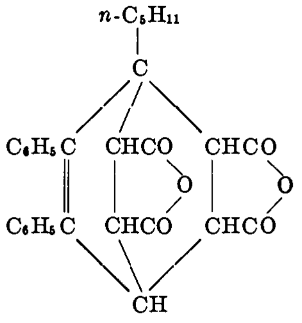
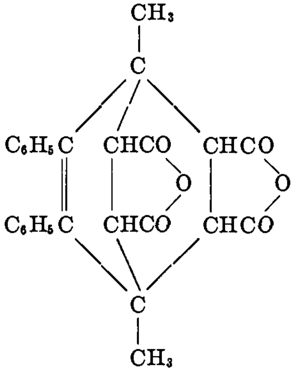
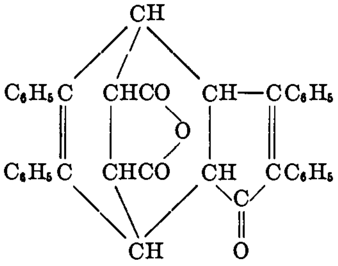
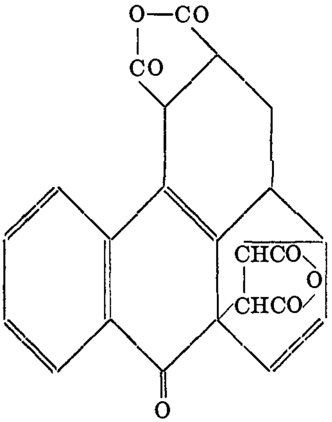
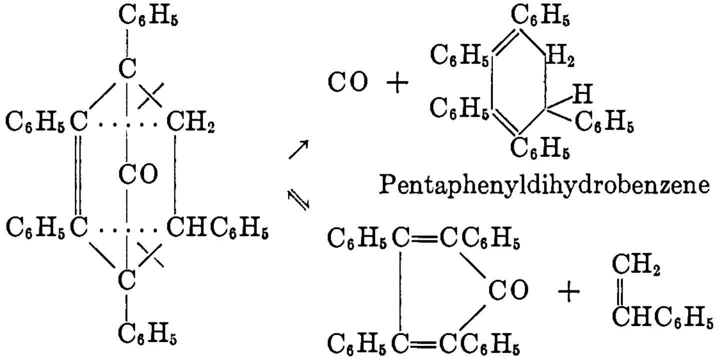
NO.	SUBSTANCE	REFERENCE
		(36)
XXXVII; R = H		(15, 18)
LXVII; R = CH_3		(22)
LXVIII; R = n-C_5H_{11}		(22)

TABLE 6—*Concluded*

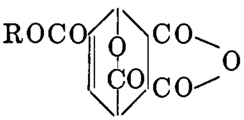
NO.	SUBSTANCE	REFERENCE
XCI		(19)
		(18)
		(34)

Taking the double-bond rule into account, it is thus possible to predict what products of heating are to be expected in similar instances. The lactone bridge ester LXXXVII would lose carbon dioxide, and the dianhydrides would lose maleic anhydride. On experiment these reactions were found to take place.

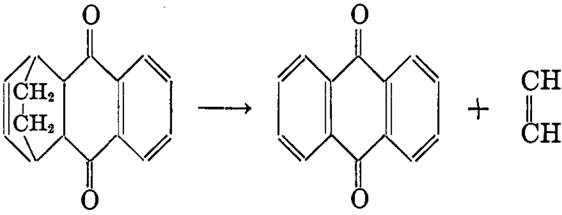


XXII Pentaphenyldihydrobenzene Tetracyclone Styrene

A considerable number of endoethylene bridge compounds of the type XCIII, formed by the diene synthesis, are likewise unstable to heat; ethylene is lost and a dihydroaromatic substance obtained (35). It should furthermore be noted



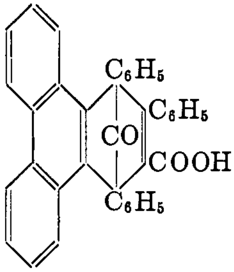
LXXXVII



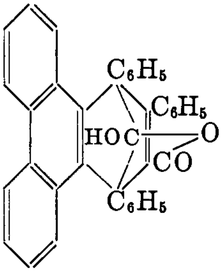
XCIII

that in these bridged compounds the ethylenic linkage affects *both* bonds holding the bridge. This was not the case with the large-membered ring ketones VIII and XII considered in the first part of this paper. This difference in linkage affords a partial explanation of why the bridge was not lost when they were submitted to high-temperature distillation. Finally, saturated six-membered bridged rings should be stable when heated. The terpene ketones are, for they can be distilled.

In the case of acetylenic addends, the bridge bonds come under the influence of two double bonds, i.e., they are in the β-position; thus, they will be weakened to a much greater degree, and it would be expected that the bridge would be



LXXXV

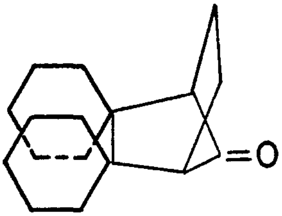


XCIV

lost more easily, as is, indeed, found to occur. Conversely, it would be very difficult or impossible to isolate the bridged compound. The only exception, the acid LXXXV, can be accounted for by assuming that the carboxyl group has formed a ring with the bridge. On account of the observation that this acid did not dissolve as expected, even in alcoholic alkali, Dilthey (40) devised such a ring structure (XCIV).

It may be noted that practically all of the carbonyl bridge compounds examined have phenyl groups at the ends of the ethylenic linkage. No method has yet been discovered for reducing this double bond, so that comparable saturated carbonyl bridge compounds are unknown. When the simplest indene having a carbonyl bridge (XLIX) is reduced by hydrogen in the presence of the very active platinum oxide catalyst, only the double bond in the side chain is affected (56); the indane L results.

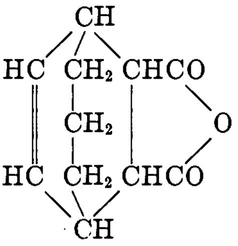
It is believed that in order for reduction to take place (at least in aromatic nuclei) the molecule to be reduced must be adsorbed on the surface of the catalyst in a planar configuration (92). Thus, the catalytic reduction of a hindered biphenyl derivative, in which rotation about the bond connecting the two phenyl groups was impossible, could not be accomplished even by the most drastic conditions of temperature and pressure (93). A similar situation is met in the compound under discussion. The two phenyl groups attached to the doubly bound carbons cannot lie in the plane of the double bond (*cf.* *o*-terphenyl (91)). This would offer considerable hindrance toward the double bond being adsorbed on any plane catalytic surface. In addition, the carbonyl group not only offers hindrance to adsorption but also forces the cyclohexene ring into the "bed"

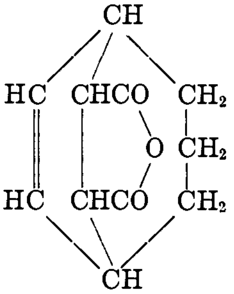


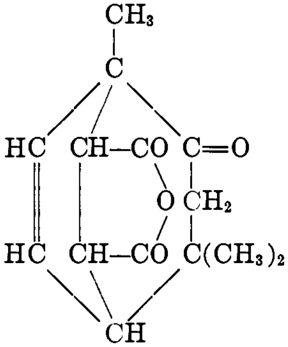
form, such that it also hinders adsorption. Thus, assuming the correctness of the adsorption hypothesis, it would appear that the reduction by catalytic methods of the ethylenic double bond bearing two phenyl groups is most unlikely to take place.

Summarizing, the behavior of the bridged molecules in a six-membered ring having an ethylenic linkage is in accord with and explicable in the light of the double-bond rule. *The behavior of the bridge is dependent upon its relation to the double bond, and not on the nature of the atoms forming the bridge.* As Norton states, it is to be emphasized "that the bridge, as such, does not confer special properties on the atoms included in the bridge, although the natural human tendency appears to be that one will tend to place the more reactive portion of the molecule in the bridge on drawing the structure of such a bridged compound" (70).

Cycloheptadiene and eucarvone form addition products XCV and XCVI with maleic anhydride (3, 60, 85). Each of these substances can be considered either as a six-membered ring with a three-atom-chain bridge, or as a seven-membered ring with a two-atom-chain bridge (XCVa). Little is known of their chemical behavior, probably on account of the small amounts available.


XCV


XCVa


XCVI

In the light of the foregoing evidence, it would be expected that on being heated these substances would either (*a*) dissociate into their components or (*b*) undergo cleavage of the three-carbon-atom system, analogous to the bridge in the six-carbon-atom types. While it is recorded in the literature (2) that XCV dissociates into its components, no experimental details are given.

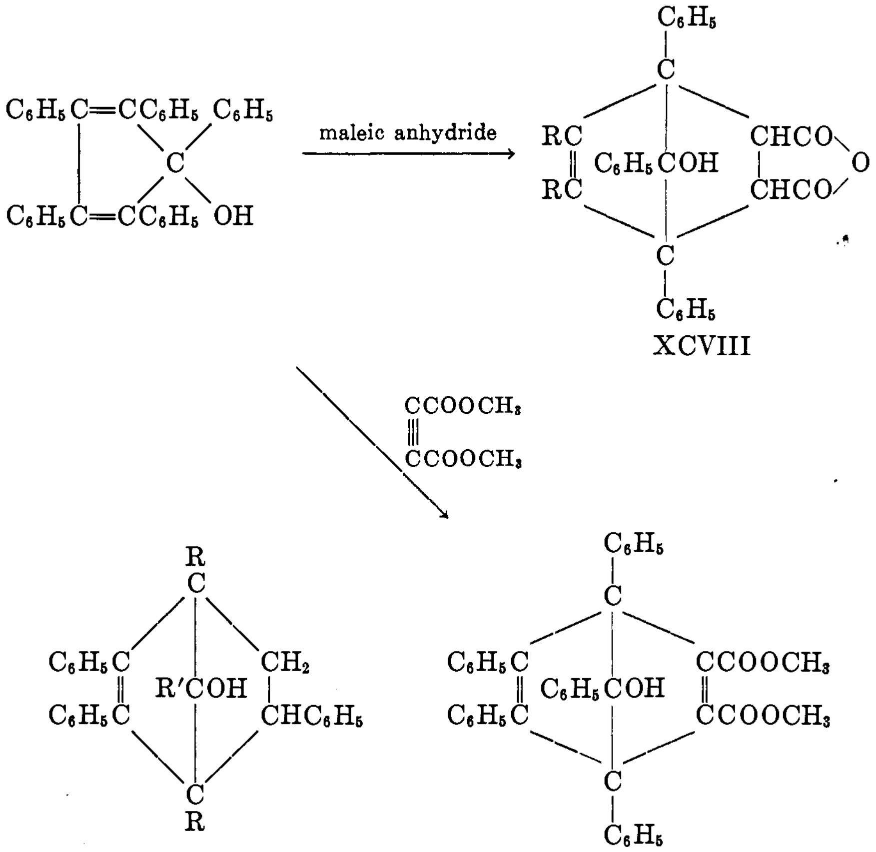
V. Carbinol Bridge Compounds

Since the substances having a carbinol bridge $R{-}\overset{|}{\underset{|}{C}}{-}OH$ have all been prepared in connection with the carbonyl bridge work and have certain comparable properties, it is proper that they be included in any survey covering the entire field.

Only a small number of this type (XCVII, XCVIII, XCIX) of substance is known. They have all been obtained either (*1*) by the action of a Grignard reagent on a carbonyl bridge compound (19, 20) or (*2*) by a direct diene synthesis (20, 21). Those in the six-membered-ring series, secured by the first procedure, can only be obtained if there is no hydrogen alpha to the bridge carbonyl. The only known example of a substance (XIII) in which the carbinol bridge is across an eight-membered ring has already been described (page 214); it had no unusual properties (14).

The carbinol bridge compounds are collected in table 7.

Since this type of substance was prepared solely to learn its behavior when heated, there are only a few other known facts. The hydroxyl group was replaced by chlorine when the carbinol was treated with acetyl chloride (19); the chloride C lost hydrogen chloride when heated, but the nature of the product has not been determined.

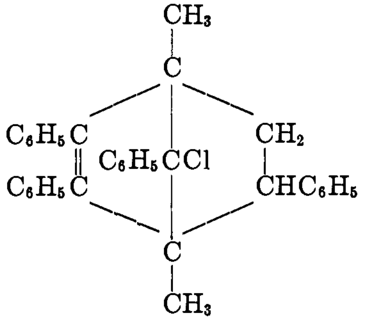


XCVIII

XCVII

XCIX

The behavior of the carbinols on heating is interesting. A variety of products is obtained, most of which are cleavage fragments. Usually it appears that the molecule has dissociated into a diene and an ethylenic compound—a reverse diene synthesis. The diene component then undergoes further changes.



C

TABLE 7

Six-membered ring compounds with a carbinol bridge

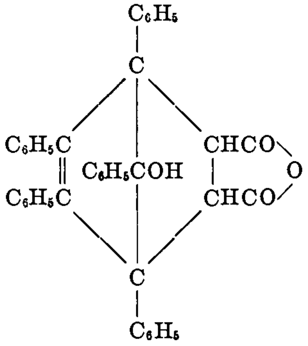
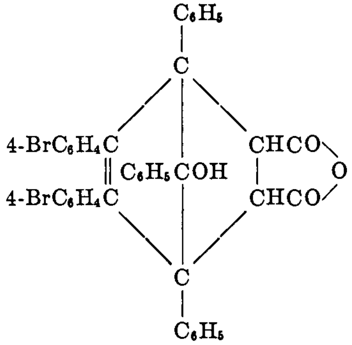
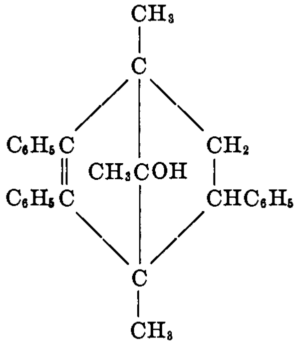
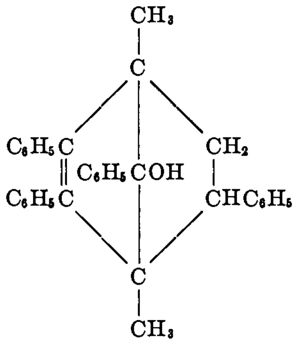
NO.	SUBSTANCE	REFERENCE
CI		(20)
XCVIII; R = 4-BrC_6H_4		(21)
XCVII; R,R′ = CH_3		(19)
XCVII; R = CH_3 R′ = C_6H_5		(19)

TABLE 7—*Continued*

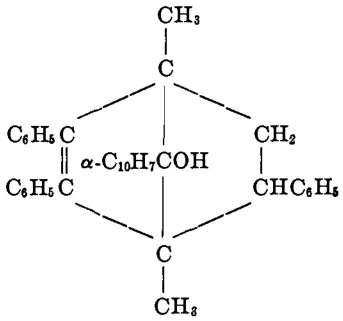
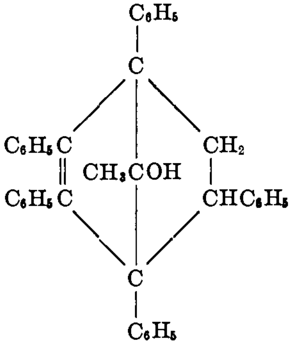
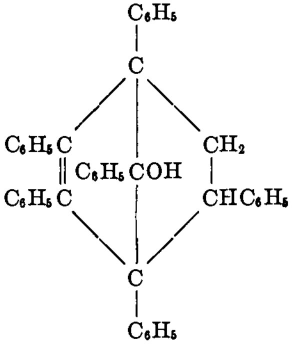
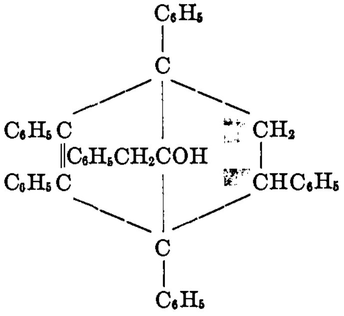
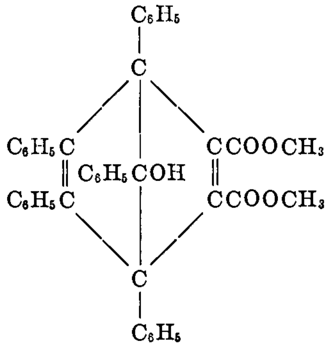
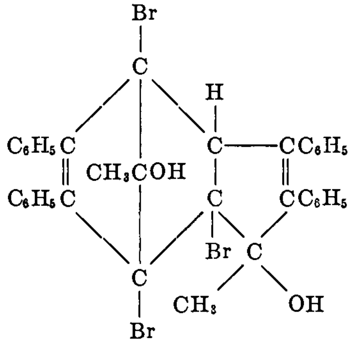
NO.	SUBSTANCE	REFERENCE
XCVII; R = CH_3 R′ = α-$C_{10}H_7$		(19)
XCVII; R = C_6H_5 R′ = CH_3		(20)
CV		(20)
CVI		(20)

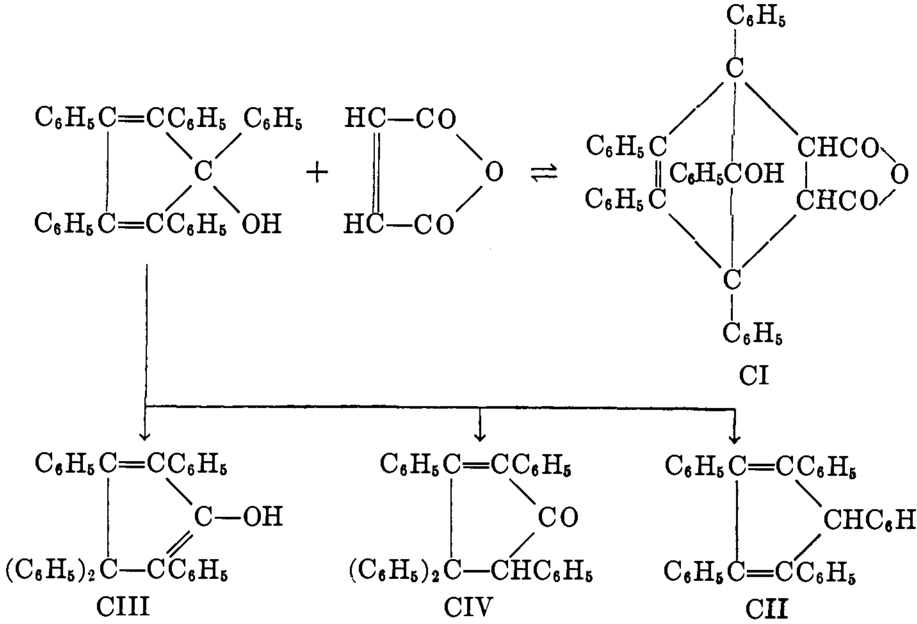
TABLE 7—*Concluded*

NO.	SUBSTANCE	REFERENCE
XCIX		(20)
LXIII		(8)

Pentaphenylcyclopentadienol (Ziegler's carbinol) and maleic anhydride gave an addition product having a carbinol bridge, CI (XCVIII; R = C_6H_5) (20). When this addition product was heated *in vacuo*, a complex mixture was formed; among the easily recognized products were water, maleic anhydride, benzaldehyde, and pentaphenylcyclopentadiene (CII). There were also two isomers, CIII and CIV, which are also isomers of the carbinol. When Ziegler's carbinol was heated by itself under the same conditions, it gave the two isomeric substances, CIII and CIV, and pentaphenylcyclopentadiene. It seems obvious that the complex bridge compound must have dissociated into its components; a secondary reaction of the regenerated Ziegler's carbinol then gave rise to the cyclopentene derivatives.

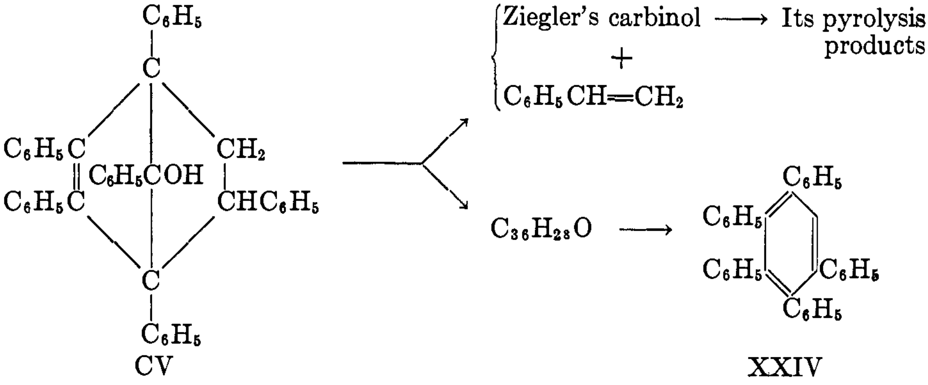
The pair of isomers CIII and CIV are interconvertible; they are formed from Ziegler's carbinol by a 1,3-rearrangement of a phenyl group (20). A brominated homolog of Ziegler's carbinol showed a similar behavior (21).

When the carbinol CV (XCVII; R,R′ = C_6H_5) was heated, there were formed the same substances that resulted from Ziegler's carbinol alone, plus styrene and an oxygen-containing substance, $C_{36}H_{28}O$, the structure of which has not yet


CI

CIII CIV CII

been determined. The oxygen atom is inactive (not ketonic or acidic), but when the substance is treated with perchloric acid, water is removed and pentaphenylbenzene (XXIV) is formed (20). The fate of the bridge is uncertain, but it is

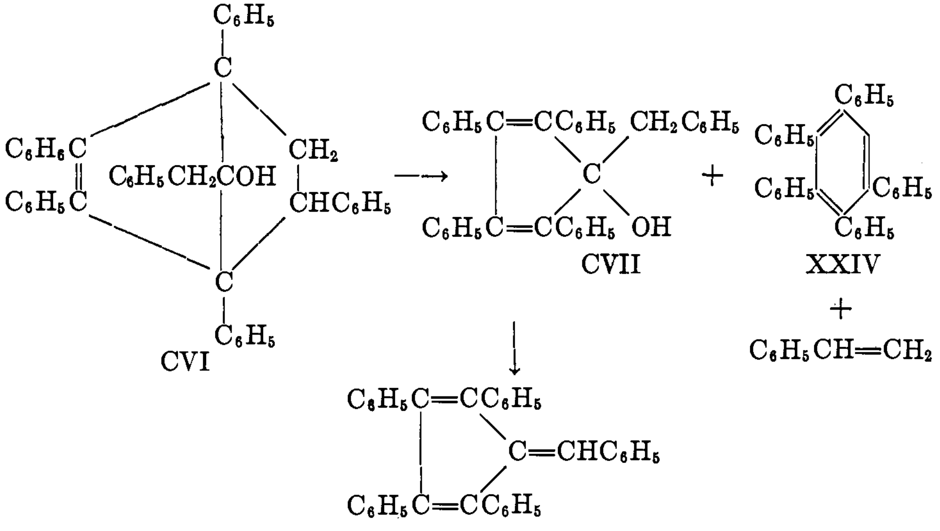


CV

XXIV

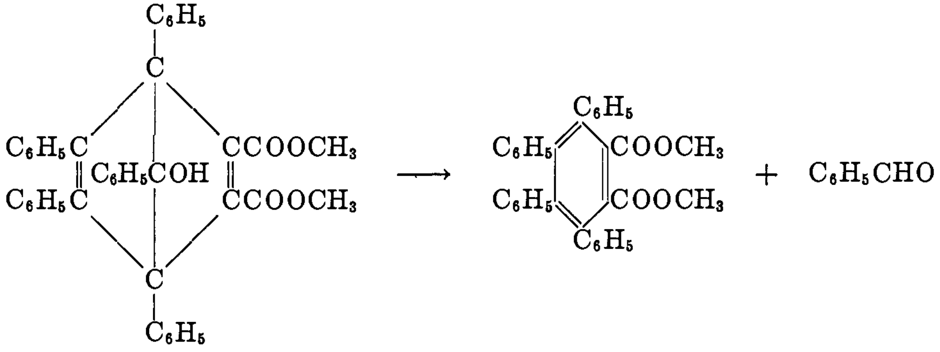
obvious that the oxygen appears in the unknown substance. It is also clear that the bridge must have been cleaved in some way before the addition product could dissociate into its components. By analogy with the behavior of the carbonyl bridge compounds, the formation of pentaphenylbenzene was taken as an indication of the presence of a six-membered ring in the addition product.

The carbinol CVI, on pyrolysis, yielded styrene, pentaphenylbenzene, the carbinol CVII, and the corresponding fulvene CVIII. In this instance, the carbinol CVII appears to be more stable, so that it could be isolated. The use of this benzyl compound affords proof that the formation of pentaphenylbenzene does not involve the bridge carbon or aryl group attached thereto. It was not possible to determine the fate of the bridge in this instance (20).



CVI, CVII, XXIV, CVIII

In order to have a more favorable example in which one mode of cleavage would be expected to predominate, the addition product (XCIX) of Ziegler's carbinol and acetylenedicarboxylic ester was prepared (20). This substance would be expected to lose the bridge very easily, because it is attached to carbon atoms which are located beta to two sets of double bonds, both of which favor cleavage of the same single bonds. This expectation was realized, for the reaction was clean, giving but two products, benzaldehyde and tetraphenylphthalic ester.



XCIX

In this instance, the fate of the bridge is clear—it appears as benzaldehyde.

It should be pointed out that it requires a much higher temperature to decompose the carbinol bridge compounds than is needed for the other types discussed. Presumably this is accounted for in the other types by the formation of substances that require no rearrangement of atoms or groups to be stable molecules. In the case of the carbinols, the first cleavage product is an unstable form of an aldehyde. Since this is not a normal product, it requires a greater amount of energy to bring about the cleavage. Thus, the isolation of the ester XCIX, formed with an acetylenic addend, is possible.

In summation: When six-membered cyclic substances having a carbinol bridge and one ethylenic linkage are heated, they resemble other similarly constituted compounds, differing only in the nature of the bridges. The molecule decomposes in two ways: either it dissociates into its components, which may undergo further changes, or it loses the bridge and gives a complex aromatic compound or substances closely related to it. The bridge appears as an aldehyde, which can be isolated as such in favorable circumstances.

When the carbinol bridge compound contains two ethylenic linkages, but one mode of decomposition occurs—that in which the bridge is eliminated.

The enthusiastic collaboration of my former graduate students at McGill University and the valuable aid of my colleagues in the Synthetic Organic Research Laboratory is hereby gratefully acknowledged.

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