CARBONYL BRIDGE COMPOUNDS

C. F. H. ALLEN[1]

Rochester Institute of Technology, Rochester, New York

Received July 1, 1961

CONTENTS

I. Nomenclature 653
II. General 653
A. Infrared Absorption 653
B. Revision of Structures 653
C. The Saturated Series 654
D. Dimer Dissociation 654
E. Zelinski's Supposed Bridged Ketone 655
III. Use of Simple Ethylenic Compounds 656
IV. Polyhalogenated Compounds 657
V. Polycyclic Series 657
VI. Macrocyclic Series 658
VII. Inferred Bridged Ketones 661
VIII. Properties 661
IX. References 663

I. NOMENCLATURE

The preparation of carbonyl bridge compounds consists of the addition of a cyclopentadienone to an ethylenic compound. Since the cyclopentadienones bear so many substituents, the names become cumbersome. They have, therefore, been simplified; a cyclopentadienone becomes a "cyclone." The common tetraphenylcyclopentadienone is tetracyclone. Unless otherwise indicated, other cyclones have phenyl groups in the 2- and 5-positions. Thus, anisylcyclone is 3,4-bis-(4-methoxyphenyl)-2,5-diphenylcyclopentadienone, piperonylcyclone is the analogous 3,4-bis-(3,4-methylenedioxyphenyl) compound. Acecyclone and phencyclone are the polynuclear dienones derived from dibenzyl ketone and acenaphthenequinone and phenanthrenequinone, respectively.

II. GENERAL

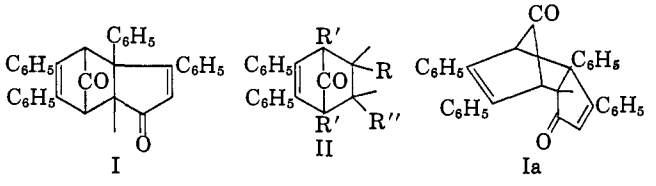
In the fifteen years since the earlier review of the chemistry of carbonyl bridge compounds (6) there have been a considerable number of advances which it is appropriate to summarize at this time, as outlined in the table of contents.

A. INFRARED ABSORPTION

During an investigation of infrared absorptions of compounds having small sized rings, a number of carbonyl bridged structures were included (7). The first one to be done was the "bimolecular product" (I) which initiated the original work. Surprisingly, this had two bands for carbonyl groups—the usual ketone at 5.99 and a second at 5.64 μ. The first one is part of the α,β-unsaturated ketonic system, which also shows up as such in the ultraviolet (8), but the second is new. Accordingly, a study was made of a number of carbonyl bridge compounds of known structure (II), and the value 5.64 μ (1770 cm.$^{-1}$) found to be characteristic for such a transannular bridge across a six-membered ring. This subsequently was confirmed by other investigators and is now a diagnostic tool (40, 43, 51, 57, 60).

B. REVISION OF STRUCTURES

The bimolecular product (I) undoubtedly has the endo *cis* configuration (shown in Ia) because (1) the diene synthesis is *cis*, and (2) there are no interfering

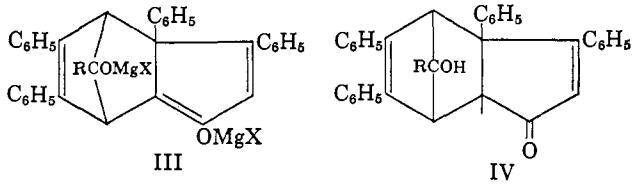


groups as there would be in the *exo* isomer. For convenience plane formulas will be used in this paper, unless the other style is desirable for clarity.

When the substance (I) was treated quantitatively with methylmagnesium iodide, two equivalents of reagent were consumed with evolution of one equivalent of methane (*i.e.*, one active hydrogen and one addition). The products of such reactions with various Grignard reagents were ketocarbinols and were assigned the structure of indenols, on the assumption that addition had occurred preferentially at the indenone carbonyl group, and the observation that they lost carbon mon-

[1] Formerly Kodak Research Laboratories, Eastman Kodak Company, Rochester, New York.

oxide when heated. However, they all showed the infrared carbonyl band at 6.0 μ only, corresponding to a carbonyl group conjugated with a double bond (*i.e.*, an α,β-unsaturated ketone); this was confirmed by the ultraviolet absorption. The inevitable conclusion that the Grignard reagent preferentially attacked the bridge had to be drawn. This behavior is now in line with that of all the homologs of the bimolecular product, rather than an exception as previously suggested (7). There is, therefore, no longer any mystery regarding the structure (III) of the organomagnesium compound (9, 21). Since the endocarbinols (IV) are not carbonyl bridged compounds, the structures LXV, pp. 247–248 (6) are now changed to the isomers (IV).

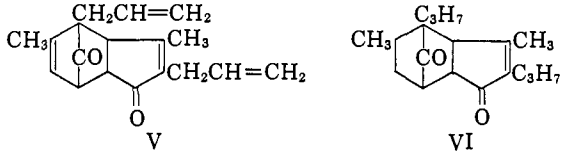


The conversion of the carbinols to hydrocarbons has been discussed; it is still postulated as proceeding by way of a carbonyl bridged indenol.

C. THE SATURATED SERIES

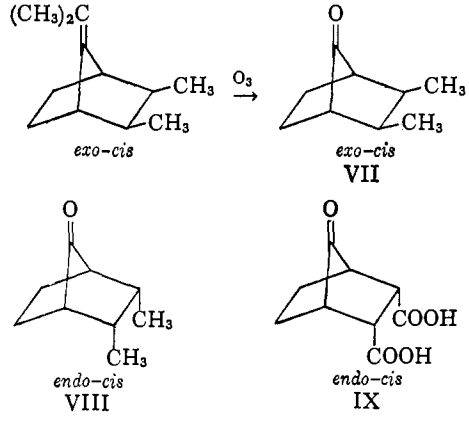
A characteristic property of all the compounds having a carbonyl bridge across an unsaturated six-membered ring is their easy loss of the bridge as carbon monoxide when heated. In each instance the unsaturation bears a particular relation to the bridge. Other bridges in analogous compounds having a similar relation show a similar behavior. Therefore it is not a peculiarity of the nature of the bridge, but its location in respect to the double bond. The conclusion is obvious; it may be predicted that in an analogous *saturated* compound, the bridge will not be lost; the substance will be stable to heat, *i.e.*, distillable.

First attempts to prepare such a substance by catalytic reduction of the known carbonyl bridge compounds were unsuccessful, owing to the presence of bulky aryl substituents on the double bond. Fortunately, the dimer (V) of allethrolone (42) became available, and made it possible to test this point. Catalytic reduction of this dimer resulted in saturation of the three isolated ethylenic linkages (VI). Both carbonyl groups remained intact, as shown by the absorption spectra.



The reduced compound distilled unchanged, thus verifying the prediction (26). Further instances with simpler molecules have since been described and amply confirm the conclusion.

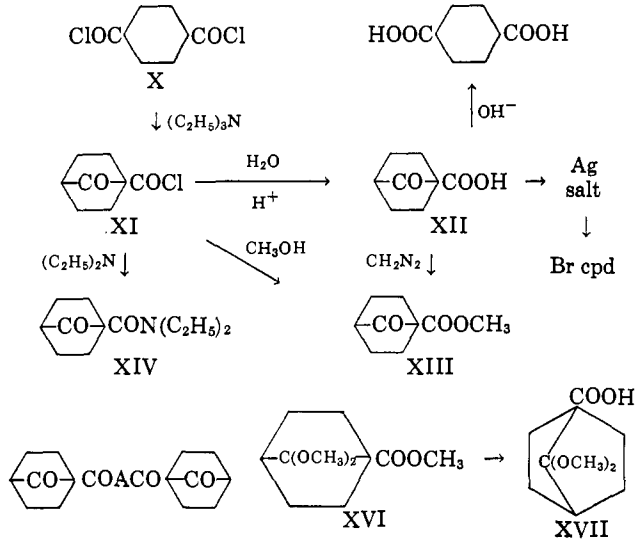
The first instance dealt with the pair of *exo-cis* and *endo-cis*-2,3-dimethyl bicyclo[2.2.1]-7-heptanones (VII, VIII) (57). These were prepared from the adducts of dimethylfulvene and maleic anhydride by selective reduction and other appropriate manipulations, the last step being ozonolysis.



Both ketones distilled without decomposition, had infrared bands in the 5.64 μ region, and gave isomeric 2,4-dinitrophenylhydrazones. An *endo-cis* acid (IX) and its dinitrophenylhydrazone were also prepared.

The second type was acidic. Distillation of hexahydroterephthaloyl chloride (X) gave the bicyclic bridged chloride (XI), which showed infrared absorption in the right range and had the expected chemical properties (acetal formation, alkaline cleavage of the bridge; formation of acids, esters and amides) (40). The reactions are summarized in Chart I. The acid (XII), having a carboxyl at the bridgehead (38), could not be decarboxylated (13, 40).

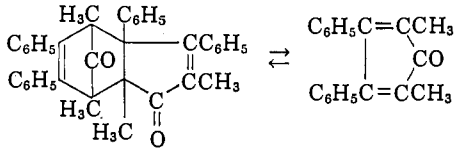
CHART I



D. DIMER DISSOCIATION

The earliest discovered cyclopentadienones were

known only in the form of their dimers, "bimolecular products"; not until the discovery of the tetraphenyl derivative was a monomer known. The latter did not dimerize. A study was undertaken, therefore, to uncover any factors affecting this behavior; as a result the limits of the reaction were determined (23). It was found that one group consisted of substances that were known only in the dimeric form (colorless solid); a second, only as the monomeric dienone (colored solid); and a third which was dimeric (colorless solid), but was dissociated when dissolved (deeply colored solutions, the intensity of color increasing as the temperature was raised) and gave intermediate molecular weight values.



From the facts it was concluded that any cyclopentadienone having fewer than three substituents will exist only as the dimer. When there are three groups, the dienones will exist as the nondissociating dimer except in the extreme case in which there are two aryl groups adjacent to the carbonyl. When all four positions are substituted, a dissociable dimer results when the 2- and 5-positions bear a methyl and an alkyl; otherwise the substance is a monomer, except that chlorine atoms and phenoxy groups do not interfere with dimerization. These observations have been very useful in selecting the appropriate dienone for a desired reaction; the most easily accessible is the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone.

E. ZELINSKI'S SUPPOSED BICYCLO[2.2.1]HEPTANONE

Many years ago Zelinski (61) heated the mixed barium hexahydroterephthalates, and prepared a semicarbazone in small yield from the oily distillate. The carbonyl compound was not regenerated or identified. As already has been announced (7) on repetition of this work, no fraction of the oily distillate had an infrared band at 5.64, now known to be characteristic of compounds having a carbonyl bridge across a six-membered ring. However, there was a band at 5.87, typical of aldehydes, and benzaldehyde was identified by direct comparison of its 2,4-dinitrophenylhydrazone, and by the infrared spectra of both it and its derivative (13). The amount was small, of the order of 11 per cent. As first obtained the dinitrophenylhydrazone was not "homogeneous." When subjected to paper chromatography, exceedingly small or trace amounts of four other derivatives were found. One of them was a tolualdehyde.

It already has been pointed out (59) that bicyclo[2.2.1]heptanone would be unlikely, since conversion of dicarboxylic acids to ketones proceeds by way of a β-keto acid, and that Zelinski's would not be susceptible to decarboxylation, having the carboxyl group at a bridgehead (38).

TABLE I

SUBSTANCES, STRUCTURES, AND REFERENCES

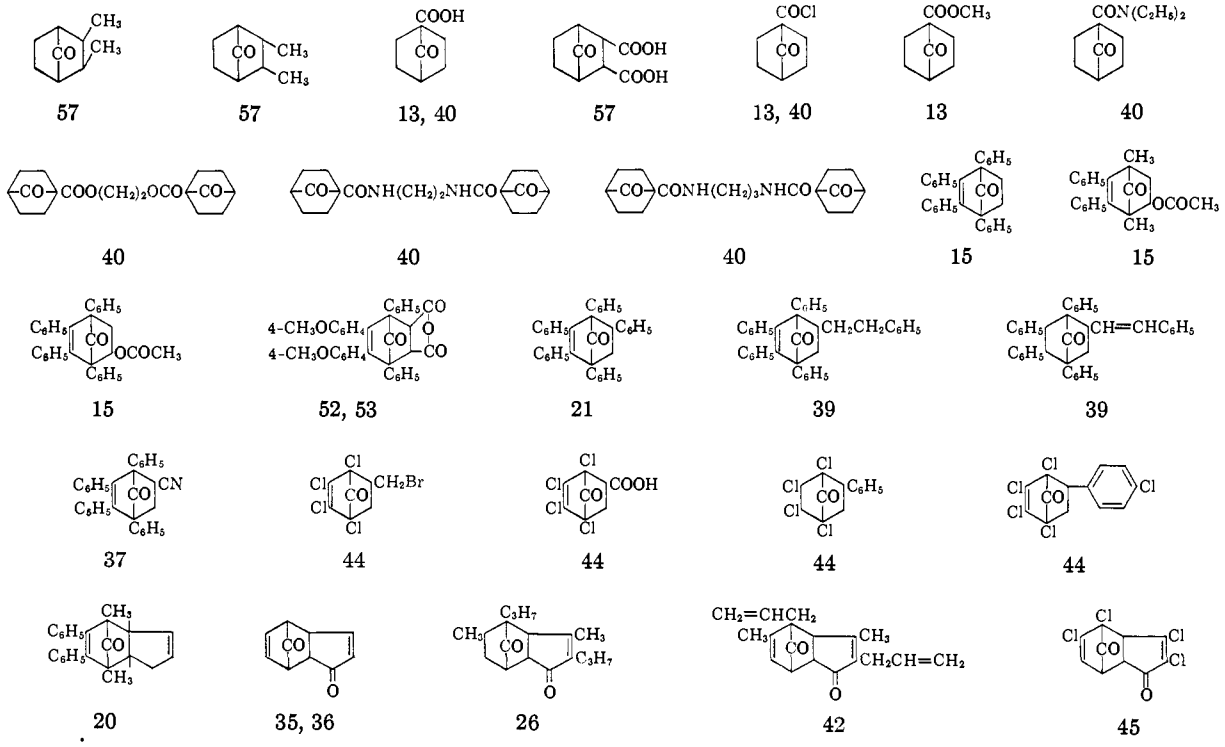
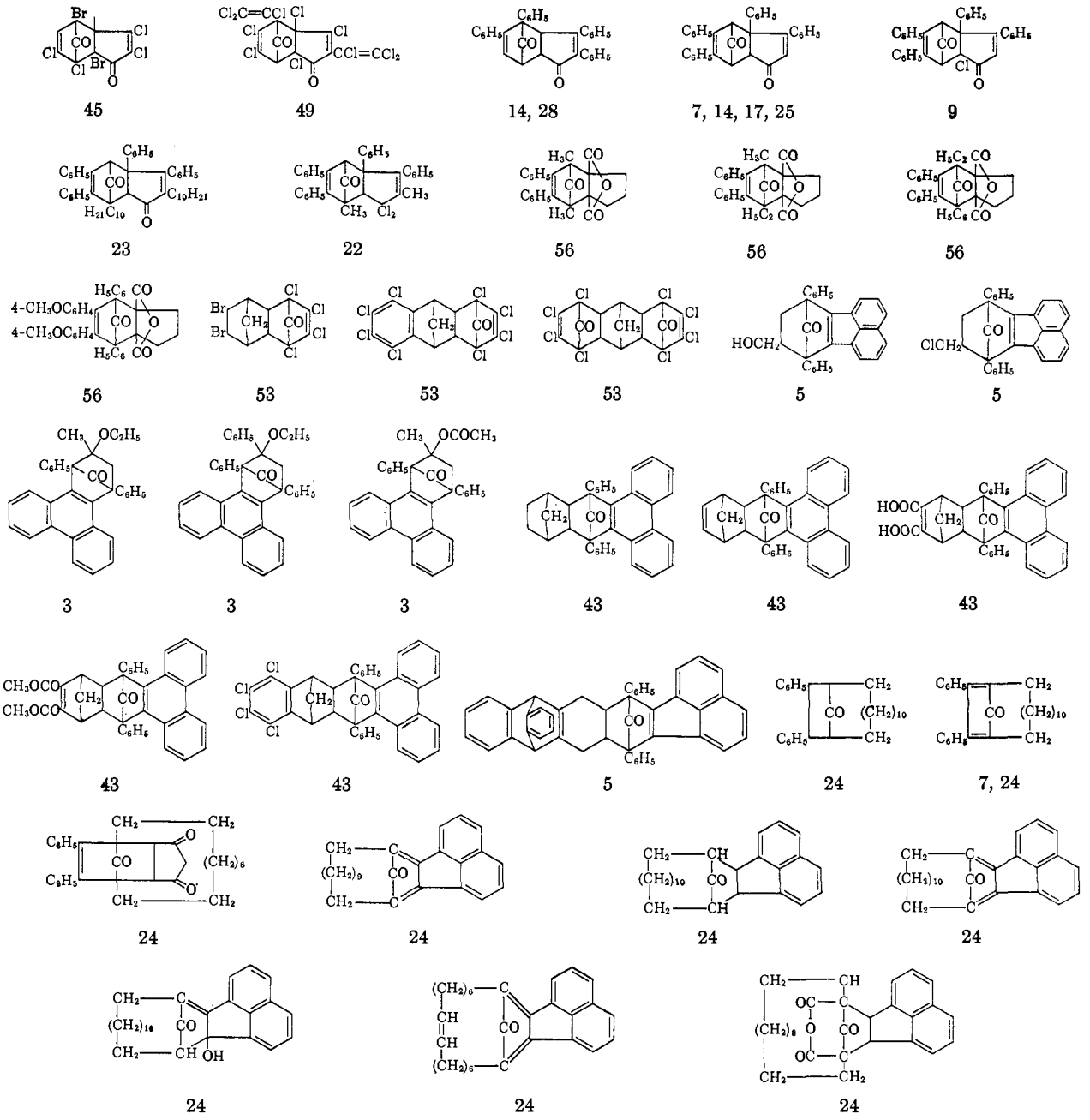
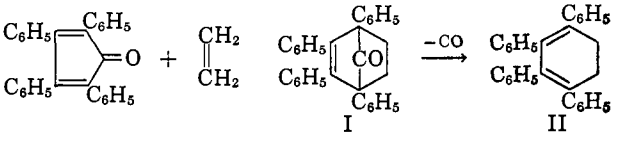


TABLE I *Concluded*



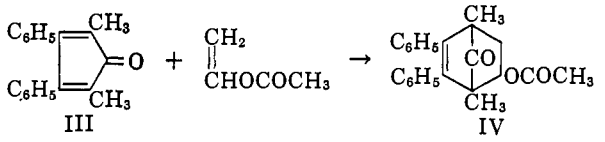
III. USE OF SIMPLE ETHYLENIC COMPOUNDS

The results of a study of the reactions of cyclones and simple ethylenic compounds (vinyl ethers and esters) have appeared in several papers (1–5). The components, in a sealed tube, were heated at elevated temperatures (150–200°). As should have been expected, the products had no carbonyl bridge, the drastic conditions favoring decarboxylation and aromatization. That this is largely a matter of temperature has been shown by others from the study of the reaction between ethylene and tetracyclone (15). At 100°, using an aluminum chloride catalyst, the expected adduct (I) results, whereas at 180° (but without the catalyst) tetraphenyldihydrobenzene (II) is formed by loss of the bridge.



Furthermore, adducts (IV) are formed quantitatively from vinyl acetate and tetracyclone and the dissociating dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (III) at 100° for 24 hr. (15).

For allyl alcohol and for allyl chloride the Russian authors found that by operating at 200° for 30 hr., ad-

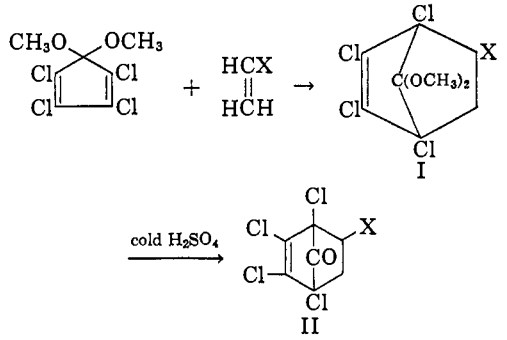


ducts retaining the bridge were obtained with acecyclone (5). According to the abstract (1) their work may be summarized by stating that "the stability of the bridge is not solely determined by the double bond in the β-position but depends on the nature of the reacting radical." Phencyclone differs from all others; many dienophiles add with greater facility, giving normal products with the bridge. This difference "must be explained by the specificity of its structure and the specificity of the addition product formed, and on the basis of the previously reported diene synthesis with several substituted cyclones and ethylene dienophilic agents of type CH_2:CHX it is suggested that the reactions involve the primary addition of the CH_2– end of the reagent to one of the conjugated carbon atoms of the cyclone to give a tautomeric system in the incipient bridge, between C:CO⁻—C and ⁻C—CO—C forms, to the latter of which is then drawn the electronophilic α-C atom of the addend to complete the synthesis. In all cases the final products were hydrocarbons, resulting from the loss of the endocarbonyl bridge and HX. The loss of the endocarbonyl bridge appears to be a simple elimination of carbon monoxide by electron transfer from the terminal carbon atom of the original conjugated-bond system of the cyclone to the oxygen of the carbonyl group. The loss of HX may be simultaneous with the loss of carbon monoxide or at another period; the data on hand do not permit a definite conclusion. Phencyclone, in being able to yield complete adducts, must be regarded in a different light from the other cyclones; its adducts are stable up to their melting points, when carbon monoxide is lost. This stability may be examined by the tendency to form the stable phenanthrene-type ring system. Thermal decomposition of its adducts in high-boiling solvents gave a hydrocarbon derivative of tricyclone; attempts to produce the loss of only carbon monoxide, to be followed by dehydrogenation, failed."

It should be noted that while adducts have been obtained with allyl compounds, simple styrenes in boiling toluene for 24 hr. give only the fluoranthene derivatives resulting from decarbonylation (58).

IV. POLYHALOGENATED COMPOUNDS

With the relatively recent availability of polychlorinated cyclopentenes and pentadienes (46, 48), Zincke's early work (62) has been considerably amplified. A number of new carbonyl bridge compounds have been prepared, but a very extensive number of related substances having a $>CCl_2$ bridge have been described (47). These are a potential source of carbonyl bridge compounds, for replacement of these chlorine atoms can lead to an oxo group. Such a change has been described already; treatment of the dihalo compound with methanolic sodium methoxide gives a ketal (I) which is hydrolyzed easily to the oxo derivative (II) by cold sulfuric acid. The ketals may also be formed directly from a dimethoxycyclopentadiene (44). Ketal formation from carbonyl bridged compounds, a charac-



X = C_6H_5, 4-ClC_6H_4, CH_2Br, COOH.

teristic reaction of the latter (16, 40), is of some use as their source.

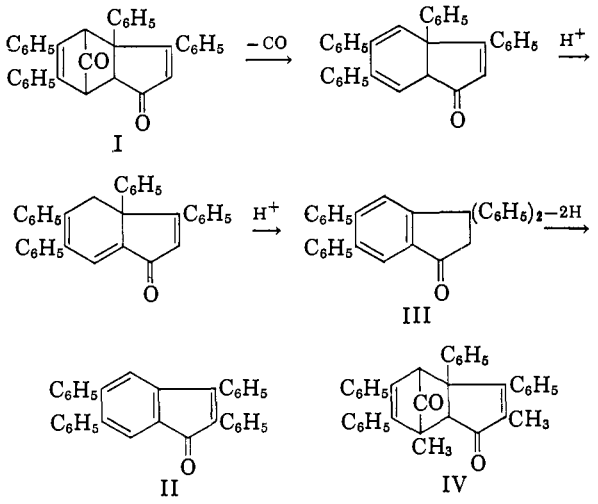
V. POLYCYCLIC SERIES

The preparation of multicyclic carbonyl bridge compounds in the indene series always involves the addition of a cyclopentadienone ("cyclone") to itself or to some other cyclopentene.

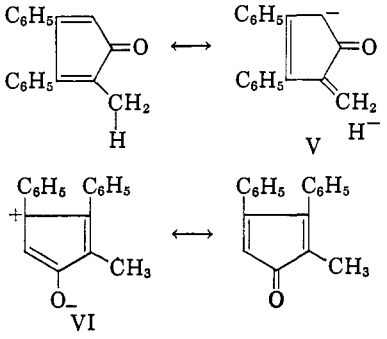
The bimolecular product from anhydroacetonebenzil (17) is the dimer (I) of 3,4-diphenylcyclopentadienone. It gave oxygen-containing products when treated with chromic acid (10,14); the identity of the regenerated substance with the original dimer was not recognized at the time, and it was thought that an isomer was obtained. When the infrared spectra of the dimer and supposed isomer were found to be identical, there were no longer any isomeric dimers to be explained (25). In accordance with its method of preparation, and by analogy with all the later discovered dissociable dimers, the dimer was assigned the structure (I) having an angular phenyl group. Upon decarbonylation an indanone resulted, which by sulfur dehydrogenation gave the authentic indenone (XXII), the structure of which has been proved by both degradation and synthesis (11, 17). Since it appeared that the angular phenyl group had moved from position 3a to 2, a 1,3-phenyl shift was assumed. The indenone, however, upon catalytic reduction, did not regenerate the indanone from which it had been made, but gave an isomer (27). The indanone from the dimer was then thoroughly investigated, and found to have the *gem*-diphenyl structure (III) (25). Hence, there have been two 1,2-shifts of a phenyl group instead of one 1,3-shift. The course of the reactions from dimer to indenone is summarized in Chart II.

A revision of structures in previous papers has had to

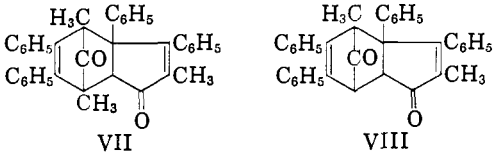
CHART II



be made, but the only one of immediate concern is that of the dimer (I) which has the angular phenyl group as originally written (17). The presence of the angular phenyl group (at position 3a) was proved in the 2,7-methyl homolog (IV) by stepwise degradation terminating in 2,3,5-triphenyltoluene (19). The location of the methyl group in IV at position 7 rather than at 4 is preferred for several reasons.

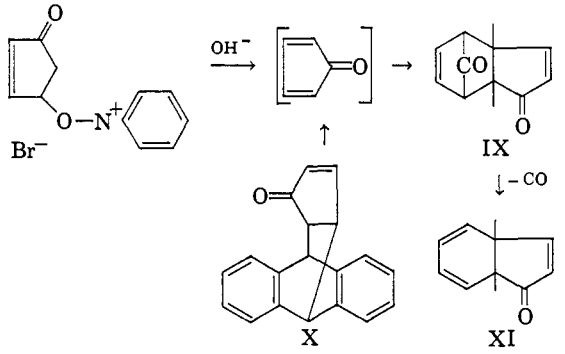


The contributor V, expressing the hyperconjugative influence of the methyl group, is responsible for the small polarization of the diene system; the contributor VI shows the polarization of the dienophile. The polarizations make the rate of formation of VII faster than that of the isomer, VIII, in absence of contrary influences. Since the steric requirements also favor



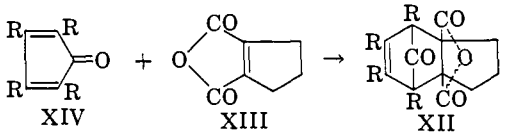
VII, the rate of formation of VIII should be much slower.

An unsubstituted bridged indenone is the recently discovered dimer (IX) of cyclopentadienone. It was obtained in two ways: (a) the 1,2-adduct of 3,5-dibromocyclopentene and pyridine-N-oxide was decomposed by cold alkali (36); (b) Thiele's dioxime was submitted to an interchange reaction with levulinic acid (35). It has been suggested that the reaction proceeds by way of cyclopentadienone which at once dimerizes. The transitory existence was inferred during pyrolysis of the anthracene adduct (X) of cyclopentadienone at 350° (34). The product was the indenone (XI), as would

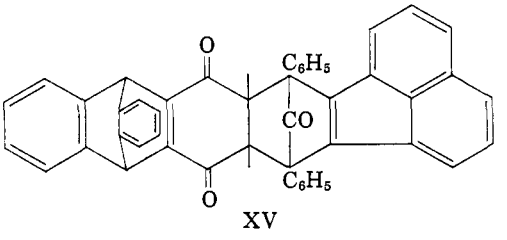


be expected by loss of the bridge. In conformation the bridged compound (IX) was decarbonylated to the same compound.

A new type (XII) of anhydride in the bridged indanone series was prepared (56), using the cyclopenteneanhydride (XIII) and the dienones (XIV) from the dissociable dimers of dialkylanhydroacetonebenzil (18, 23, 56), as well as 3,4-dianisyl-2,5-diphenylcyclone.



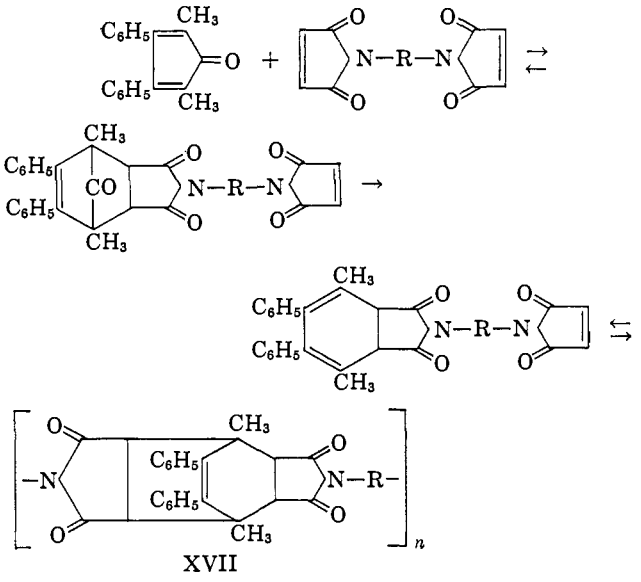
An example of a very complex polynuclear quinone having a carbonyl bridge is 7,16-diphenyl-7,16-endomethano-9,14-endo-*o*-phenylene-7,7a,9,14,15a,16-hexahydro-17-oxoacenaphtho[1,2-b]naphthacene-8,15-quinone (XV) (5).



Utilizing the dimethyldienone (XVI) from its dissociating dimer (18) a polymeric imide (XVII) has been prepared from arylenebismaleimides, varying in the nature of R, as shown in the scheme which includes XVII (41).

VI. MACROCYCLIC SERIES

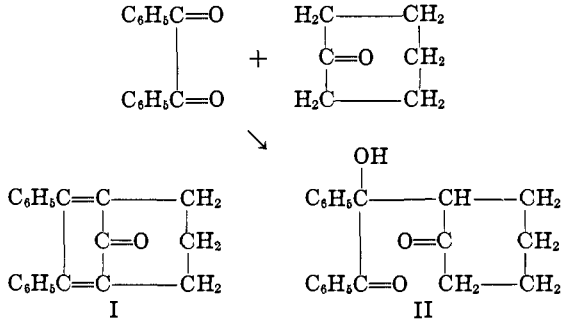
Compounds with Two Double Bonds.—Quite a variety of unsaturated macrocyclic compounds having a carbonyl bridge are now known. The point of immediate importance is the behavior of the carbonyl bridge.



XVII

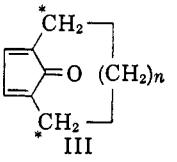
Briefly summarized, the latter is not lost by decarbonylation except in the case where it is in a six-membered ring having a double bond in the β,γ-position at both ends. Unsaturation elsewhere has no effect. Its behavior, thus, parallels that of all the other known analogs. The interesting chemical reactions of these macrocyclic compounds will now be outlined.

More than twenty years ago the first unsuccessful attempt was made to prepare a carbonyl bridge compound containing a double bond at the bridgehead. A bis aldol-like condensation between benzil and cyclohexanone to give I could not be realized, even though benzil does condense twice with suitable open-chain ketones; instead, the 1:1 addition product (II) was obtained.



I II

A planar structure such as I is unlikely because of the strain which would be introduced in its formation by the distortion of bond angles and/or distances; no substances with this unusual arrangement have yet been described. Such a structure also violates Bredt's rule (38) in the form in which it is commonly expressed. However, it is now known that the rule, which was based on a study of small ring systems, is not applicable to macrocyclic rings. The non-formation of the substance I may be attributed to the inability of the reactive groups to come within bond-forming distance of each other. A sufficiently long chain should be able to connect the atoms in such a way as to obviate that difficulty; from a study of models it was evident that such a bridged ring structure would be free from strain if one ring were sufficiently large. Ignoring the spatial requirement of the carbonyl group, the lowest member of the series of cyclanones that should form a structure of type I would be cyclononanone. An additional factor, however, must be considered. It is an inherent property of the ethylenic bond that its substituent atoms must lie approximately in the same plane as the double bond itself. Thus, the C* in III must lie in the plane of the dienone ring.



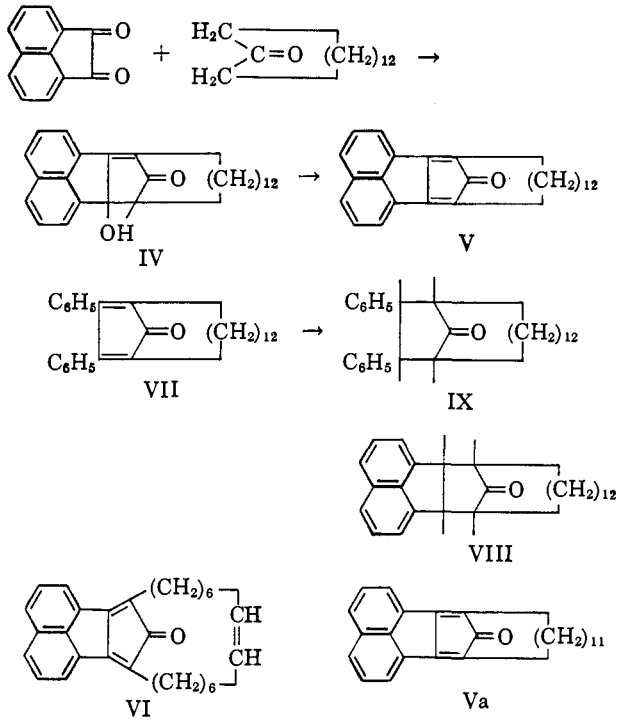
III

The aliphatic ring then must be sufficiently large to accommodate the oxygen atom without excessive steric hindrance. Examination of models shows this limit to be in the region of cyclotetradecanone or cyclopentadecanone. This is in agreement with views on the conformation of cyclic ketones—that the oxygen atom lies roughly inside the ring in the range C_{10} to C_{12}. These conclusions were tested by reactions of acenaphthenequinone and benzil with cyclononanone, cyclodecanone, cyclotetradecanone, cyclopentadecanone, and civetone according to a procedure previously described (24). Only in the case of the latter three ketones was condensation to a cyclopentadienone of the general type of I achieved.

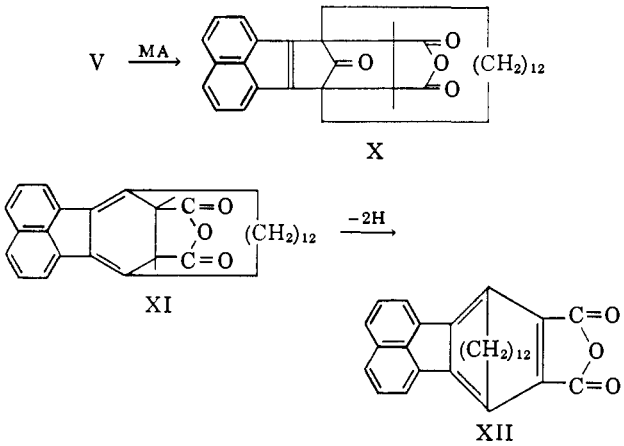
Acenaphthenequinone and cyclopentadecanone in methanol, with potassium hydroxide as a catalyst, at room temperature, gave the carbinol, IV. The carbinol is dehydrated by boiling with acetic acid to give V. If the original reaction mixture is refluxed, a molecule of water is lost, and the doubly unsaturated ketone (V) is obtained directly.

Cyclotetradecanone gives the analog Va in low yield, while civetone gives the triply unsaturated ketone VI. Benzil and cyclopentadecanone give VII.

Grignard analysis of these dienones shows one addition, indicating the presence of a carbonyl group, which is confirmed by infrared analysis. They do not form dinitrophenylhydrazones, probably because of spatial considerations. Quantitative catalytic reduction of V and VII shows two double bonds in each, and gives the tetrahydro derivatives, VIII and IX, respectively. In view of these facts, and from a comparison of the ultraviolet absorption spectra, the structures V, VII, VI, and Va are assigned to these products. The ketones V and VII are essentially coplanar; therefore, the diene system should be quite open to dienophilic reagents. That this is indeed the case is demonstrated

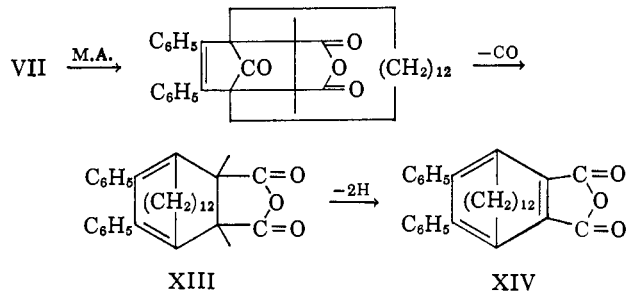


by the ready addition of maleic anhydride. The ketone, V, and the anhydride give the addition product, X, at room temperature. This adduct now has a six-membered ring with a carbonyl bridge, and, in analogy to similarly constituted compounds, is readily decarbonylated to XI, which, in turn, may be hydrogenated to the aromatic 7,10-endododecano-fluoranthene-8,9-dicarboxylic anhydride (XII). This anhydride was obtained directly from V and acetylenedicarboxylic acid.



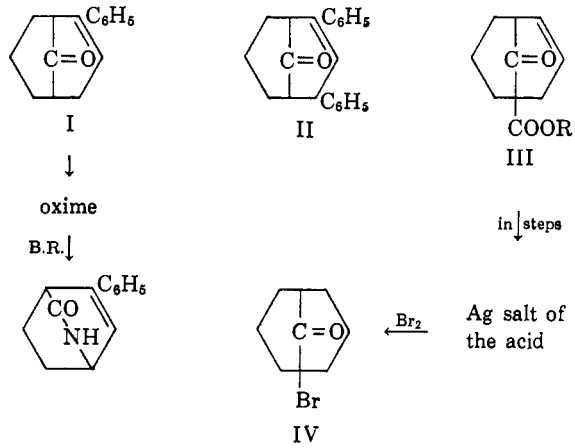
In an analogous series of reactions, the cyclic ketone, VII reacts with maleic anhydride to give an endocarbonyl compound, which is decarbonylated to the anhydride, XIII; the latter, in turn, is dehydrogenated to the anhydride of 17,18-dicarboxyl-15,16-diphenylbicyclo[12.2.2]octadeca-14,16,17-triene (XIV).

The physical and chemical properties of all these compounds are very similar to those of their open-chain analogs, especially in regard to their ultra-



violet absorption spectra. The large polymethylene bridge does not confer special properties on the molecule. However, although the dienones contain a crossed conjugated system, it has not, up to the present, been found possible to bring about a Michael addition reaction by addition of cyanoacetamide, *p*-toluenesulfinic acid, or ethyl malonate using alcoholic solutions and an alkaline catalyst. This may be attributed to the two substituents on the carbon atom in the *beta* position relative to the carbonyl group. The substances described constitute a new class of compounds; they have *two* double bonds at a bridgehead which are not part of an aromatic system, and which, in addition, are conjugated with a carbonyl group.

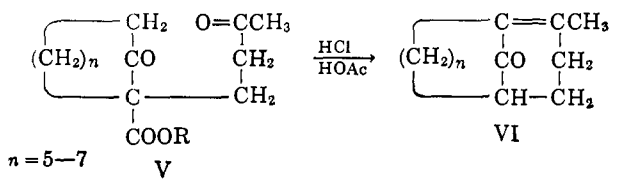
Compounds with One Double Bond.—The bicyclic macrocyclic ketones I–III having one double bond β,γ- to the carbonyl bridge have been further studied (31–33) since the first review paper (6). They can all be distilled, and all form 2,4-dinitrophenylhydrazones. The only way to break the bridge is by means of a Beckmann rearrangement! Although silver bromide



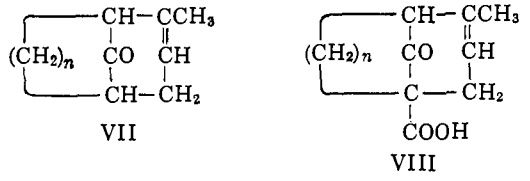
precipitated when the saturated bromoketone (IV) was treated with silver nitrate, no unsubstituted ketone could be obtained (33).

Intramolecular ring closure of certain complex macrocyclic keto esters (V) leads to monoethylenic bicyclic ketones (VI) having the double bond at the bridgehead (54, 55). This result shows that Bredt's rule applies only to small ring compounds; in other words, a double bond may be at a bridgehead in a

bicyclic system if the ring is large enough. These ketones (VI) can be distilled without change.



The only unusual property is the inactivity of the carbonyl group toward reagents (semicarbazide, Girard reagent). This lack of activity has been attributed to spatial effects. However, closely related ketones in which the double bond is not at the bridgehead (VII) do show the carbonyl reactions; the inactivity of the former (VI), then, may be connected with the α,β-unsaturated system.

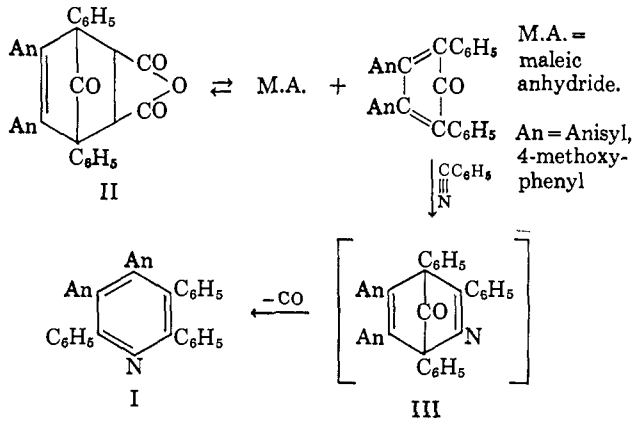


It may be noted that in these cases the double bond is in the β,γ-position relative to the carbonyl *at only one end*, hence its effect is insufficient to activate the cleavage of the bridge.

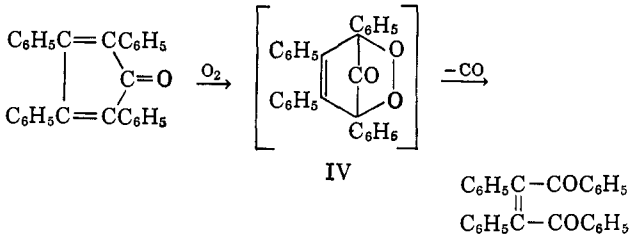
The behavior of the acids (VIII) is also of interest, in view of the current opinion that a carboxyl group at a bridgehead, even in a β-keto acid, does not lose carbon dioxide. If the large, outer ring contains eight atoms, the acid sublimes unchanged (54). If the ring has more than eight atoms, the acid can be decarboxylated in quinoline (at 245°); this behavior suggests that the larger ring is nonplanar. An extensive account of these and related compounds from nitromalonic aldehyde is given elsewhere (38).

VII. INFERRED CARBONYL BRIDGE COMPOUNDS

In a great many instances the transitory formation of a carbonyl bridge compound from the components of a diene synthesis is inferred by analogy on account of the nature of the products; identification of carbon monoxide is a confirming criterion. Among such are the many products derived from acecyclone by the Russian group (1–5), and an analogous number used to characterize styrenes (59). Two unusual instances may be cited. (1) The production of a pentaarylated pyridine (I) (51, 52) from the maleic anhydride adduct (II) and benzonitrile is explicable when the reversibility of the diene synthesis is recalled. The regenerated cyclone adds to benzonitrile in the usual fashion, but the dissociating temperature of the anhydride is high enough so that decarbonylation of the adduct (III) occurs (effect of two β,γ-ethylenic linkages).



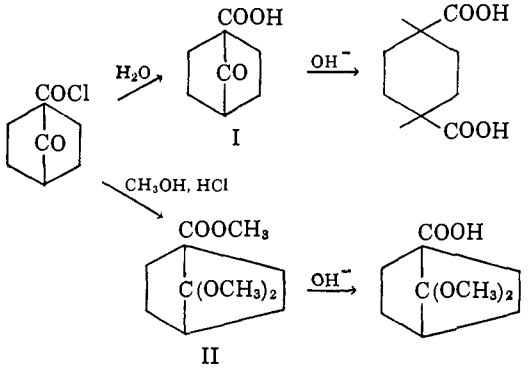
(2) A relatively simple carbonyl bridge compound (IV) was inferred (but was not isolated) as being an intermediate in the photo-oxidation of tetracyclone, since the products were carbon monoxide and dibenzoylstilbene (30).



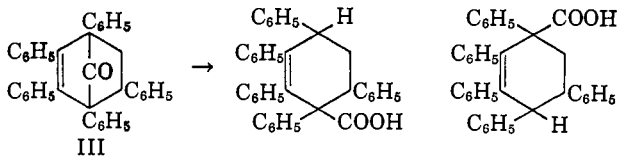
VIII. PROPERTIES OF CARBONYL BRIDGE COMPOUNDS

Characteristic reactions of carbonyl bridge compounds are (a) decarbonylation when heated, (b) cleavage of the bridge by alkali, (c) ketal formation. The decarbonylation reaction has been the most widely studied, as already has been outlined. Two instances of cleavage of the bridge by alkali were given in the first review (6); since then further work was shown the general nature of the reaction. 1-Carboxy[2.2.1]cycloheptan-7-one (I) is hydrolyzed readily to a mixture of hexahydroterephthalic acids, as is its dimethylketal methyl ester (II) at a slower rate (40). Since this is a saturated compound, the cleavage is not connected with the presence of a double bond.

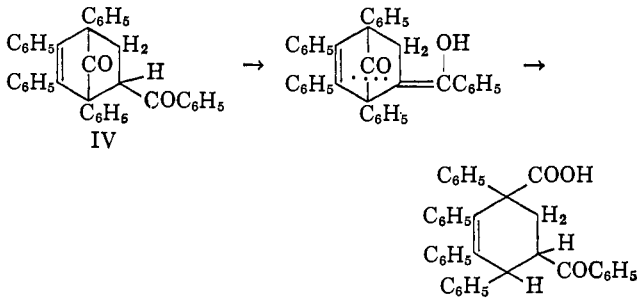
A number of polyarylated polycyclic derivatives



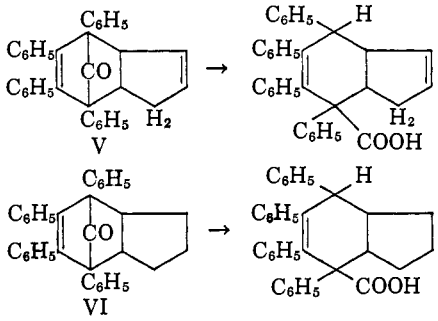
have been found to form acids similarly on treatment with basic reagents (12, 20). Substances having un-



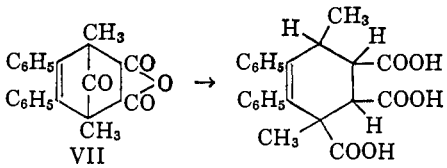
symmetrical structures (III, IV) give two acids unless other factors, such as enolization, are involved; in this case only one acid results.



The symmetrical indene (V) and indane (VI) each give a single acid.

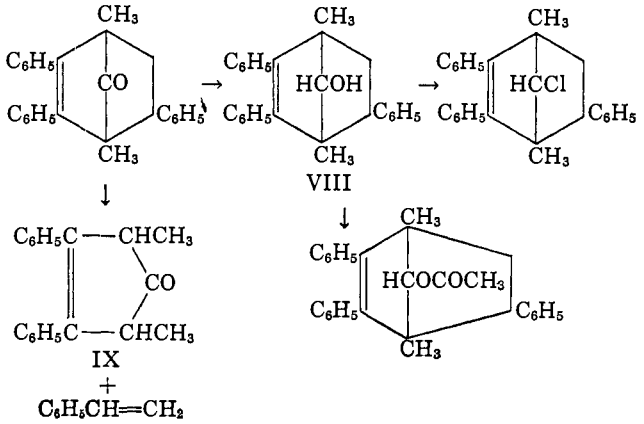


The bridged anhydride (VII) gives a tribasic acid (20).

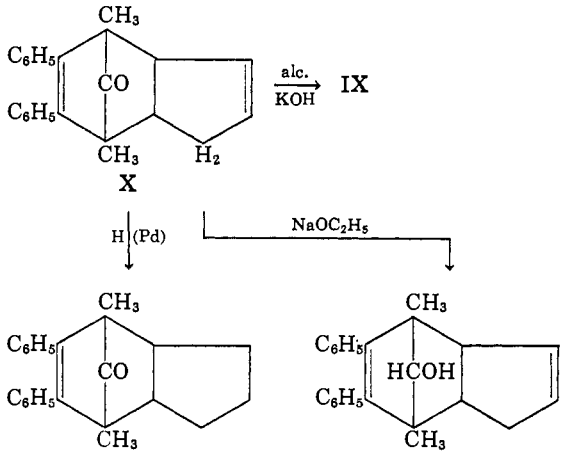


While most carbonyl bridge compounds give acids upon alkali treatment, there are a few complications (20). Those having methyl groups, instead of phenyl, at the bridgehead, in part, undergo reduction when treated with sodium ethoxide in dry ethanol, a bridge carbinol (VIII) resulting. The latter is distillable unchanged.

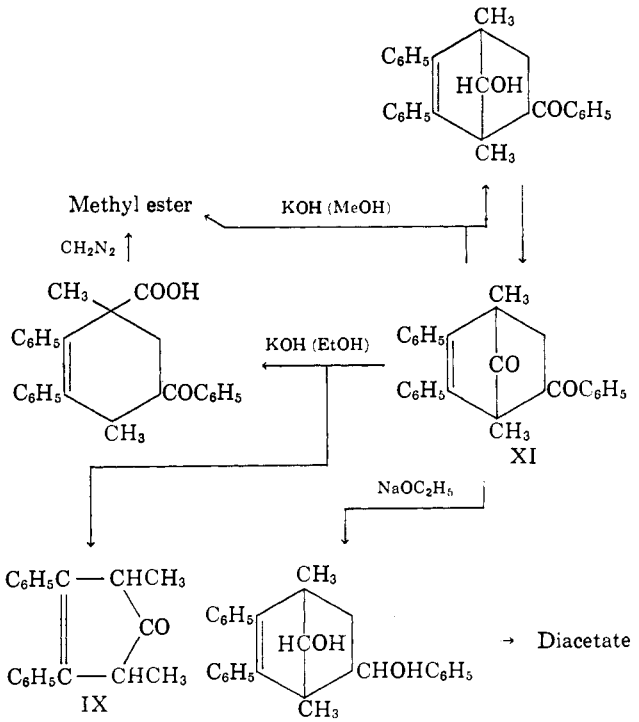
With ethanolic potassium hydroxide, however, reduction and dissociation to the cyclopentenone (IX) takes place. The other product is assumed to be styrene, since the same two products result when the carbinol is



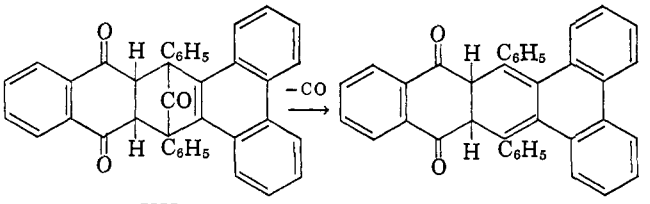
distilled. Analogously the indene (X) gave a carbinol, or the same cyclopentenone, IX.



The bridged ketone (XI) gives all the foregoing types of products (20).

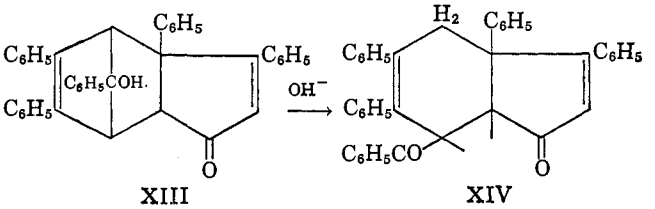


A polynuclear quinone (XII) was decarboxylated during the alkali treatment (12).



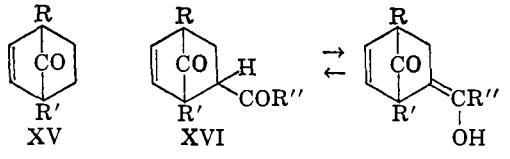
XII

A supposed tricyclic carbinol (12), later (8) shown to be an isomeric indenone (XIII) without a carbonyl bridge, gave the ketone (XIV) by what amounts to the reversal of an aldol-type condensation.



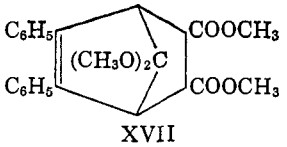
XIII XIV

In summary, if there are phenyl groups at the ends of the bridge (XV, R = C_6H_5), the latter is cleaved at one end, so that the product is a carboxylic acid. If there are methyl groups at the ends of the bridge, reduction to a carbinol takes place. If there are methyl groups or hydrogen at one or both ends of the bridge, and a side chain containing an unsaturated linkage of such a nature that upon enolization a double bond can be formed between the ring and the side chain (XVI, R, R′ = CH_3, H), all possible types of reaction can be expected. The keto group in the side chain may be reduced to give a carbinol.



XV XVI

Ketal formation already has been mentioned in the preceding section dealing with "action of alkali." As usual, ketals are formed when the carbonyl bridge compounds are treated with methanol and an acid. Only methyl ketals have been made, since they were obtained as by-products (40). The first one known was a ketal diester (XVII) (16).



XVII

The clerical assistance of Misses Glenda Didas and Judy Witzel is gratefully acknowledged.

IX. REFERENCES

(1) Abramov, V. S., *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 330 (1945); *Chem. Abstracts*, **40**, 5024 (1946).

(2) Abramov, V. S., *Doklady Akad. Nauk, S.S.S.R.*, **63**, 637–640 (1948); *Chem. Abstracts*, **43**, 2585 (1949).

(3) Abramov, V. S., and Pakhomova, A. P., *J. Gen. Chem. USSR, Eng. tr.*, **24**, 1187 (1954).

(4) Abramov, V. S., and Shapshinskaya, L. A., *Doklady Akad. Nauk, S.S.S.R.*, **59**, 1291 (1948); *Chem. Abstracts*, **43**, 2614 (1949).

(4a) Abramov, V. S., and Shapshinskaya, L. A., *Zhur. Obshchei Khim.*, **22**, 1450 (1952); *Chem. Abstracts*, **47**, 10488 (1953).

(5) Abramov, V. S., and Tsyplenkova, N. P., *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 60 (1949); *Chem. Abstracts*, **39**, 1639 (1945).

(6) Allen, C. F. H., *Chem. Rev.*, **37**, 209 (1945).

(7) Allen, C. F. H., Davis, T. J., Stewart, D. W., Van Allan, J. A., and Williams, J. L. R., *J. Org. Chem.*, **20**, 306 (1955).

(8) Allen, C. F. H., Davis, T. J., Stewart, D. W., and Van Allan, J. A., *J. Org. Chem.*, **20**, 310 (1955).

(9) Allen, C. F. H., and Gates, J. W., Jr., *J. Am. Chem. Soc.*, **64**, 2123 (1942).

(10) Allen, C. F. H., and Gates, J. W., Jr., *J. Am. Chem. Soc.*, **64**, 2439 (1942).

(11) Allen, C. F. H., and Gates, J. W., Jr., *J. Am. Chem. Soc.*, **65**, 419 (1943).

(12) Allen, C. F. H., Jones, J. E., and Van Allan, J. A., *J. Am. Chem. Soc.*, **68**, 708 (1946).

(13) Allen, C. F. H., Reynolds, G. A., Webster, S. K. and Williams, J. L. R., *J. Org. Chem.* **27**, 1447 (1962).

(14) Allen, C. F. H., and Rudoff, H., *Can. J. Research*, **B15**, 321 (1937).

(15) Allen, C. F. H., Ryan, R. W., Jr., and Van Allan, J. A., *J. Org. Chem.*, **27**, 778 (1962).

(16) Allen, C. F. H., and Sheps, L. J., *Can. J. Research*, **11**, 178 (1934).

(17) Allen, C. F. H., and Spanagel, E. W., *J. Am. Chem. Soc.*, **55**, 3773 (1933).

(18) Allen, C. F. H., and Van Allan, J. A., *J. Am. Chem. Soc.*, **64**, 1260 (1942).

(19) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **10**, 333 (1945).

(20) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **11**, 268 (1946).

(21) Allen, C. F. H., and Van Allan, J. A., *J. Am. Chem. Soc.*, **68**, 2387 (1946).

(22) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **14**, 1051 (1949).

(23) Allen, C. F. H., and Van Allan, J. A., *J. Am. Chem. Soc.*, **72**, 5165 (1950).

(24) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **18**, 882 (1953).

(25) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **20**, 315 (1955).

(26) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **20**, 323 (1955).

(27) Allen, C. F. H., and Van Allan, J. A., *J. Org. Chem.*, **20**, 328 (1955).

(28) Allen, C. F. H., and Van Allan, J. A., *J. Am. Chem. Soc.*, **77**, 2315 (1955).

(29) Allen, C. F. H., Ryan, R. W., Jr., and Van Allan, J. A., see ref. 15.

(30) Bikaless, N. M., and Becker, E. I., *J. Org. Chem.*, **21**, 1405 (1956).

(31) Cope, A. C., Fawcett, F. S., and Munn, G., *J. Am. Chem. Soc.*, **72**, 3399 (1950).

(32) Cope, A. C., and Herrmann, E. C., *J. Am. Chem. Soc.*, **72**, 3405 (1950).
(33) Cope, A. C., and Synerholm, M. E., *J. Am. Chem. Soc.*, **72**, 5229 (1950).
(34) DePuy, C. H., and Lyons, C. E., *J. Am. Chem. Soc.*, **82**, 631 (1960).
(35) DePuy, C. H., and Ponder, B. W., *J. Am. Chem. Soc.*, **81**, 4629 (1959).
(36) DePuy, C. H., and Zaweski, E. F., *J. Am. Chem. Soc.*, **81**, 4920 (1959).
(37) Doering, R. F., Miner, R. S., Jr., Rothman, L., and Becker, E. I., *J. Org. Chem.*, **23**, 520 (1958).
(38) Fawcett, F. S., *Chem. Rev.*, **47**, 219 (1950), esp. pp. 240 ff.
(39) Grummitt, O., and Becker, E. I., *J. Am. Chem. Soc.*, **70**, 149 (1948).
(40) Hatchard, W. R., and Schneider, A. K., *J. Am. Chem. Soc.*, **79**, 6261 (1957).
(41) Kraiman, E. A., U. S. Patent 2,890,206; *Chem. Abstracts*, **53**, 17572 (1959).
(42) LaForge, F. B., Green, N., and Schecter, M. S., *J. Am. Chem. Soc.*, **74**, 5392 (1952).
(43) Mackenzie, K., *J. Chem. Soc.*, 473 (1960).
(44) McBee, E. T., Dively, W. R., and Burch, J. E., *J. Am. Chem. Soc.*, **77**, 385 (1955).
(45) McBee, E. T., and Meyers, R. K., *J. Am. Chem. Soc.*, **77**, 88 (1955).
(46) McBee, E. T., Smith, D. K., and Ungnade, H. E., *J. Am. Chem. Soc.*, **77**, 559 (1955).
(47) McBee, E. T., and Ungnade, H. E., *Chem. Rev.*, **58**, 249 (1958).
(48) Newcomer, J. S., and McBee, E. T., *J. Am. Chem. Soc.*, **71**, 946 (1949).
(49) Newcomer, J. S., and McBee, E. T., *J. Am. Chem. Soc.*, **71**, 952 (1949).
(50) Newcomer, J. S., and McBee, E. T., U. S. Patent 2,597,016; *Chem. Abstracts*, **47**, 4366 (1953).
(51) Norton, C. J., Dissertation, Harvard University (1955).
(52) Peláez, R. M., *Anales real soc. españ. fís. y quím.*, **49B**, 603; Publs. inst. quím. "Alonso Barba," **7**, 166 (1953); *Chem. Abstracts*, **49**, 1592 (1955).
(53) Peláez, R. M., "Coloq. problemas sintesis Diels-Alder, Soc. españ. fís. y chím.," Madrid, 1953, p. 109; *Chem. Abstracts*, **49**, 1592 (1955).
(54) Prelog, V., Barman, P., and Zimmermann, M., *Helv. Chim. Acta*, **32**, 1284 (1949).
(55) Prelog, V., Ruzicka, L., Barman, P., and Frenkiel, L., *Helv. Chim. Acta*, **31**, 92 (1948).
(56) SenGupta, S. C., and Bhattacharyya, A. J., *J. Ind. Chem. Soc.*, **33**, 29 (1956); *Chem. Abstracts*, **51**, 1131 (1957).
(57) Wilder, P., Jr., and Winston, A., *J. Am. Chem. Soc.*, **78**, 868 (1956).
(58) Williams, J. L. R., Borden, D. G., and Laakso, T. M., *J. Org. Chem.*, **21**, 1461 (1956).
(59) Woodward, R. B., Brutsky, F. J., and Baer, H. J., *J. Am. Chem. Soc.*, **70**, 4216 (1948).
(60) Woodward, R. B., and Katz, T. J., *Tetrahedron*, **5**, 75 (1959).
(61) Zelinski, N. D., *Ber.*, **34**, 3798 (1901).
(62) Zincke, T., and Meyer, K. H., *Ann.*, **367**, 1 (1909).