

# THE CHEMISTRY OF EIGHT-MEMBERED CARBOCYCLES

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## I. INTRODUCTION

The unique chemical behavior of benzene led chemists many years ago to speculate about the nature of the closed conjugated system of four double bonds which would be present in 1,3,5,7-cyclooctatetraene. The synthesis of cyclooctatetraene was reported in 1911-13 by Willstätter (159, 165), but the validity of the synthesis was questioned over a period of several years (6, 66, 73, 74, 155). Numerous syntheses were proposed for the preparation of eight-membered carbocycles and introduction of the double bonds in a stepwise manner, but the only successful ones gave benzocyclooctatetraenes. In 1940 a group of investigators, under the direction of Julius Walter Reppe, at the I. G. Farbenindustrie laboratories at Ludwigshaven, Germany, found that cyclooctatetraene can be

prepared by the polymerization of acetylene in the presence of certain nickel catalysts. Interest in cyclooctatetraene was revived by the reports of this work which began to appear shortly after World War II. Willstätter's synthesis was confirmed (34, 35), other syntheses of cyclooctatetraene were devised, and several groups of workers began investigations of its physical and chemical nature.

Studies of organic compounds containing large rings resulted in the synthesis of numerous eight-membered carbocycles, as, for example, the classic studies of the preparation of large carbocycles by Ruzicka and by Ziegler. Eight-membered carbocycles have also resulted from certain reactions which have been found to bring about ring-enlargement of six- and seven-membered ring compounds.

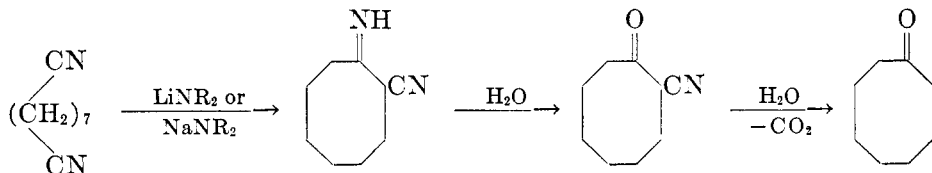
This review was written as a result of the potential commercial availability of cyclooctatetraene from acetylene and with the knowledge that cyclooctatetraene can be converted to the great majority of eight-membered carbocycles which have been prepared by various methods. It was written primarily to furnish a convenient compilation of the eight-membered carbocycles which have been prepared, but critical discussions of methods of preparation, molecular configuration, and chemical reactivity have been included. The bi- and polycyclic compounds—many of which would be extremely difficult to prepare by other methods—which have been prepared from eight-membered ring compounds have also been tabulated. It should be noted that the structures of many of the products of the reactions described herein, particularly those involving polycyclic ring systems, have not been proved conclusively, and a large amount of work remains to be done on proofs of such structures, determination of molecular configurations, and reaction mechanisms.

## II. PREPARATION OF EIGHT-MEMBERED CARBOCYCLES

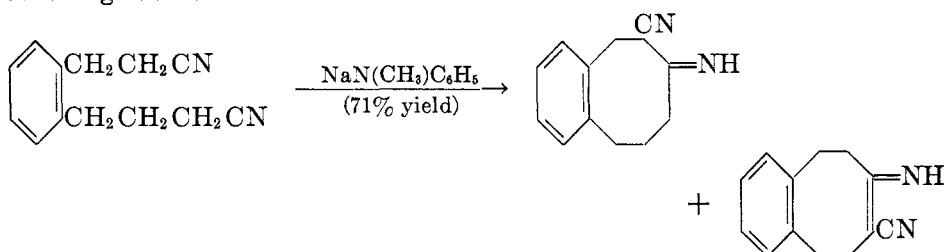
### A. BY INTRAMOLECULAR RING-CLOSURE

In the classic study of the preparation of large carbocycles by ring-closure of dicarboxylic acids, Ruzicka and Brugger (125) obtained cyclooctanone in 21 per cent yield by dry distillation of the thorium salt of azelaic acid. This procedure has since been used frequently as a source of cyclooctanone (42, 63, 122, 166, 167) and of alkylcyclooctanones, such as 1,1,8-trimethylcyclooctanone (144, 145). Ricinoleic acid upon oxidation and treatment in the above manner was found to give mixtures of cycloheptanone and cyclooctanone (99).

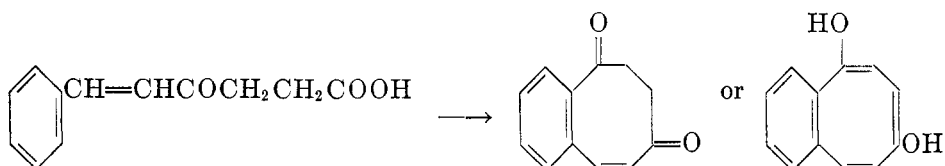
In the preparation of large carbocycles by intramolecular condensations of dinitriles, it was found that ring-closure of azelanitrile can be accomplished in yields of 90 per cent when sodium or lithium derivatives of secondary amines are used as condensing agents (138, 168, 169, 170, 171). The product of this ring-closure is readily hydrolyzed and cyclooctanone is produced in a 75 per cent yield from the dinitrile (171). The overall reaction is as follows:



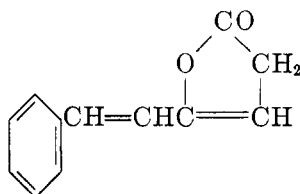
This intramolecular condensation was employed by Fry and Fieser (56) in the following reaction:



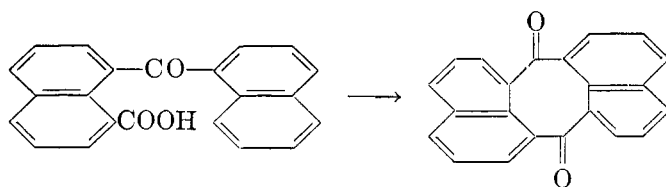
Several examples of the preparation of eight-membered rings by cyclodehydration have been reported. Sen and Roy (140) assigned cyclooctabenzene structures to products obtained by heating benzylidene derivatives of levulinic acid with acetic anhydride. The product formed in this manner was found to give a mono-phenylhydrazone and a dibenzoyl derivative, to be soluble in caustic, and to decolorize bromine and potassium permanganate solutions. These facts were regarded as evidence for tautomerism between enol and keto forms and the reaction was written as follows:



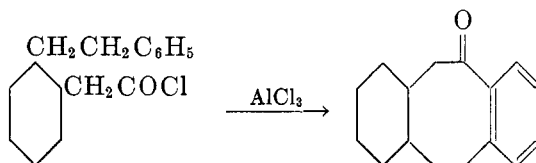
Subsequent investigators (112a) showed that oxidation of the product of this reaction gives benzoic acid rather than phthalic acid and that two molar equivalents of hydrogen are absorbed upon catalytic hydrogenation to give a material containing a lactone ring. On the basis of these observations, the product was assigned the following structure:



Knapp (81) reported that the ring-closure of naphthaloylnaphthoic acids to give eight-membered ring compounds can be accomplished in low yields by treatment with phosphorus pentoxide, aluminum chloride, or concentrated sulfuric acid.

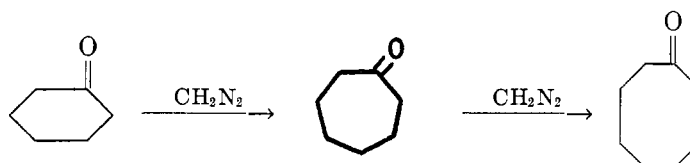


One example of intramolecular ring-closure by the Friedel-Crafts reaction to give an eight-membered carbocycle has been reported (23). The reaction is as follows:



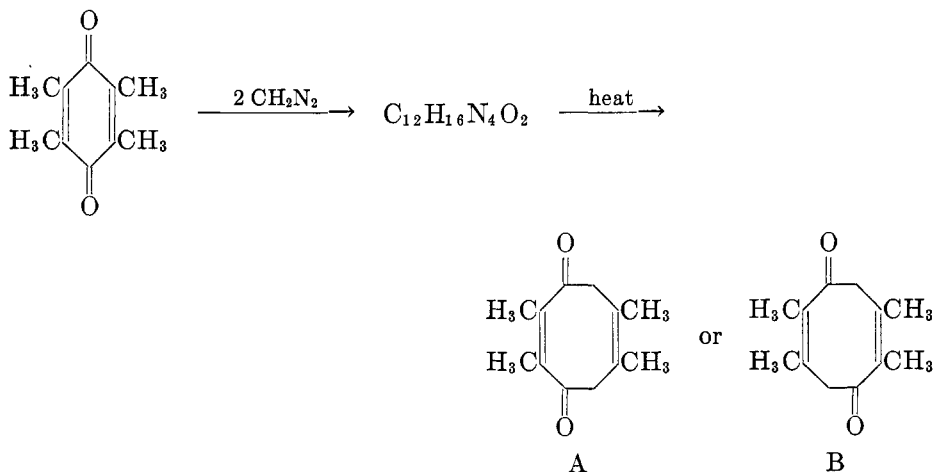
#### B. BY RING-ENLARGEMENT

Mosettig and Burger (94) found that alicyclic ketones undergo ring-enlargement when treated with diazomethane. By this method, cycloöctanone was obtained from cycloheptanone (1, 83) in yields of 37-55 per cent and from cyclo-



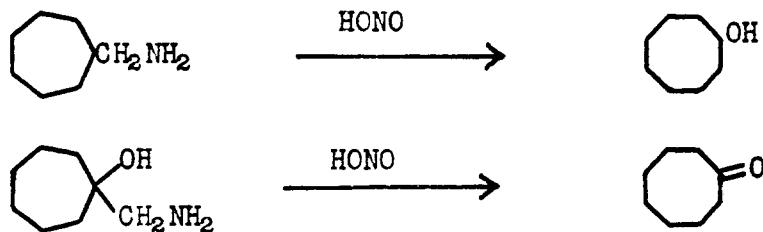
hexanone (5) in a yield of 15 per cent. Ring-enlargement by this method was successfully applied to 2-chlorocycloheptanone (147), 3-methylcyclohexanone (98), 3-methylcycloheptanone (98), and  $\alpha$ -tetralone (150) to give the corresponding cycloöctanone in low yields. An attempt to prepare a cycloöctanedione from 1,4-cyclohexanedione and diazomethane was unsuccessful (155).

Smith and Pings (143) treated duroquinone with diazomethane and obtained as one of the products a compound ( $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_2$ ) which lost nitrogen on heating to give a material believed to be an eight-membered diketone (A or B).



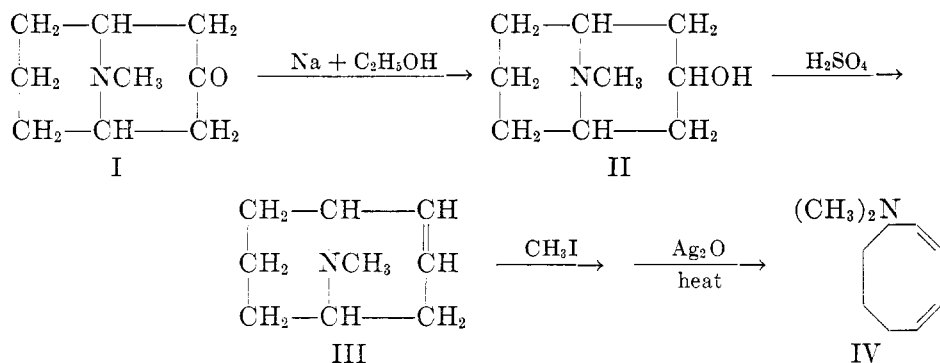
Wallach (156) found that ring-enlargement occurred when aminomethylcycloheptane, obtained by the reduction of the cyanohydrin of cycloheptanone,

was treated with nitrous acid, cyclooctanol being produced. When the cyanohydrin was carefully reduced to the aminomethylcycloheptanol before the reaction with nitrous acid, the product was cyclooctanone (149).

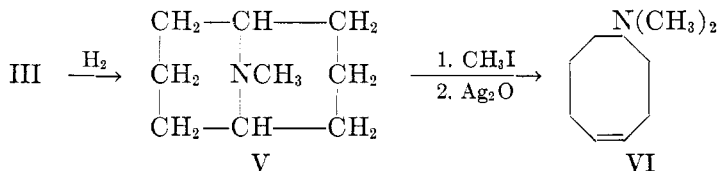


### C. BY CLEAVAGE OF THE BRIDGE OF BICYCLIC COMPOUNDS

The first eight-membered carbocycles were prepared by degradation of certain alkaloids containing bicyclic ring systems. In the original synthesis of cyclooctatetraene by Willstätter (164, 165), pseudopelletierine (I) was converted to *N*-methylgranatoline (II) by reduction of the ketone group, the product dehydrated to give *N*-methylgranatenine (III), and exhaustive methylation carried out to give the eight-membered carbocycle,  $\alpha$ -des-dimethylgranatenine or *N,N*-dimethyl-2,4-cyclooctadien-1-ylamine (IV).

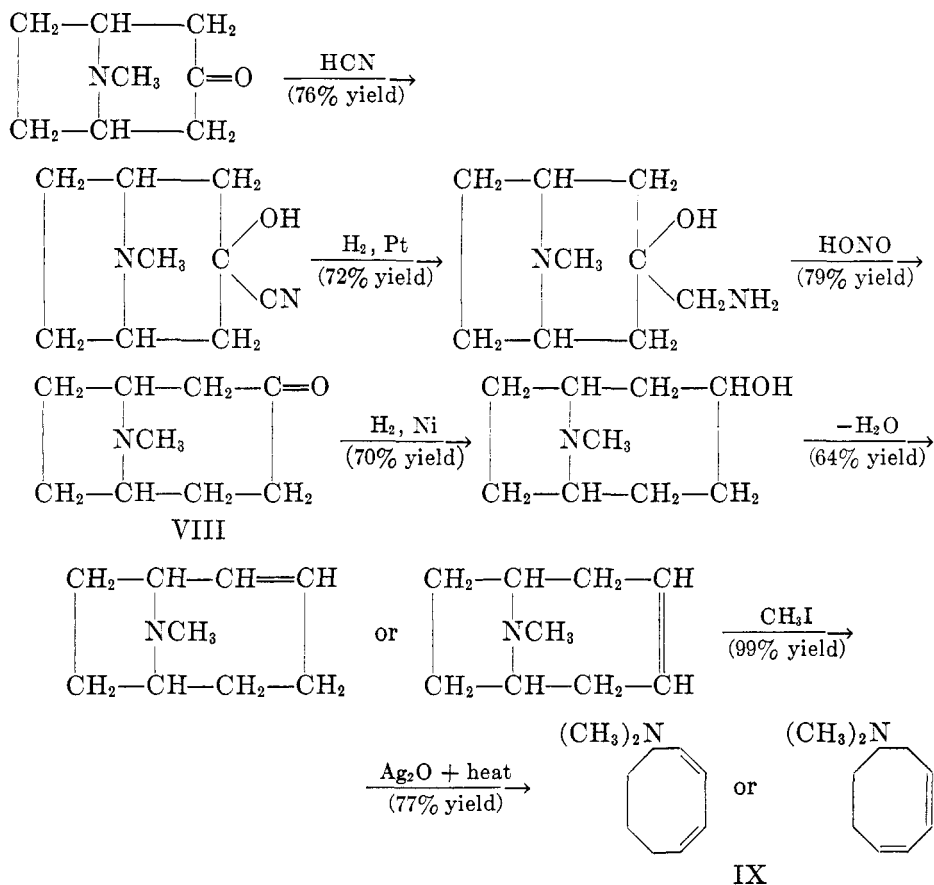


The *N*-methylgranatenine (III) was also hydrogenated to *N*-methylgranatanine (V) and converted to *N,N*-dimethyl-4-cycloocten-1-ylamine (VI) by exhaustive methylation.

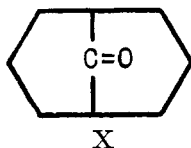


These reactions were also carried out by Cope and Overberger (34, 35) in their repetition of Willstätter's cyclooctatetraene synthesis.

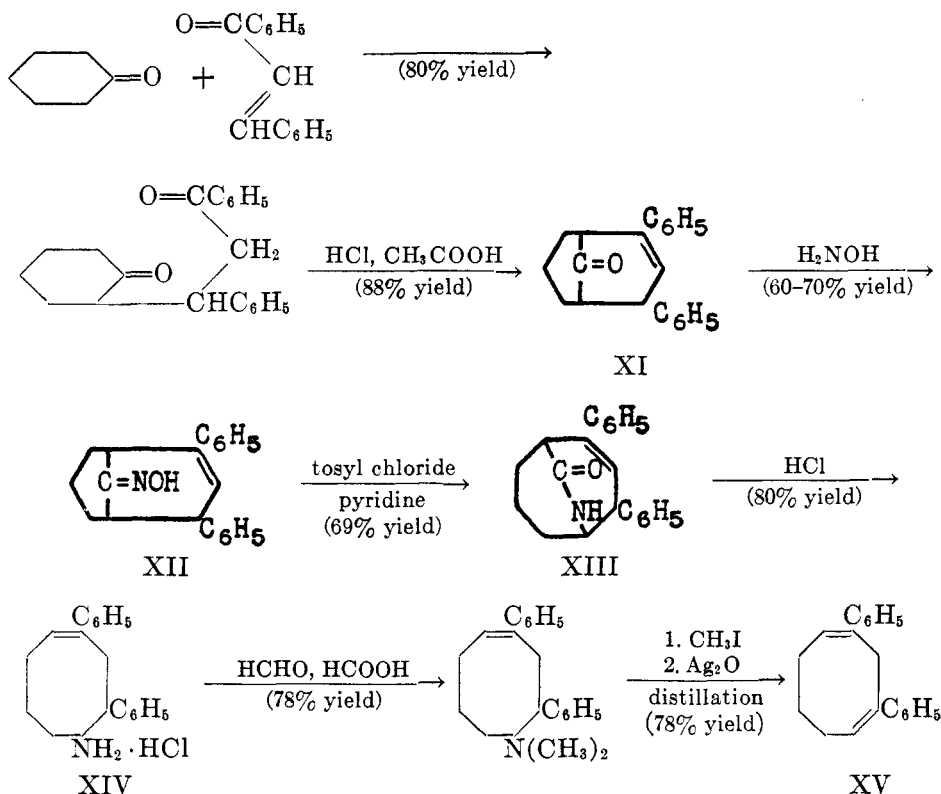
The difficulty with which pseudopelletierine is obtained led to the synthesis of the eight-membered carbocycle from the more readily available alkaloid, tropinone (33). Tropinone (VII) was converted to the cyanohydrin, the cyanohydrin hydrogenated, and the product treated with nitrous acid to bring about ring-enlargement. The resulting product, R-homotropinone (VIII), an isomer of pseudopelletierine, was converted to *N,N*-dimethylcyclooctadienylamine (IX) in the same manner as was pseudopelletierine.



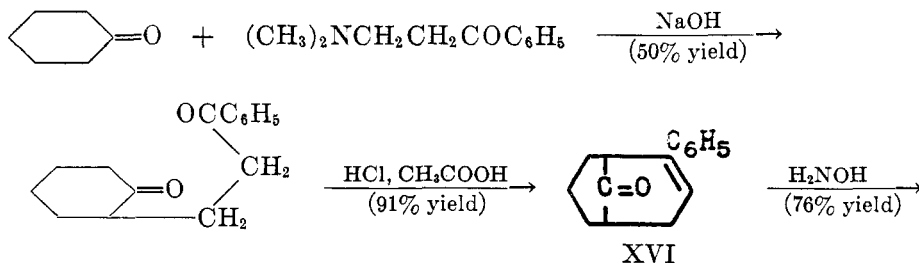
A search for a still more convenient source of eight-membered ring compounds led to their synthesis by removal of the carbonyl bridge of the bicyclo[3.3.1]-nonan-9-one ring system (X) (26, 30).



2,4-Diphenylbicyclo[3.3.1]non-2-en-9-one (XI) was prepared by the Michael addition of cyclohexanone to benzalacetophenone, followed by cyclization with acids. Cleavage of the bridge was accomplished by conversion to the oxime (XII), rearrangement to the lactam (XIII), and hydrolysis. Exhaustive methylation of the resulting amine (XIV) gave 2,4-diphenyl-1,4-cyclooctadiene (XV).



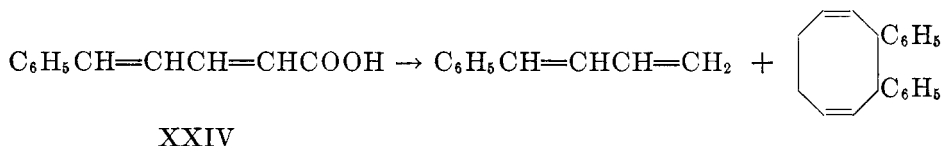
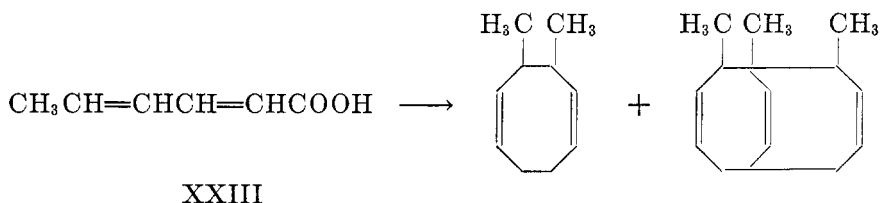
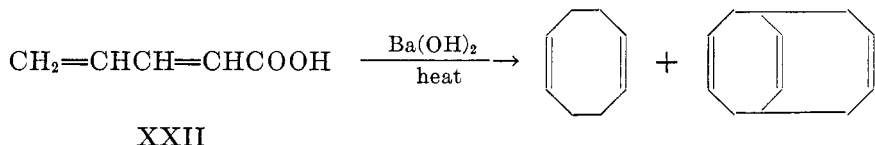
2-Phenylbicyclo[3.3.1]non-2-en-9-one (XVI) was prepared by treatment of cyclohexanone with  $\beta$ -dimethylaminopropiophenone, followed by an acid-catalyzed cyclization. Cleavage of the bridge in the manner described above led to the formation of phenyl-1,3-cyclooctadiene (XVII).



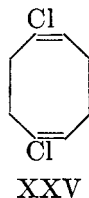




several 2,4-pentadienoic acids with barium hydroxide and isolated products to which were assigned structures containing eight-membered ring systems. The reaction was applied to  $\beta$ -vinylacrylic acid (XXII), sorbic acid (XXIII), and 4-phenyl-2,4-pentadienoic acid (XXIV) with the results indicated in the following equations:



Chloroprene has been observed to dimerize on standing or on heating in the presence of polymerization inhibitors to give a mixture of dimers, from which an eight-membered cyclic diolefin has been isolated (16, 24, 36, 54). The evidence for a 1,5-cyclooctadiene structure consists of hydrogenation to give cyclooctane (16, 24, 54), dehalogenation to give 1,5-cyclooctadiene (24, 37, 54), and ozonization followed by oxidation to give succinic acid (16). The chlorine atoms were shown to be in the 1,6-positions (36), a fact which identifies the eight-membered cyclic chloroprene dimer as 1,6-dichloro-1,5-cyclooctadiene (XXV). The best yield (22 per cent) of the eight-membered diene was obtained by heating



chloroprene under pressure in the presence of phenothiazine and Darco at 80°C. for 120 hr. (54).

Other 1,5-cyclooctadienes which have been isolated from dimers of 1,3-dienes are 1,5-cyclooctadiene from 1,3-butadiene in 1–15 per cent yields (54, 172, 174), 1,2,5,6-tetrachloro-1,5-cyclooctadiene from 2,3-dichloro-1,3-butadiene in 13

per cent yield (54), and 1,2,5,6-tetramethyl-1,5-cyclooctadiene from 2,3-dimethyl-1,3-butadiene in 5 per cent yield (174).

#### E. BY POLYMERIZATION OF ACETYLENE

In studying the reactions of acetylene under pressure, German investigators under the direction of J. W. Reppe found that four or more molecules of acetylene will condense in the presence of certain nickel catalysts to give cyclic polymers (13, 38, 68, 71, 76, 114, 115, 116, 117, 118, 119, 120, 142). The main product of the reaction was shown to be cyclooctatetraene.

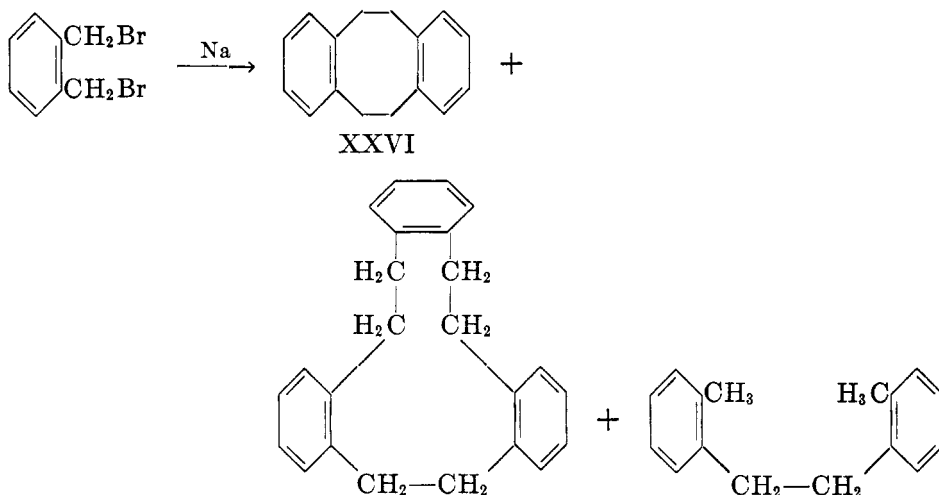
These investigators (38, 119) found that when nickel cyanide, calcium carbide, or ethylene oxide, and tetrahydrofuran were placed in a stirred autoclave and acetylene introduced continuously at a constant pressure of 15–20 atm. (5 atm. of nitrogen was used as diluent) at 60–70°C., there was a slow absorption of acetylene for 30–60 hr. The product was shown to contain mainly cyclooctatetraene and small amounts of benzene, naphthalene, azulene, and hydrocarbons corresponding to empirical formulas of  $C_{10}H_{10}$  and  $C_{12}H_{12}$ . The product obtained from a typical reaction in a 4- to 5-l. autoclave was reported to consist of 30–50 g. of benzene, 320–400 g. of cyclooctatetraene, and 30–50 g. of higher-boiling hydrocarbons and residue. The yields of cyclooctatetraene based on the amount of acetylene absorbed averaged about 70 per cent but yields as high as 90–95 per cent were reported (71, 76, 114, 115, 117, 142).

When the reaction was carried out at higher temperatures, proportionately larger amounts of the higher-boiling hydrocarbons were obtained (120). At 90–100°C. the product consisted of 140 g. of cyclooctatetraene, 40 g. of crude  $C_{10}H_{10}$ , 25 g. of crude  $C_{12}H_{12}$ , and 15 g. of higher-boiling hydrocarbons. At 120–130°C. a 70-g. fraction consisting mainly of the  $C_{10}H_{10}$  material was obtained. Upon removal of small amounts of azulene from the product of the reaction carried out at 90–100°C., by extracting a petroleum ether solution with phosphoric acid, an orange-yellow hydrocarbon,  $C_{10}H_{10}$ , and a bright yellow hydrocarbon,  $C_{12}H_{12}$ , were obtained. By similar purification of the product from the reaction at 120–130°C., a bright yellow hydrocarbon,  $C_{10}H_{10}$ , was obtained. The two  $C_{10}H_{10}$  hydrocarbons were considered by the German workers to be stereoisomeric cyclodecapentaenes and the  $C_{12}H_{12}$  was considered to be cyclododecahexaene (13, 38, 71, 76, 114, 115, 117, 120).

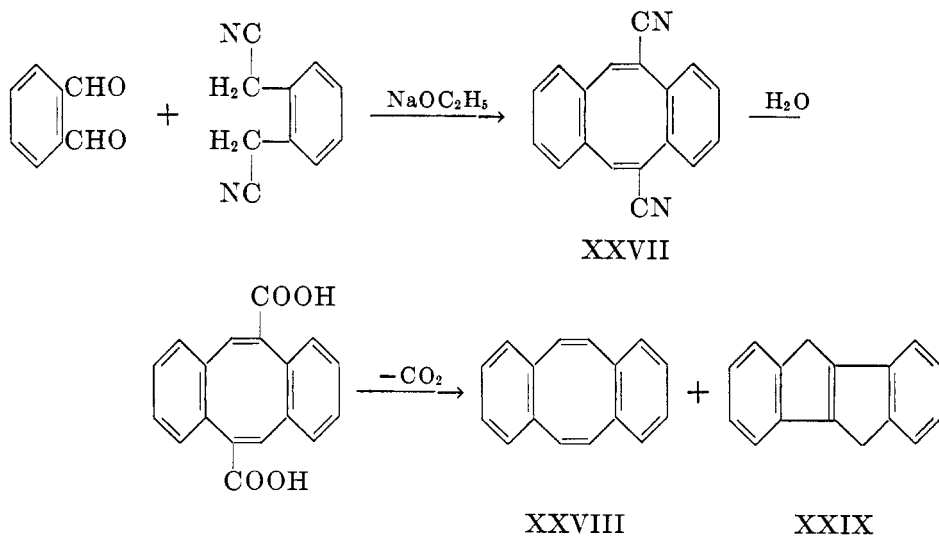
Subsequent work by two independent groups of workers (27, 40) resulted in the isolation of vinylcyclooctatetraene and 1-phenyl-1,3-butadiene, both having a  $C_{10}H_{10}$  empirical formula, from the higher-boiling fractions from cyclooctatetraene preparations. Upon comparison of the properties of mixtures of these hydrocarbons with the properties reported by the German workers for their  $C_{10}H_{10}$  material, it is evident that they also had a mixture of these two hydrocarbons. The orange-yellow  $C_{10}H_{10}$  apparently contained a higher ratio of vinylcyclooctatetraene, which is golden-orange in color, while the bright yellow  $C_{10}H_{10}$  contained a higher ratio of colorless 1-phenyl-1,3-butadiene. In the light of these findings, it is doubtful that the  $C_{12}H_{12}$  material is the single compound cyclododecahexaene.

## F. BY MISCELLANEOUS METHODS

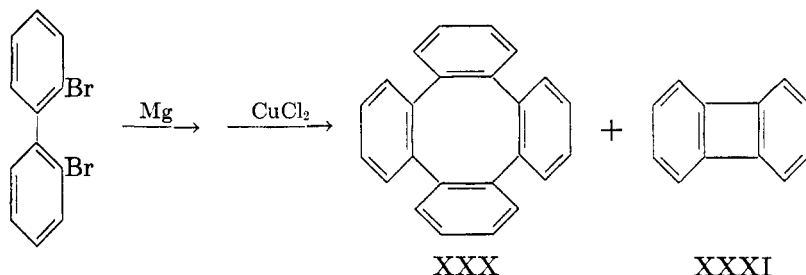
The reaction of  $\alpha, \alpha'$ -dibromo-*o*-xylene and sodium was reported (7) to give an eight-membered carbocycle, 5,6,11,12-tetrahydrocycloocta[*a,e*]dibenzene (XXVI), in 6 per cent yield along with smaller amounts of two other hydrocarbons. At high dilution, a 30 per cent yield was obtained (28).



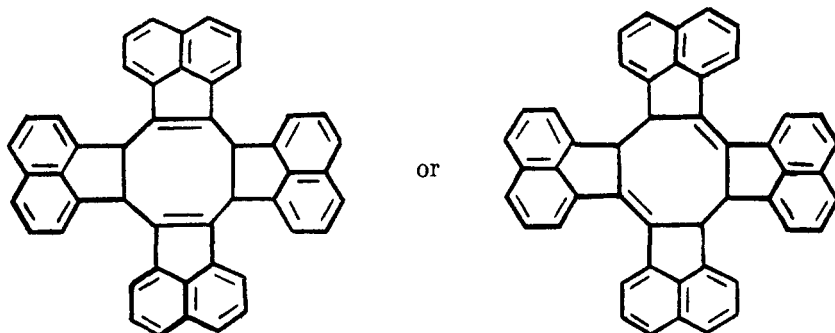
Fieser and Pechet (52) showed that *o*-phthalaldehyde and *o*-phenylenediacetonitrile will condense to give cycloocta[*a,e*]dibenzene-5,12-dicarbonitrile (XXVII) in 47 per cent yield. Hydrolysis followed by decarboxylation gave two products, cycloocta[*a,e*]dibenzene (XXVIII) and 5,10-dihydroindeno[2,1-*a*]indene (XXIX).



The action of cupric chloride on the Grignard reagent prepared from 2,2'-dibrombiphenyl was reported (113) to give a 16 per cent yield of tetraphenylene, which was assigned a cycloöcta[*a,c,e,g*]tetrabenzene structure (XXX), and a 4 per cent yield of diphenylene (XXXI).

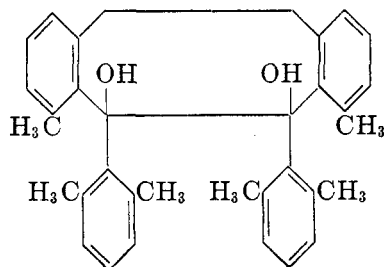


In the study of the polymerization of acenaphthene at high temperatures (45), a very high-melting crystalline compound, C<sub>48</sub>H<sub>28</sub>, was obtained in 4-5 per cent yield. The material, fluorocyclene, was considered to have one of the two following structures:



Subsequent work (44, 46, 47) showed that fluorocyclene can be produced in yields of 25-38 per cent when the acenaphthene is heated at high temperatures in the presence of lead oxides.

By the addition of aryllithium compounds to diaryl ketones (50), products were obtained which were assigned cycloöcta[*a,e*]dibenzene structures. For example, the product from the addition of 2,6-dimethylphenyllithium to bis(2,6-dimethylphenyl) ketone was assigned the following structure:



Similar products were reported to be formed by the addition of phenyllithium and mesityllithium to mesityl ketone.

Pyrolysis of tetrafluoroethylene was reported to produce mixtures of poly-fluorinated cycloparaffins (69). It was suggested that one distillation fraction of such a pyrolysis was hexadecafluorocyclooctane, although no structural evidence was given.

Treatment of caoutchouc with nitric acid or lead nitrate was reported to give a carboxylic acid which was believed to be 5,6-dinitrocyclooctene-1-carboxylic acid (3).

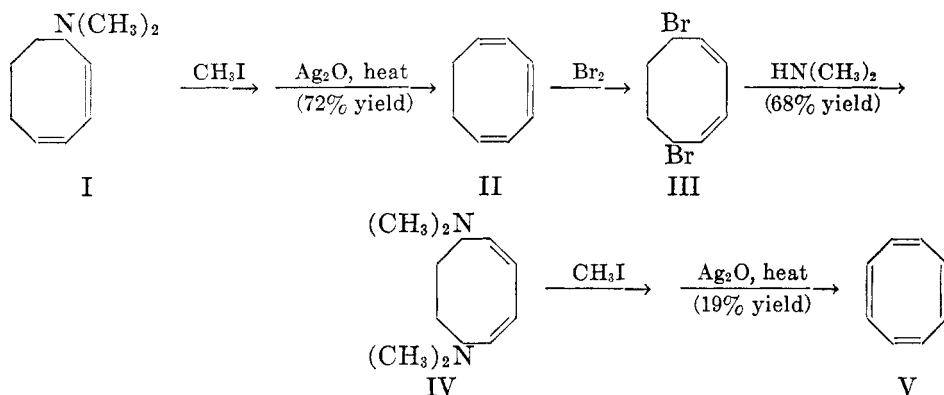
Several unsuccessful attempts have been made to synthesize cyclooctadi-benzene compounds, such as the condensation of 2,2'-biphenylcarboxaldehyde with ethyl succinate (112), ring-closure of 1,4-di(2-iodophenyl)-1,3-butadiene (112) by the Ullmann reaction, and intramolecular coupling of the diazonium salt of 1-(2-aminophenyl)-4-phenyl-1,3-butadiene (4).

### III. PROPERTIES OF EIGHT-MEMBERED CARBOCYCLES

#### A. CYCLOOCTATETRAENE

##### 1. Preparation

The first synthesis of cyclooctatetraene was carried out in 1911-13 by Willstätter, Waser, and Heidelberger (159, 165) by the stepwise introduction of double bonds into the eight-membered carbocycle which was obtained by degradation of pseudopelletierine (see page 107). The double bonds were introduced by first subjecting the  $\alpha$ -des-dimethylgranatenine (I) (IV of page 107) to exhaustive methylation to produce a cyclooctatriene (II). Addition of bromine to II, followed by treatment of the dibromocyclooctadiene (III) with dimethylamine, gave *N,N,N',N'*-tetramethyl-5,7-cyclooctadiene-1,4-diamine (IV). Exhaustive methylation gave a yellow hydrocarbon,  $C_8H_8$ , which was believed to be cyclooctatetraene (V).

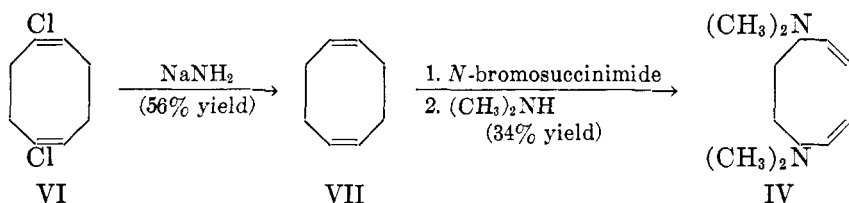


A number of years later, the validity of the suggested 1,3,5,7-cyclooctatetraene structure was challenged. Similarities between Willstätter's product and styrene were pointed out (6, 66, 155). The observations that cyclooctene is converted to styrene on catalytic dehydrogenation (66) and that the Hofmann ex-

haustive methylation procedure when applied to diaminobutanes gives ethylacetylene and methylallene in addition to 1,3-butadiene (74) were considered as evidence that Willstätter's product may not have been cyclooctatetraene. A mechanism whereby styrene might have been formed was postulated (73).

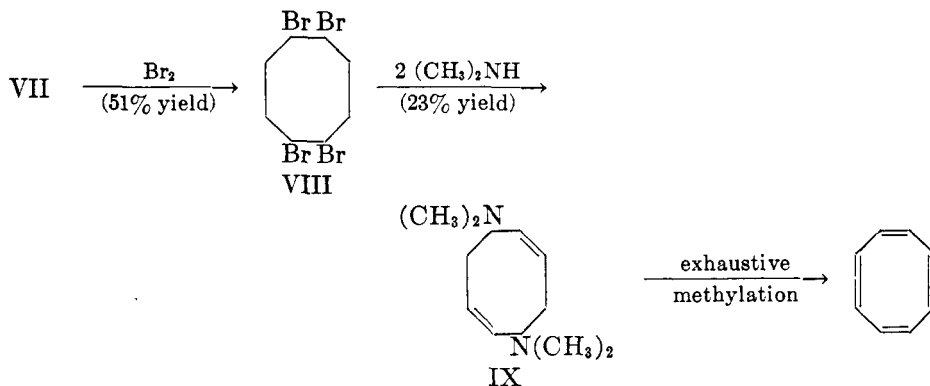
In 1940 Reppe discovered that cyclooctatetraene can be prepared by polymerization of acetylene in the presence of nickel catalysts (see page 112). The physical constants of the cyclooctatetraene prepared from acetylene and of the material prepared by Willstätter were not in absolute agreement, but could easily be accounted for by the fact that Willstätter had a very small amount of material and was unable to purify it to the same degree as did Reppe. Cope and Overberger (35) repeated Willstätter's synthesis from pseudopelletierine and showed that the product is identical with the cyclooctatetraene prepared from acetylene. Thus, Willstätter's synthesis was confirmed and accordingly deserves its place in classic synthetic organic chemistry.

Cope and Bailey (24) prepared cyclooctatetraene from the eight-membered cyclic chloroprene dimer (VI). VI was dehalogenated to 1,5-cyclooctadiene (VII), the diene treated with two molar equivalents of *N*-bromosuccinimide, and the resulting dibromo compound, which was not isolated, treated with dimethylamine to give *N,N,N',N'*-tetramethyl-5,7-cyclooctadiene-1,4-diamine (IV).



IV proved to be identical with the intermediate (IV of page 107) obtained from pseudopelletierine and was converted to cyclooctatetraene in the same manner.

Cyclooctatetraene was also prepared from VII by adding two molar equivalents of bromine, treating the tetrabromocyclooctane (VIII) with dimethylamine to give *N,N,N',N'*-tetramethyl-2,6-cyclooctadiene-1,5-diamine (IX), and then using exhaustive methylation (174).



An attempt was made (165) to prepare cyclooctatetraene directly from the dibromocyclooctadiene (III) by dehydrohalogenation, but only bicyclic and tricyclic compounds were obtained.

## 2. Structure and molecular configuration

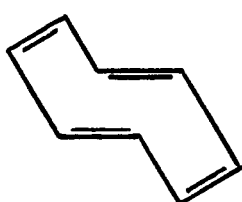
Reppe (38, 71, 76, 115, 116, 117, 119, 142) concluded that the product obtained by polymerization of acetylene is 1,3,5,7-cyclooctatetraene on the basis of its chemical and physical properties. Hydrogenation in acetic acid with palladium and charcoal catalysts showed the presence of four double bonds and the product was shown to be cyclooctane. The equivalence of the four double bonds, an essentially zero dipole moment, and the Raman spectrum, which shows only seven lines out of a possible forty-two, were considered to indicate that the molecule has a high degree of symmetry. The infrared spectrum shows no absorptions due to methylene groups and one single and sharp absorption due to CH groups, which was considered to indicate equivalence of the CH groups. These observations were subsequently substantiated by other infrared and Raman spectra studies (85, 86, 87, 88).

Because of its relationship to benzene, cyclooctatetraene has attracted considerable attention in regard to its resonance stabilization and possible aromatic character. From the heat of combustion of cyclooctatetraene, resonance energies of 25.3 (104) and 28 (38, 91) kcal./mole were calculated. Even less resonance energy is indicated by the calculated value of  $-34.35 \pm 0.34$  kcal./mole (111) for the heat of isomerization of cyclooctatetraene to styrene, which has a resonance energy of 46 kcal./mole (101). X-ray diffraction methods (78, 79) and molecular and diamagnetic susceptibility measurements (103, 104) indicate the presence of little or no resonance energy. The C=C absorption in the infrared spectrum at  $1639\text{ cm}^{-1}$  (88) (A.P.I. Project 44, Infrared Spectrogram 739) is not shifted from the position of an unconjugated double bond (8), which indicates that there is little of the usual interaction between conjugated double bonds. This is also borne out by the ultraviolet absorption spectrum (A.P.I. Project 44, Ultraviolet Absorption Spectrograms 180 and 207), which does not show distinct absorptions but only an increasing general absorption toward the shorter wave lengths.

The chemical reactivity of cyclooctatetraene shows it to be olefinic in character and, qualitatively, to have little resonance stabilization. It adds halogens readily, undergoes the Diels-Alder reaction, and is readily oxidized and reduced. Eloffson (48) showed that cyclooctatetraene is reduced polarographically at a voltage (half-wave potential  $-1.5\text{ v.}$ ) much lower than aromatic hydrocarbons, in fact, lower than any known simple olefinic or acetylenic hydrocarbon. This was interpreted to indicate that the molecule is highly polarized or polarizable. It is the first quantitative measurement indicating that cyclooctatetraene, rather than being stabilized by resonance, is even more reactive than might be expected.

While it is now generally agreed that cyclooctatetraene consists only of an eight-membered ring system with conjugated double bonds, there is disagree-

ment concerning the geometric configuration of the molecule. The possible molecular configurations which have been given the most consideration are the chair form ( $D_{2h}$ ), tub or boat form ( $D_{2d}$ ), and the crown forms ( $D_{4d}$  or  $D_4$ ). The two crown forms differ in that the  $D_{4d}$  form contains bonds of equal length (which would be the result of considerable resonance), while the  $D_4$  form contains alternate single and double bonds. Of these forms, only the  $D_{2d}$  could involve a strainless configuration.

 $D_{2h}$  $D_{2d}$  $D_4$ 

By comparison of the infrared and Raman spectra of cyclooctatetraene and completely deuterated cyclooctatetraene and by interpretation with the help of the product rule, Lippincott, Lord, and McDonald (85, 87, 88, 89) concluded that cyclooctatetraene has the  $D_4$  structure. An interpretation of the spectra in terms of the  $D_{2d}$  structure was given (88), but the serious difficulty is encountered that this structure should have all of the infrared-active fundamentals present also in the Raman spectrum, which is contrary to the observation of several strong infrared bands with no counterparts in the Raman spectrum. The possibility that cyclooctatetraene has two structures in equilibrium was ruled out on the basis of the simplicity of the spectra.

An x-ray diffraction study (78, 79) on a crystal of cyclooctatetraene confirmed the alternating single-double bond structure and the bond lengths were found to be typically aliphatic (1.34 Å. and 1.54 Å.) with a C=C—C angle of 125°C. The data obtained were reported to fit the  $D_{2d}$  structure. The data from electron diffraction analyses of the cyclooctatetraene vapor have been interpreted to fit both the crown structure (9, 10, 11, 137) and the  $D_{2d}$  structure (72).

Many of the thermodynamic functions of cyclooctatetraene have been calculated and measured (86, 104, 111, 139), but it was concluded that these would be of no value in distinguishing between the  $D_4$  and  $D_{2d}$  structures. In the course of their investigations of cyclooctatetraene, Pink and Ubbelohde (103, 104) observed a transition accompanied by a color change at about 98°K. Subsequent heat capacity measurements over a range of temperatures showed no anomalies near 98°K. and no color change was observed (139).

In summary, the physical and chemical properties of cyclooctatetraene are consistent with the 1,3,5,7-cyclooctatetraene structure, in which there is little resonance stabilization. There is not, however, complete agreement among investigators as to the molecular configuration, although the most thorough dis-



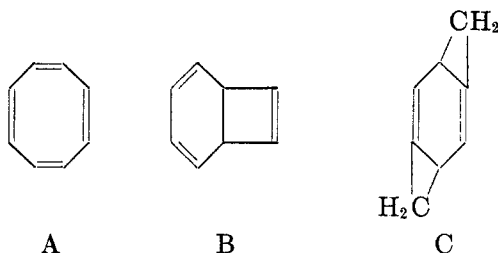
cussions and experimental data published to date indicate the crown ( $D_4$ ) configuration.

### 3. Reactions

Most of the work which has been done on the chemistry of cyclooctatetraene was carried out in Germany during World War II at the I. G. Farbenindustrie laboratories at Ludwigshaven. Descriptions of the work, which was done under the direction of Julius Walter Reppe, began to appear shortly after the close of the war in the form of reports written by teams of American and British experts who visited Germany. Many of these FIAT, BIOS, and PB Reports represent interrogations of chemists who recited experimental results from memory, with the result that it is not always clear whether their statements are opinions or proved facts.

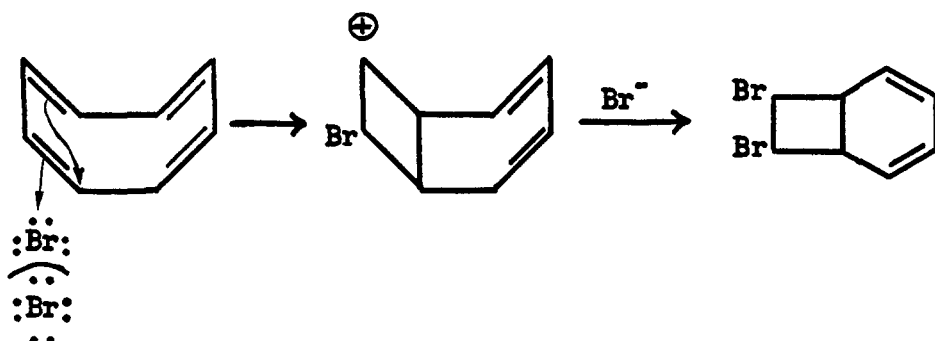
The reports (71, 76, 115, 116, 142) which are believed to contain the most factual information are based on a manuscript which eventually appeared in book form (117). The chapter on cyclopolyolefins in the book by Copenhaver and Bigelow (38) appears to contain all of the pertinent information on cyclooctatetraene which appeared in PB Reports. Reppe, Schlichting, Klager, and Toepel (119) and Reppe, Schlichting, and Meister (120) reported the experimental procedures and, what is more important, the yields. It becomes evident from these papers that many of the yields and suggested possibilities contained in the PB Reports were somewhat exaggerated. These two papers (119, 120) plus the book by Copenhaver and Bigelow (28) furnish an adequate survey of the work done by the Germans on cyclooctatetraene.

Many of the reactions of cyclooctatetraene result in rearrangement of the carbon skeleton. The German workers attempted to explain the structures of the reaction products by suggesting that cyclooctatetraene reacted as if it existed in three forms, A, B, and C.



In the face of all of the physical evidence which favors structure A (see page 117), it is undoubtedly incorrect to suggest that cyclooctatetraene exists in these three forms. It is unnecessary to write such forms to explain the reactions, since rearrangements of unstable intermediates probably occur rather than rearrangement of the cyclooctatetraene. One paper (55) has appeared in which a plausible mechanism is given for the transition to the bicyclo[4.2.0]octane ring system on addition of halogens. Cyclooctatetraene was assumed to

exist in the "tub" or all-*cis* form and the addition of bromine was represented as follows:

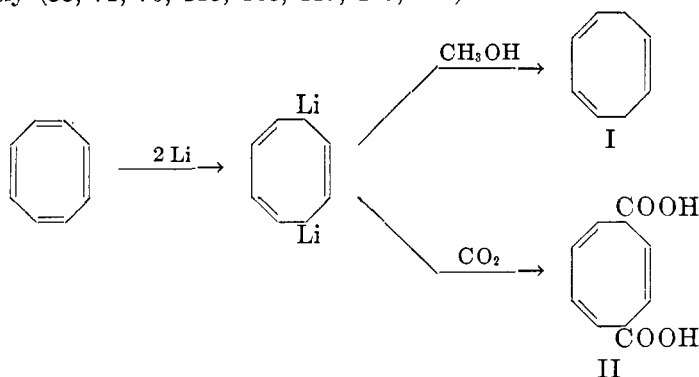


It is to be hoped that other such mechanisms will be proposed and established to explain other rearrangements of cyclic polyolefins.

#### a. Reduction

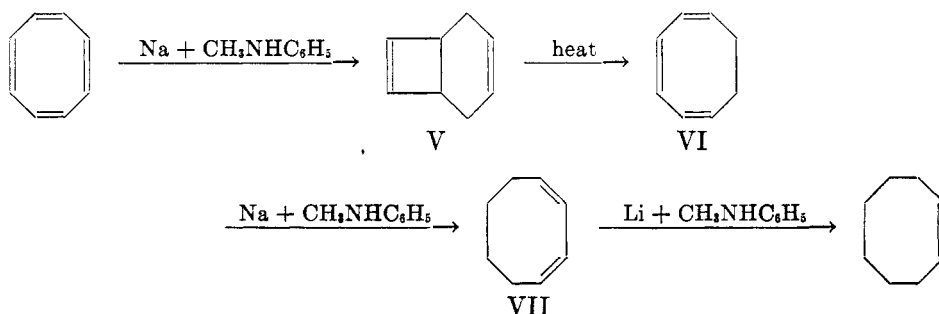
Cyclooctatetraene is readily hydrogenated over nickel, palladium, and platinum catalysts to the completely saturated cyclooctane (35, 38, 71, 76, 115, 116, 117, 118, 119, 142, 159, 165). Substituted cyclooctatetraenes are likewise smoothly hydrogenated to the corresponding substituted cyclooctane: for example, phenylcyclooctatetraene, *p*-dimethylaminophenylcyclooctatetraene, and vinylcyclooctatetraene (27, 32, 40). Since the German workers (38, 71, 76, 115, 116, 117, 118, 119, 120, 142) found that the first three double bonds of cyclooctatetraene are hydrogenated at a rate roughly ten times that of the fourth in solvents such as methanol and tetrahydrofuran and with a palladium on calcium carbonate catalyst, it is possible to interrupt the hydrogenation after absorption of three molar equivalents of hydrogen to give essentially pure cyclooctene in yields of 83–86 per cent (25, 119).

Cyclooctatetraene adds two atoms of lithium or sodium. Treatment of the addition product with methanol and with carbon dioxide was reported to give 1,3,6-cyclooctatriene (I) and 1,3,6-cyclooctatriene-5,8-dicarboxylic acid (II), respectively (38, 71, 76, 115, 116, 117, 119, 142).



However, subsequent investigators (31) showed that the product obtained by treatment of the lithium-cyclooctatetraene addition product with methanol is a mixture containing only 20–30 per cent of I along with 20–30 per cent of 1,3,5-cyclooctatriene, 17 per cent of cyclooctadienylcyclooctadienes (reducible to bicyclooctyl), 10–20 per cent of  $C_8$  hydrocarbons less saturated than the cyclooctatrienes, and 7 per cent of polymers. Structure II is probably also incorrect. A compound of this structure would not be expected to have a high melting point, whereas the product in question is reported to sublime at  $220^\circ C$ .

Cope and Hochstein (31) found that cyclooctatetraene is reduced to a mixture of 1,3,5- and 1,3,6-cyclooctatrienes with sodium and liquid ammonia in 61 per cent yield. It was suggested (174) that reduction of cyclooctatetraene in the cold with sodium and methylaniline in ether gives bicyclo[4.2.0]-3,7-octadiene (V), which rearranges on heating to 1,3,5-cyclooctadiene (VI). Treatment of VI with sodium and methylaniline was reported to give 1,3-cyclooctadiene (VII) which, in turn, gives cyclooctene upon treatment with lithium and methylaniline. The overall reduction was written as follows:

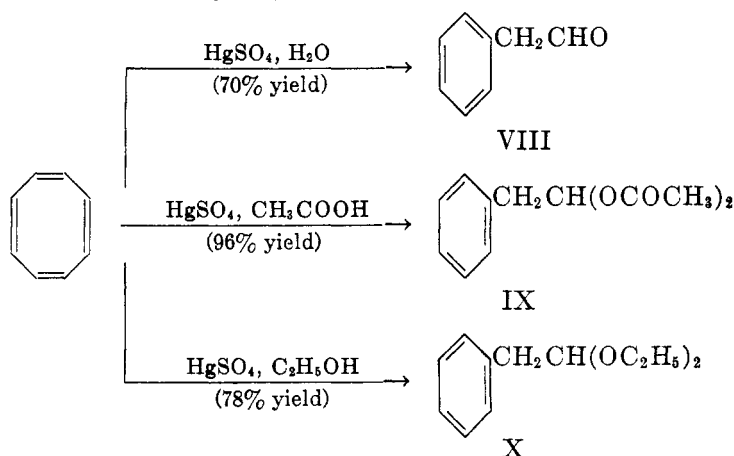


### b. Oxidation

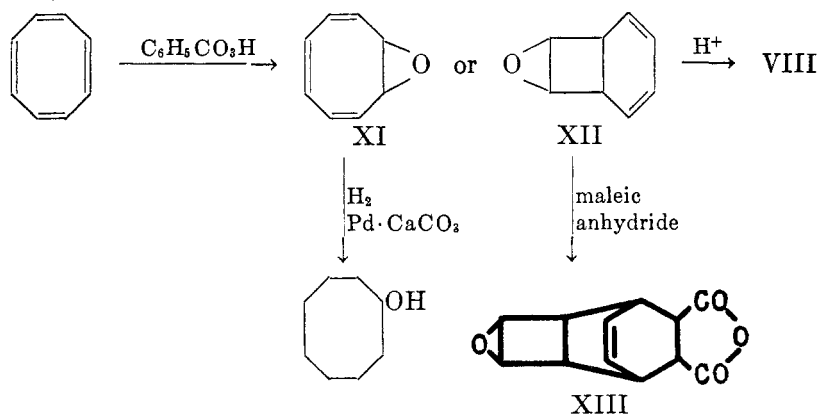
Oxidative reactions of cyclooctatetraene lead to the formation of benzene derivatives except in the case of peroxidation with perbenzoic acid (13, 38, 71, 76, 115, 116, 117, 118, 119, 142). In the gaseous phase, cyclooctatetraene is oxidized by air over vanadium, molybdenum, or titanium oxides to give benzoic acid. Yields were reported to be quantitative, although the yield reported in the only case where the experimental procedure was given (119) was 70 per cent and some benzaldehyde was isolated. Oxidation of cyclooctatetraene with chromic acid in acetic acid gives a 14.5 per cent yield of terephthalic acid and a 6 per cent yield of benzaldehyde (119). With aqueous potassium permanganate a 21 per cent yield of benzoic acid and some benzaldehyde is produced (119). Alkaline hypochlorite was reported to give terephthalaldehyde plus small amounts of benzaldehyde and benzoic acid. The yield of terephthalaldehyde was not disclosed, but it is believed to be small.

If an aqueous suspension of cyclooctatetraene is shaken with mercuric sulfate, phenylacetaldehyde (VIII) is produced. If the water is replaced by glacial acetic

acid or by absolute ethanol, the phenylethylidene diacetate (IX) and the diethyl acetal of phenylacetaldehyde (X), respectively, are formed (119).



Treatment of cyclooctatetraene in chloroform with perbenzoic acid results in the formation of the epoxide, which rearranges violently and quantitatively to phenylacetaldehyde (VIII) upon treatment with acid (13, 38, 71, 76, 115, 116, 117, 118, 119, 142). Since catalytic hydrogenation of the epoxide gives cyclooctanol and bicyclooctane systems do not give cyclooctane on hydrogenation (160), the compound was considered to be 7,8-epoxy-1,3,5-cyclooctatriene (XI). Friess and Boekelheide (55) suggested a bicyclooctadiene structure (XII) for the epoxide on the basis of its ultraviolet absorption spectrum and the uptake of one molar equivalent of hydrogen and perbenzoic acid by the maleic anhydride adduct (XIII).

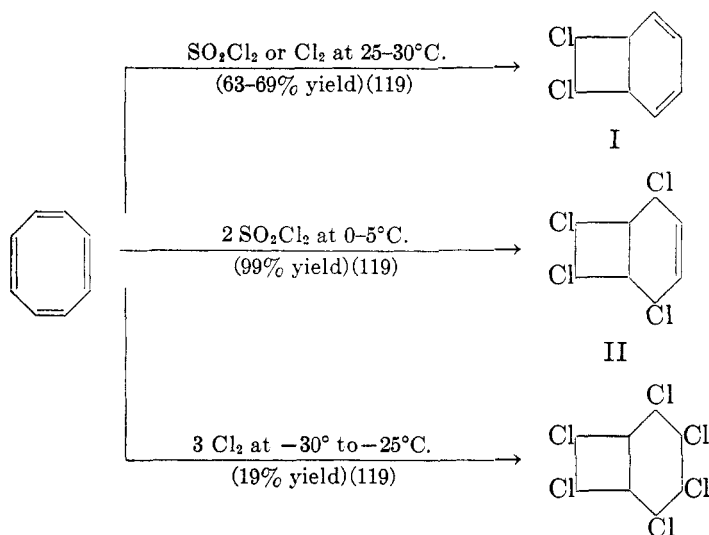


It was suggested that cleavage of the bicyclic ring system of XII during hydrogenation might be possible, owing to strain present in the molecule. It should be noted, however, that XIII or a similar polycyclic compound might arise from XI in view of the nature of the products which cyclooctatetraene forms by Diels-Alder reactions (see pages 126-133).

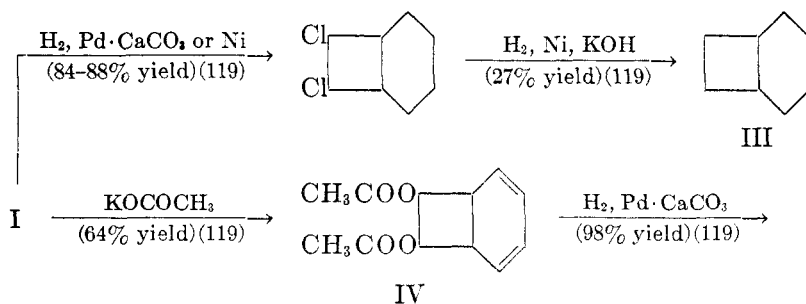
## c. Addition reactions

Willstätter and Heidelberger (159) obtained addition products of cyclooctatetraene and chlorine, bromine, and hydrogen bromide but the structures of the products were not known. Subsequent investigations (38, 71, 76, 115, 116, 117, 119, 142) have shown that the addition reactions of cyclooctatetraene result in structural rearrangement, with the formation of bicyclo[4.2.0]octane derivatives.

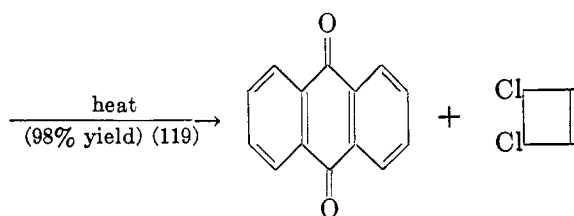
Depending on reaction conditions, chlorine adds to cyclooctatetraene to give a dichloro, tetrachloro, or hexachloro derivative.



The fact that only three moles of chlorine can be added to cyclooctatetraene was considered an indication of rearrangement to a bicyclic ring system. Proof of the structure of I was obtained by catalytic hydrogenation to bicyclo[4.2.0]octane (III) and by treatment with potassium acetate to give the diacetate (IV), followed by hydrogenation and hydrolysis to give 7,8-dihydroxybicyclo[4.2.0]octane (V), the structure of which was proved by cleavage to the known hexahydrophthalic acid and hexahydrophthalaldehyde.



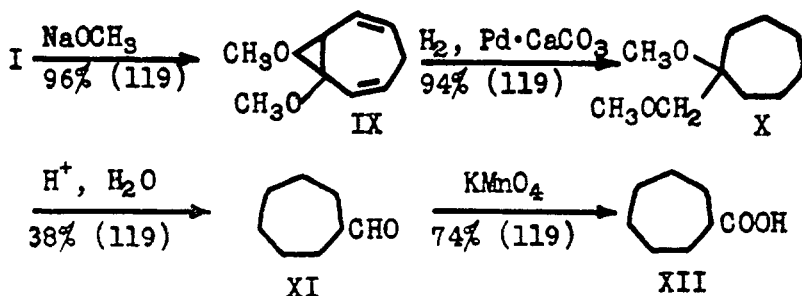




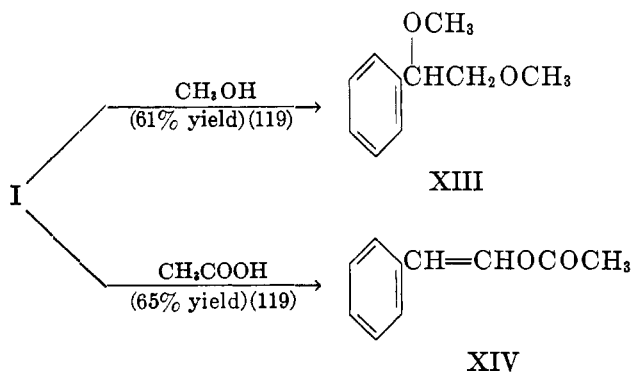
VIII

The pyrolysis of adducts of this type may be a very convenient method for preparing the four-membered ring system, particularly cyclobutenes.

Treatment of I with sodium methoxide was found to result in further rearrangement to give a product believed to be 7,8-dimethoxybicyclo[5.1.0]-2,5-octadiene (IX) (38, 71, 76, 115, 116, 117, 119, 142). The evidence cited for this structure was the absorption of three molar equivalents of hydrogen to give a compound, formulated as 1-methoxy-1-methoxymethylcycloheptane (X), which gives cycloheptanecarboxaldehyde (XI) on hydrolysis. The aldehyde was identified by its semicarbazone and by oxidation to cycloheptanecarboxylic acid (XII) and conversion to the amide.



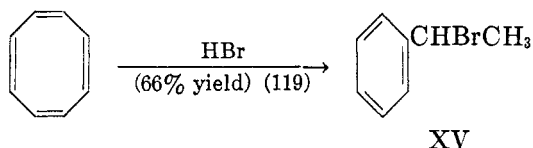
Treatment of I with alcohols or carboxylic acids results in aromatization (38, 71, 76, 115, 116, 117, 119, 142). I and methanol give the dimethyl ether of phenyl-ethylene glycol (XIII), while I and acetic acid give styryl acetate (XIV).



The addition of bromine to cyclooctatetraene also gives dibromo, tetrabromo, and hexabromo derivatives which were assumed to have the bicyclo[4.2.0]octane structures of the chlorine derivatives (38, 71, 76, 115, 116, 117, 119, 142). The dibromo compound gives alkoxy-substituted derivatives with sodium alkoxides and undergoes Diels-Alder reactions in the same manner as the dichloro derivative.

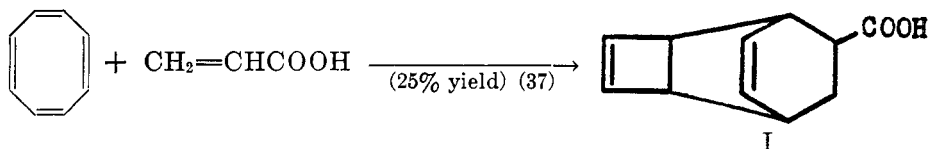
Mixed halogenated bicyclo[4.2.0]octane derivatives are obtained by addition of bromine to unsaturated chlorine addition products. These products, as well as hydrogenation products of various cyclooctatetraene-halogen addition products and their Diels-Alder adducts, are included in table 1 (see Section IV).

The addition of hydrogen bromide to cyclooctatetraene results in the formation of  $\alpha$ -bromoethylbenzene (XV), the structure of which was proved by oxidation to benzoic acid and conversion to  $\alpha$ -methoxy- and  $\alpha$ -acetoxyethylbenzenes (38, 71, 76, 115, 119).



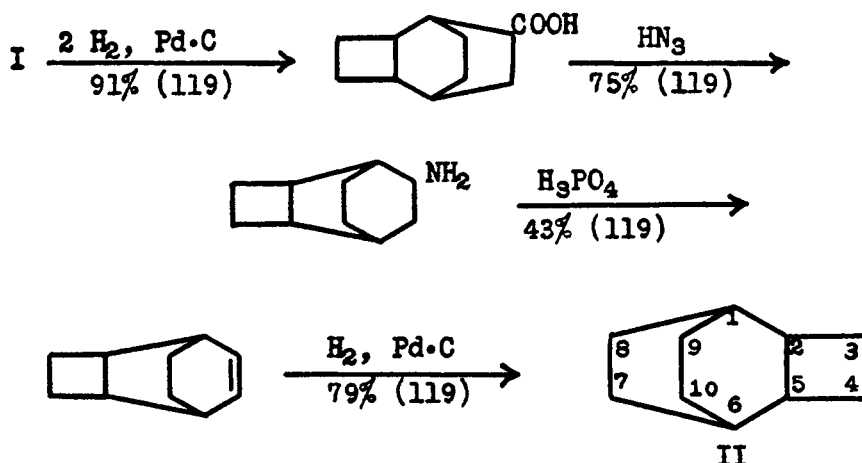
#### d. Diels-Alder reactions

Cyclooctatetraene, with its four conjugated double bonds, would be expected to react with two molar equivalents of dienophile in the Diels-Alder reaction. However, with maleic anhydride, alkyl maleates, alkyl acetylenedicarboxylates, acrylic acid, quinone, and naphthoquinone, cyclooctatetraene reacts only in a 1:1 molar ratio (38, 71, 76, 115, 116, 117, 118, 119, 142). Furthermore, all of the adducts absorb one less molar equivalent of hydrogen than is expected. These two facts indicate that structural rearrangement with the disappearance of one double bond takes place and the reaction of cyclooctatetraene and acrylic acid is written as follows:

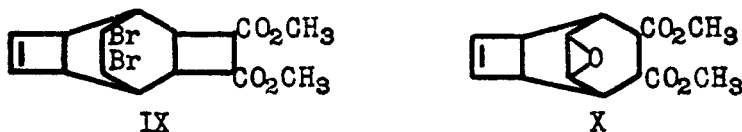


Evidence for the structure of I was obtained by hydrogenation (only two molar equivalents of hydrogen absorbed), treatment of the saturated acid with hydrazoic acid to give the amine, deamination, and hydrogenation to a saturated hydrocarbon. As the saturated hydrocarbon has an empirical formula of  $C_{10}H_{16}$ , it was assigned a tricyclic structure, tricyclo[4.2.2.0<sup>2,5</sup>]decane (II).



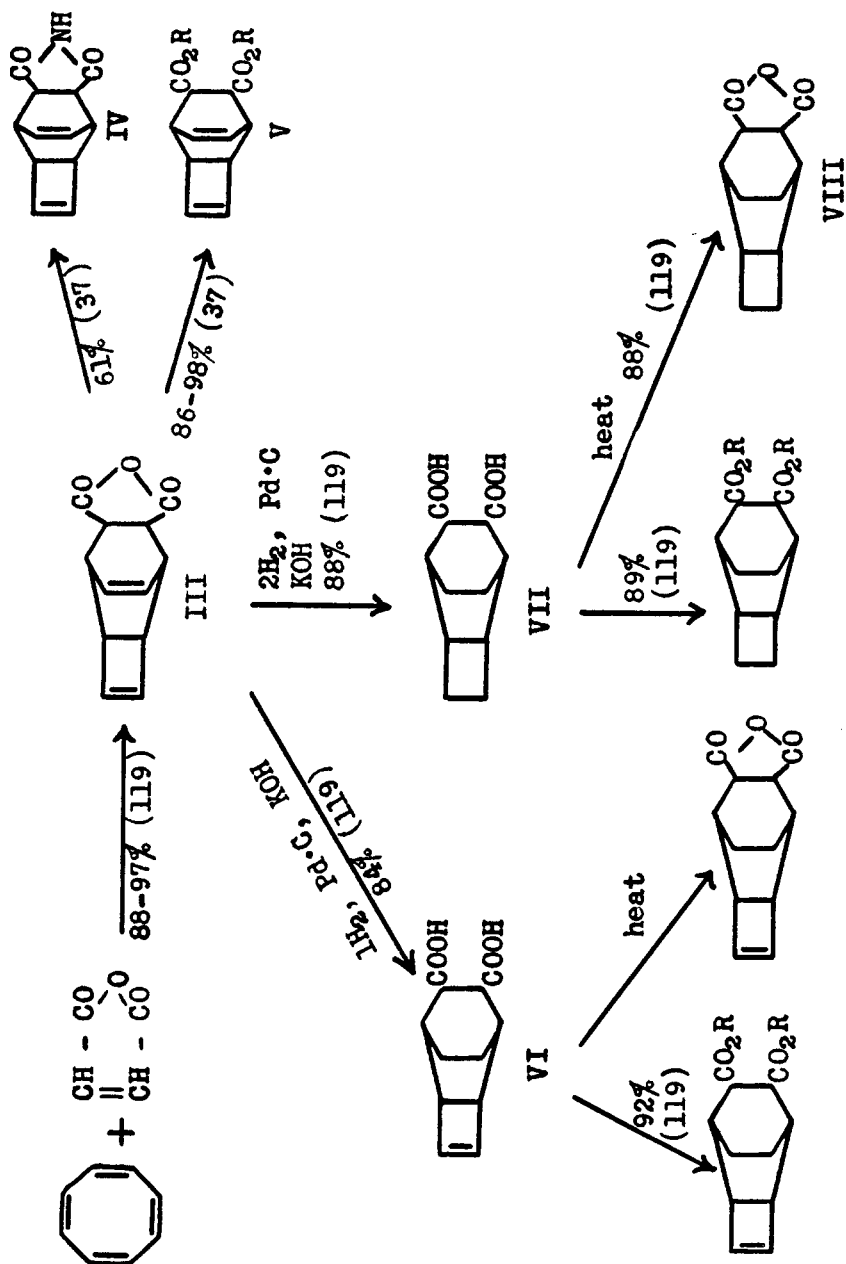


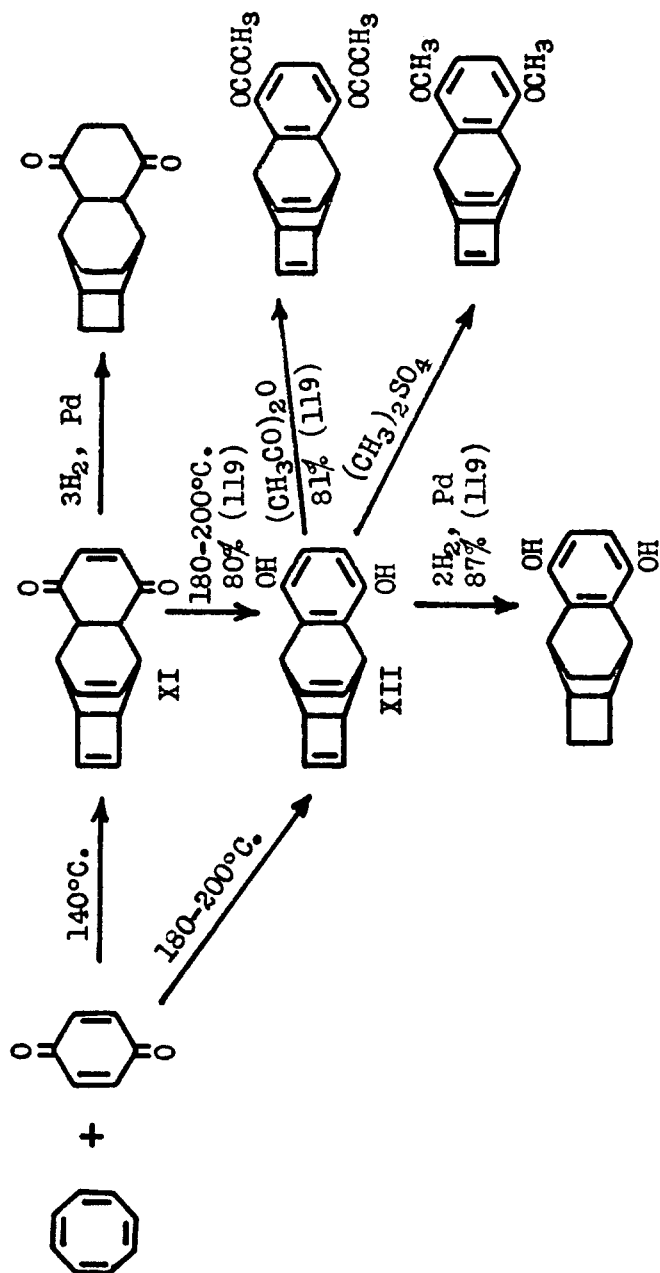
The cyclooctatetraene-maleic anhydride adduct (III) (see page 128) is readily converted to the imide (IV) and esters (V), which are crystalline in the series from methyl to isoamyl. The anhydride in dilute alkali is hydrogenated stepwise in the presence of palladium or nickel catalysts to give a dihydro- (VI) or a tetrahydro- (VII) dicarboxylic acid, both of which are easily esterified and converted to the anhydride. VI is the structure written by the German workers for the dihydro acid. There seems to be no recorded evidence for the position of the double bond, and it seems possible that the double bond in the four-membered ring would be reduced more readily than that in the six-membered ring. By addition of bromine and by treatment with perbenzoic acid, the dimethyl ester of the cyclooctatetraene-maleic anhydride adduct (IV, R = CH<sub>3</sub>) is converted to a dibromo and a monoepoxy compound, which were assigned structures IX and X. Here again, it would seem that the double bond in the cyclobutene ring might react preferentially.

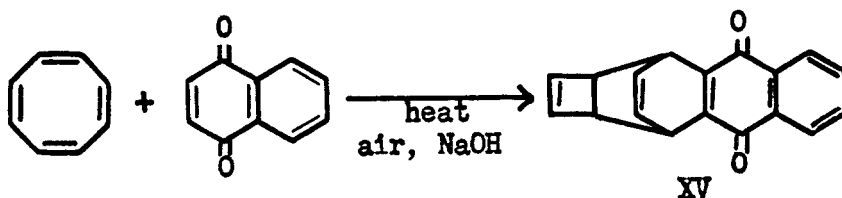
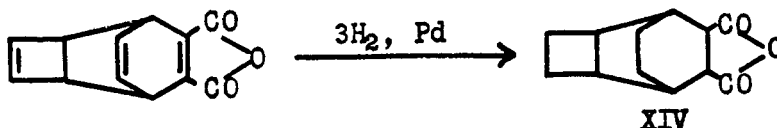
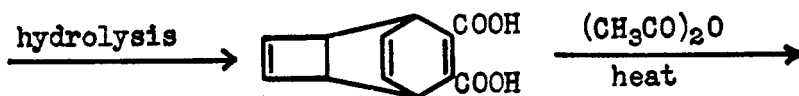
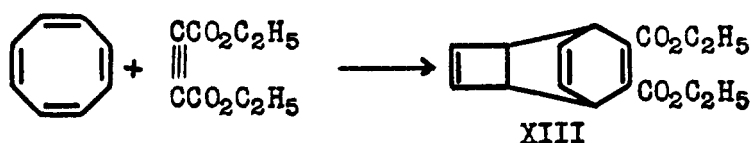


By condensing quinone and cyclooctatetraene at 140°C. in chlorobenzene, an adduct is obtained which has a quinoid structure and was assigned the structure XI (see page 129). When the adduct is prepared without a solvent at 180–200°C., an adduct with the hydroquinone structure is produced (XII). It was found that XI can be converted to XII by heating at 180–200°C. Both adducts are readily hydrogenated and XI can be converted to a diacetate and a dimethoxy derivative.

The Diels-Alder reactions of cyclooctatetraene with diethyl acetylenedicarboxylate and naphthoquinone are shown on page 130 (38, 71, 76, 115, 116, 117, 119, 142).



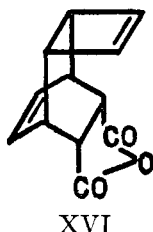




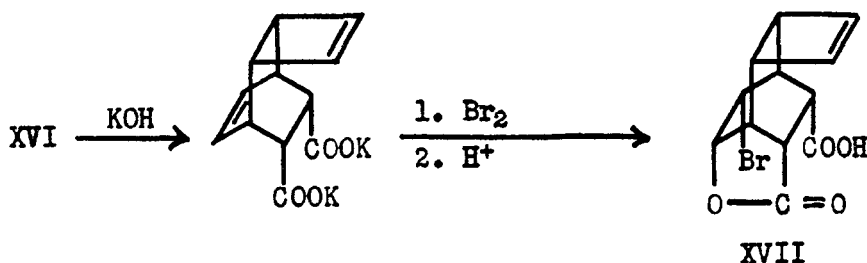
The evidence for the structures of XIII and XV consists in the formation of diethyl phthalate and anthraquinone, respectively, on pyrolysis. In the pyrolysis of 7,8-dichlorobicyclo[4.2.0]-2,4-octadiene-naphthoquinone adduct (VII of page 124), the 3,4-dichlorocyclobutene which splits out is conveniently isolated. In the pyrolysis of XIII and XV, no material has yet been isolated which corresponds to the expected 1,3-cyclobutadiene. Only resinous products, which may have been formed from 1,3-cyclobutadiene, are obtained. Product XIV was assigned a structure identical with VIII, the product obtained by hydrogenation of the cyclooctatetraene-maleic anhydride adduct. However, the reported melting point of XIV is 154–155°C. while that of VIII is 130–132°C. Whether they are structurally different or stereoisomeric is not known.

*Configuration of the Diels-Alder adducts:* Attempts were made (38, 71, 76, 115, 117, 119) to determine the exact configuration of the diene addition products of

cyclooctatetraene, and the maleic anhydride adduct was formulated as the *endo-cis* compound (XVI). In the anhydride, the carboxyl groups must be *cis*



with respect to each other. The potassium salt of the *cis*-dicarboxylic acid, which forms on careful saponification of XVI, adds chlorine or bromine to give a mono-halomonomocarboxylic acid which was formulated as XVII.



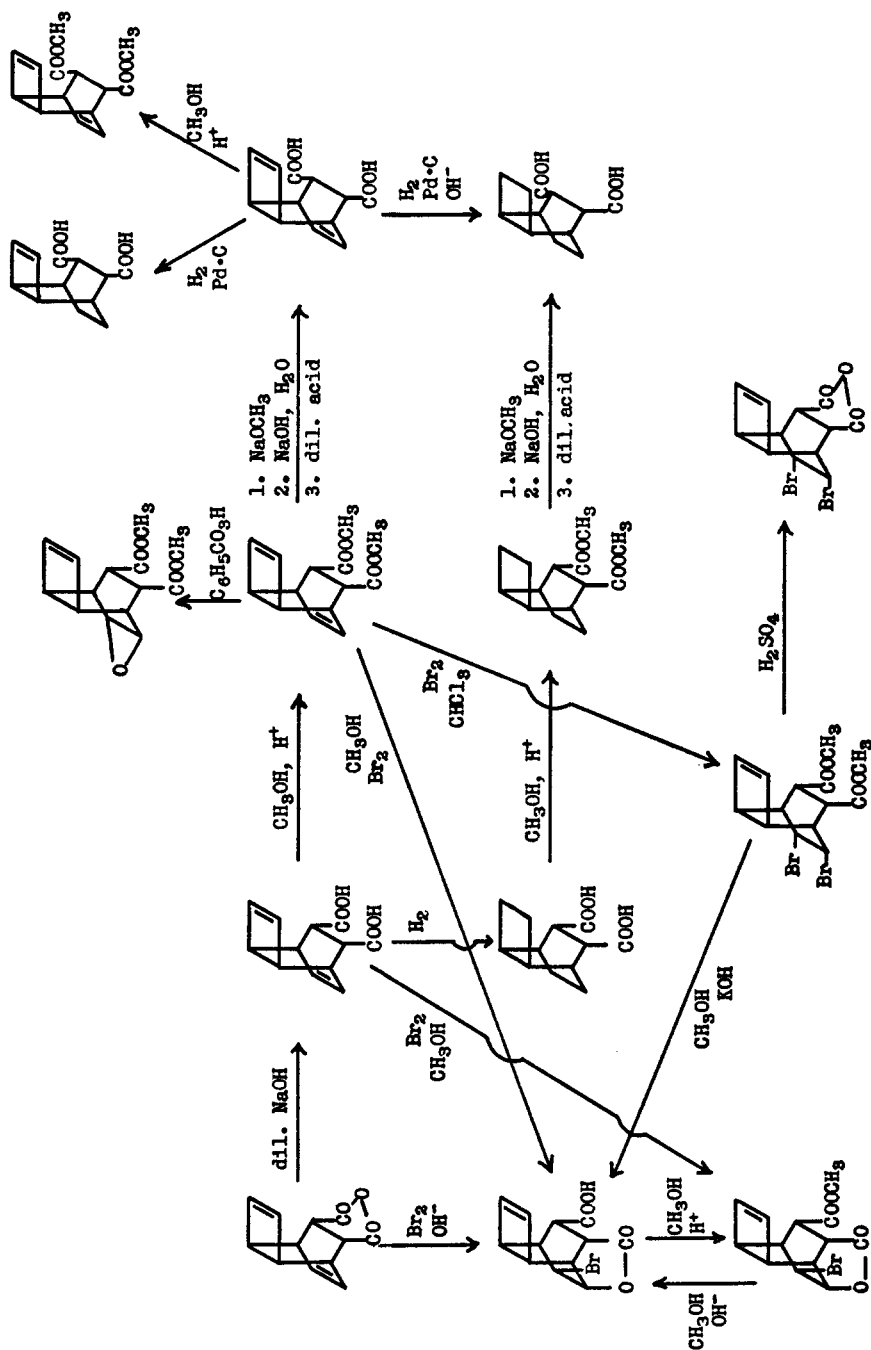
This structure was again based on the assumption that the double bond of the six-membered ring adds halogens in preference to the double bond of the four-membered ring, although it seems possible that the reverse might be true.

With the assumption that XVI represents the cyclooctatetraene-maleic anhydride adduct, a number of reactions which were carried out by the German workers were formulated as indicated in the equations on page 132. Throughout these transformations, the double bond of the six-membered ring was considered to react in preference to that of the four-membered ring.

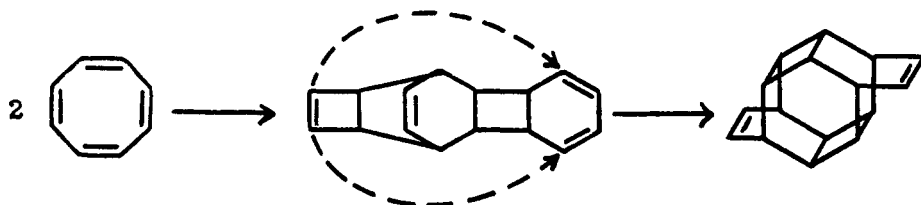
#### e. Dimerization

Cyclooctatetraene on standing and on heating dimerizes (38, 71, 76, 115, 116, 117, 119, 142) to give a mixture of at least two hydrocarbons, one of which is a solid (m.p. 43°C.) while the other is a high-boiling oil (b.p. 298°C.). The solid isomer contains three double bonds, while the liquid isomer contains two, as shown by catalytic hydrogenation. By carrying out the dimerization under nitrogen, the liquid isomer is obtained exclusively.

Dimerization of cyclooctatetraene undoubtedly occurs by a Diels-Alder condensation. The disappearance of double bonds is best explained by the formation of new rings, none of which appear to be aromatic, as no aromatic products have



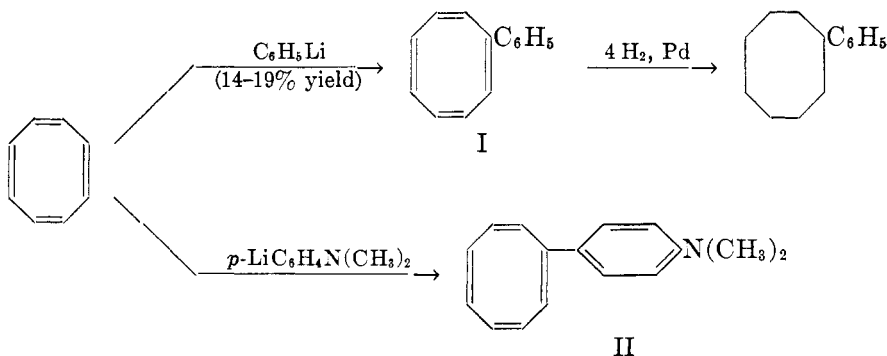
been isolated by oxidation or dehydrogenation. The German workers suggested that the dimer containing two double bonds might be explained as follows:



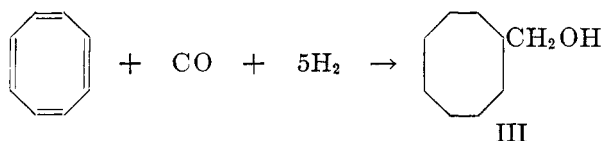
Attempts were made to polymerize cyclooctatetraene with peroxide and acid catalysts but with little success (38). Dimerization occurred in almost all attempts, although tetramerization was brought about by treatment of cyclooctatetraene with oxygen. Traces of polymers were obtained in emulsion polymerizations of mixtures of cyclooctatetraene and butadiene.

#### f. Miscellaneous reactions

The only reaction which has been found to lead to substitution of cyclooctatetraene is the reaction with organometallic compounds. Cope and Kintner (32), in an attempt to prepare phenylcyclooctatriene, found that cyclooctatetraene and phenyllithium react to give phenylcyclooctatetraene (I) and a mixture of 1,3,5- and 1,3,6-cyclooctatrienes. The structure of I was proved by comparison of the hydrogenation product with an authentic sample of phenylcyclooctane. *p*-Dimethylaminophenylcyclooctatetraene (II) is prepared from cyclooctatetraene in an identical manner.



Cyclooctatetraene is converted directly to cyclooctanemethanol (III) by the oxo reaction. Only one double bond reacts with carbon monoxide and the other three are reduced (38, 71, 76, 115, 116, 117, 142).

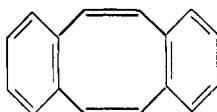


The reaction of cyclooctatetraene with carbon monoxide and water in the presence of nickel carbonyl results in the formation of a dimeric dicarboxylic acid, the same acid which is obtained from the liquid cyclooctatetraene dimer under similar conditions. The structure of this dicarboxylic acid is unknown.

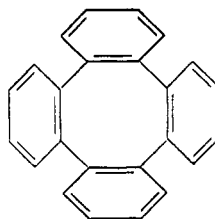
Cyclooctatetraene forms addition products with silver nitrate and with ammoniacal cuprous chloride-ammonium chloride (31, 37, 71, 76, 115, 116, 117, 119, 142). It was shown that at least three crystalline adducts with silver nitrate are formed, corresponding to  $2C_8H_8 \cdot AgNO_3$ ,  $C_8H_8 \cdot AgNO_3$ , and  $2C_8H_8 \cdot 3AgNO_3$  (31). The third complex is readily recrystallized from 20 per cent aqueous silver nitrate or alcohol and decomposed by the addition of sodium chloride to give cyclooctatetraene of high purity. Substituted cyclooctatetraenes such as phenylcyclooctatetraene and vinylcyclooctatetraene also form addition products with silver nitrate (27, 32, 40). The formation of a silver nitrate adduct has proved to be an excellent method for the separation of cyclooctatetraene from styrene (88) and of vinylcyclooctatetraene from 1-phenyl-1,3-butadiene (27, 40).

#### 4. Benzocyclooctatetraenes

During the period when the identity of Willstätter's cyclooctatetraene was being questioned, numerous attempts were made to prepare benzocyclooctatetraenes for study of the cyclooctatetraene ring. Successful syntheses of 1,2,5,6-dibenzocyclooctatetraene (I) (cycloocta[*a,e*]dibenzene, see page 113) and tetrabenzocyclooctatetraene (II) (tetraphenylene, see page 114) were carried out.

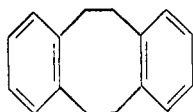


I

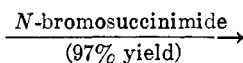


II

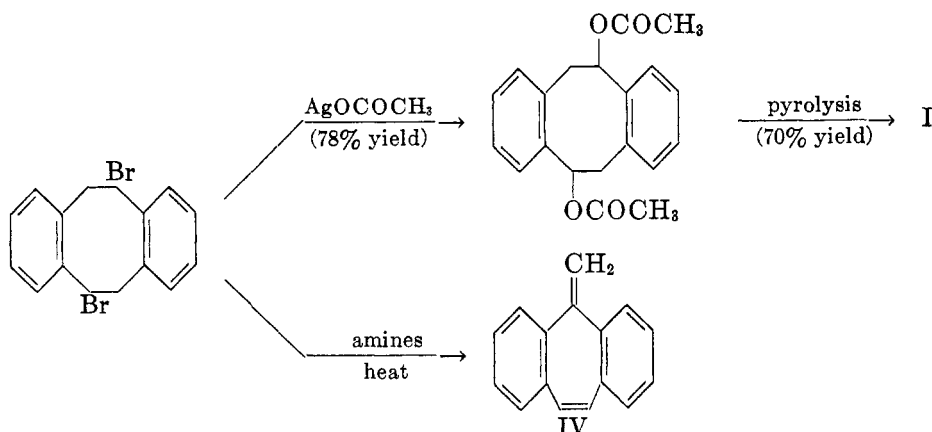
Recently, a method for introducing two double bonds in 5,6,11,12-tetrahydrocycloocta[*a,e*]dibenzene (III, see page 113) was reported which involves treatment of III with *N*-bromosuccinimide, conversion of the resulting dibromo compound to the diacetoxy compound, and pyrolysis (28). An interesting rearrangement to a seven-membered ring compound (IV) occurs when the dibromo compound is heated with amines.



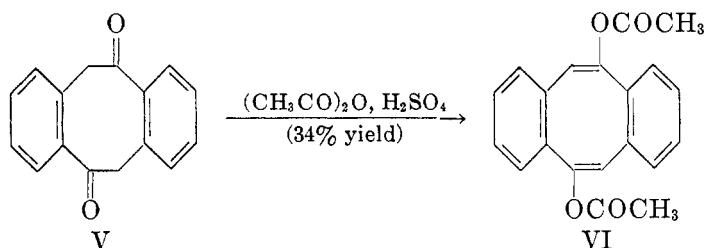
III





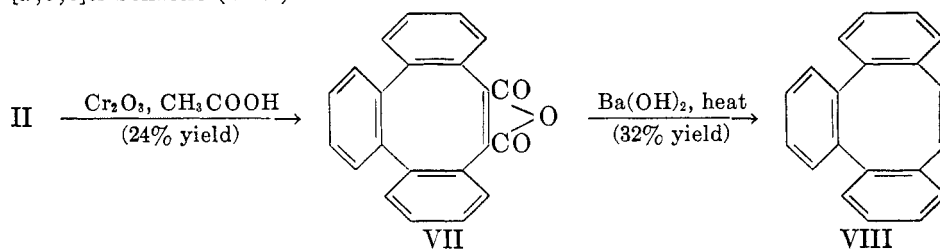


Attempts (157) to prepare I from the eight-membered diketone V (see page 110) were unsuccessful, but a product is obtained on acetylation which was assigned the cycloocta[*a,e*]dibenzene structure, VI.



I reacts chemically as an olefinic hydrocarbon; it adds bromine (77) and readily absorbs two molar equivalents of hydrogen upon catalytic hydrogenation (52). These facts, plus spectrographic examinations (52) and the observation that hydrolysis of VI gives V rather than a dihydroxy derivative, indicate that there is little resonance stabilization of the cycloocta[*a,e*]dibenzene molecule (I), owing to conjugation of the double bonds in the eight-membered ring, and hence that the molecule is not planar.

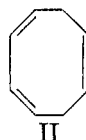
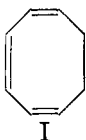
II is an exceedingly stable compound, which can be nitrated and brominated (113). It is stable to potassium permanganate in acetone (113) but is oxidized with chromic acid in acetic acid to give a dicarboxylic acid anhydride (VII). VII is decarboxylated by heating with barium hydroxide to give cycloocta[*a,c,e*]tribenzene (VIII).



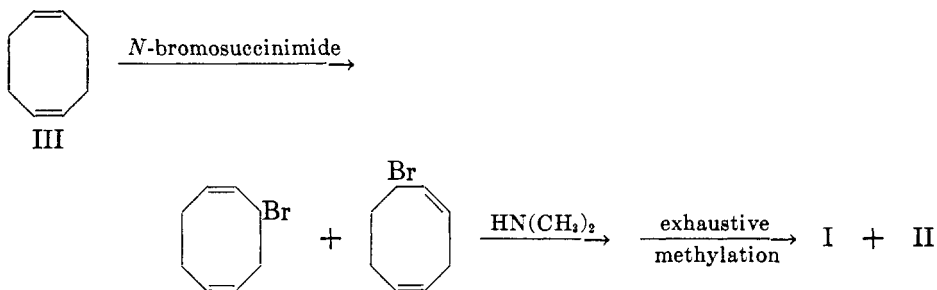
While II was found to be aromatic (as it should be since all the double bonds are present in the benzene rings), VIII was found to add bromine and to absorb one molar equivalent of hydrogen readily upon catalytic hydrogenation (141). An electron diffraction study of II showed that the eight-membered ring is not planar and that the carbon-carbon bond lengths are not equal (77). These facts indicate that there is also no resonance stabilization of II and VIII, owing to the conjugated double bonds of the cyclooctatetraene ring.

#### B. CYCLOOCTATRIENES

There are two possible cyclooctatrienes, 1,3,5-cyclooctatriene (I) and 1,3,6-cyclooctatriene (II). The triene which is produced by exhaustive methylation



of the *N,N*-dimethylcyclooctadienylamine obtained from pseudopelletierine (34, 35, 159) and from R-homotropinone (33) (see pages 107–108) was believed to be I. Cope and Bailey (24) prepared cyclooctatriene by degradation of an *N,N*-dimethylcyclooctadienylamine which was obtained from 1,5-cyclooctadiene (III) by treatment with *N*-bromosuccinimide and dimethylamine. The difference in the ultraviolet absorption spectrum of this triene and that of the triene obtained from the *N,N*-dimethylcyclooctadienylamine from pseudopelletierine was believed to be due to a mixture of I and II arising in the following manner:



Subsequent investigations showed that isomeric bromocyclooctadienes are produced in this reaction (37).

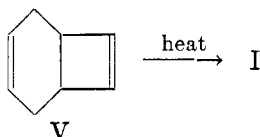
The reduction of cyclooctatetraene to cyclooctatrienes was discussed on pages 120–121. II was obtained essentially pure by fractional distillation of the sodium and liquid ammonia reduction product of cyclooctatetraene, and I was purified through its silver nitrate adduct (31). The ultraviolet and infrared absorption curves of I and II were used to determine the composition of various triene mixtures.

The isomerization of II to I by heating in the presence of potassium *tert*-butoxide was observed (31). It was also observed that I isomerizes reversibly on heating to a material which is not II. A sample of I which had been heated

for 7 hr. at 100°C. under nitrogen was found to absorb less than three molar equivalents of hydrogen upon catalytic hydrogenation to give a product containing 5-10 per cent of bicyclo[4.2.0]octane. The possibility that I isomerizes reversibly to IV was suggested.



It is noteworthy that Ziegler and Wilms (174) suggested that a bicyclo[4.2.0]-octadiene (V) is formed as the first product upon treatment of cyclooctatetraene with sodium in methylaniline (see page 121) and that V rearranges on heating to I.



It would seem in both cases, particularly in the case of IV where aromatization could take place, that either one of the other carbon-carbon bonds in the four-membered ring would break in preference to that also present in the six-membered ring.

Both I and II are very reactive compounds and are readily hydrogenated catalytically to cyclooctane (31, 33, 35, 37, 119). The reduction of I to 1,3-cyclooctadiene with sodium in methylaniline has been reported (174).

I readily undergoes the Diels-Alder reaction with maleic anhydride (31, 33, 174) and forms a crystalline addition product with silver nitrate (31). Bromine is added readily, addition apparently taking place in the 1,6-positions (35, 159, 165). Both I and II absorb oxygen rapidly from the air; I absorbs essentially one molar equivalent of oxygen to give a polymeric peroxide (31). Unsuccessful attempts were made to dehydrogenate I to cyclooctatetraene (37).

### C. CYCLOOCTADIENES

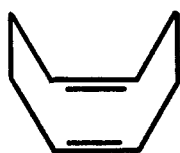
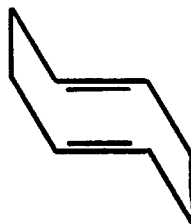
1,5-Cyclooctadienes are prepared by dimerization of 1,3-butadienes (see pages 110-111), by degradation of *N,N*-dimethyl-4-cycloöcten-1-ylamine (161, 163, 173, 174), and by dehydrobromination of 5-bromocycloöctene (174).

Willstätter and Veraguth (161, 163) reported that pyrolysis of the quaternary hydroxide of *N,N*-dimethyl-4-cycloöcten-1-ylamine gives a very unstable  $C_8H_{12}$  hydrocarbon, and that addition of two molar equivalents of hydrogen bromide to this unstable  $C_8H_{12}$ , followed by treatment with alkali or quinoline, gives a stable  $C_8H_{12}$  hydrocarbon. The unstable hydrocarbon was designated  $\alpha$ -cycloöctadiene and the stable,  $\beta$ -cycloöctadiene. Since it was found to dimerize and to polymerize very readily,  $\alpha$ -cycloöctadiene was at first believed to be 1,3-cycloöctadiene and the stable diene was believed to be either 1,4- or 1,5-cycloöctadiene. The  $\alpha$ -cycloöctadiene was actually shown to be a mixture, as it was found to give two hydrogen bromide addition products ( $C_8H_{13}Br$  and  $C_8H_{14}Br_2$

in a ratio of 1:6 parts) and two bromine addition products ( $C_8H_{11}Br$  and  $C_8H_{12}Br_2$  in a ratio of 1:5 parts). Treatment of the  $C_8H_{13}Br$  material with quinoline was found to give a  $C_8H_{12}$  hydrocarbon with only one double bond, a result which indicates that the hydrocarbon present in the smaller amount was bicyclooctene.

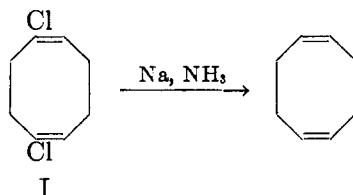
Harries (70) substantiated the observations that a mixture is formed in the degradation of the *N,N*-dimethylcyclooctenylamine. However, he showed by ozonolysis that the mixture consisted of 1,5-cyclooctadiene (at least 80 per cent) and bicyclooctene and contained essentially no 1,3-cyclooctadiene.

Ziegler and Wilms (173, 174) suggested that there are two 1,5-cyclooctadienes and that their difference is due to *cis-trans* isomerism. They reported that the degradation of *N,N*-dimethyl-4-cycloocten-1-ylamine gives a 77 per cent yield of a labile diene (m.p.  $-62^\circ C.$ ,  $n_{D}^{20} = 1.4933$ ) which polymerizes readily and adds one molar equivalent of phenyl azide in a few minutes (no mention was made of any bicyclooctene). The diene (m.p.  $-70.1^\circ C.$ ,  $n_{D}^{20} = 1.4936$ ) prepared by dimerization of 1,3-butadiene, on the other hand, is very stable and does not react with phenyl azide (phenyl azide supposedly adds to double bonds in strained ring systems only (2)). By addition of one mole of hydrogen bromide to the stable 1,5-cyclooctadiene, treatment with dimethylamine, and exhaustive methylation, the labile diene is formed. A *trans-trans* configuration, which would involve considerable strain, was suggested for the labile diene and a strain-free *cis-cis* configuration for the stable diene. Two such structures can be represented as follows:

*cis-cis**trans-trans*

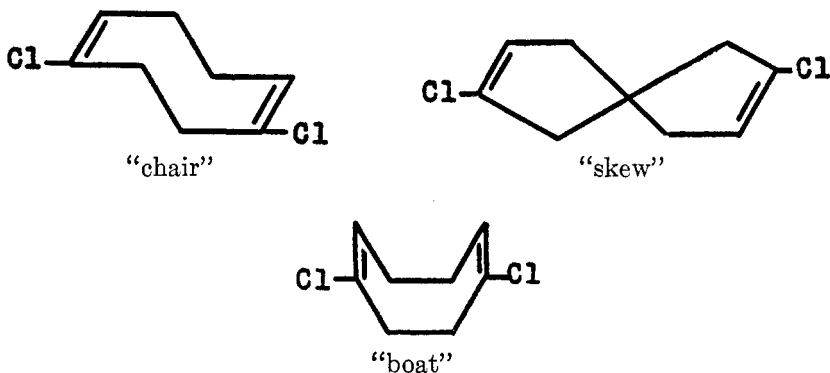
Examination of the Raman spectra (67) of these two dienes and comparison of lines with those known for *cis* and *trans* double bonds support these suggested structures.

The eight-membered chloroprene dimer (I) is readily converted to 1,5-cyclooctadiene by sodium in liquid ammonia (24, 37).

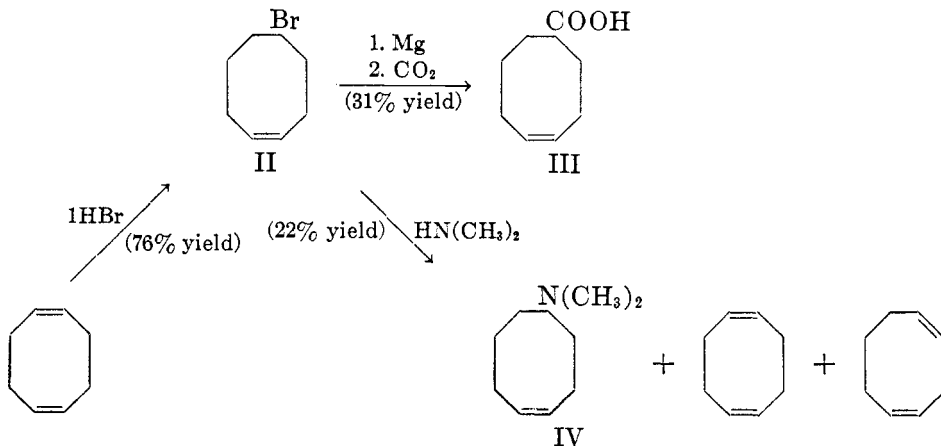


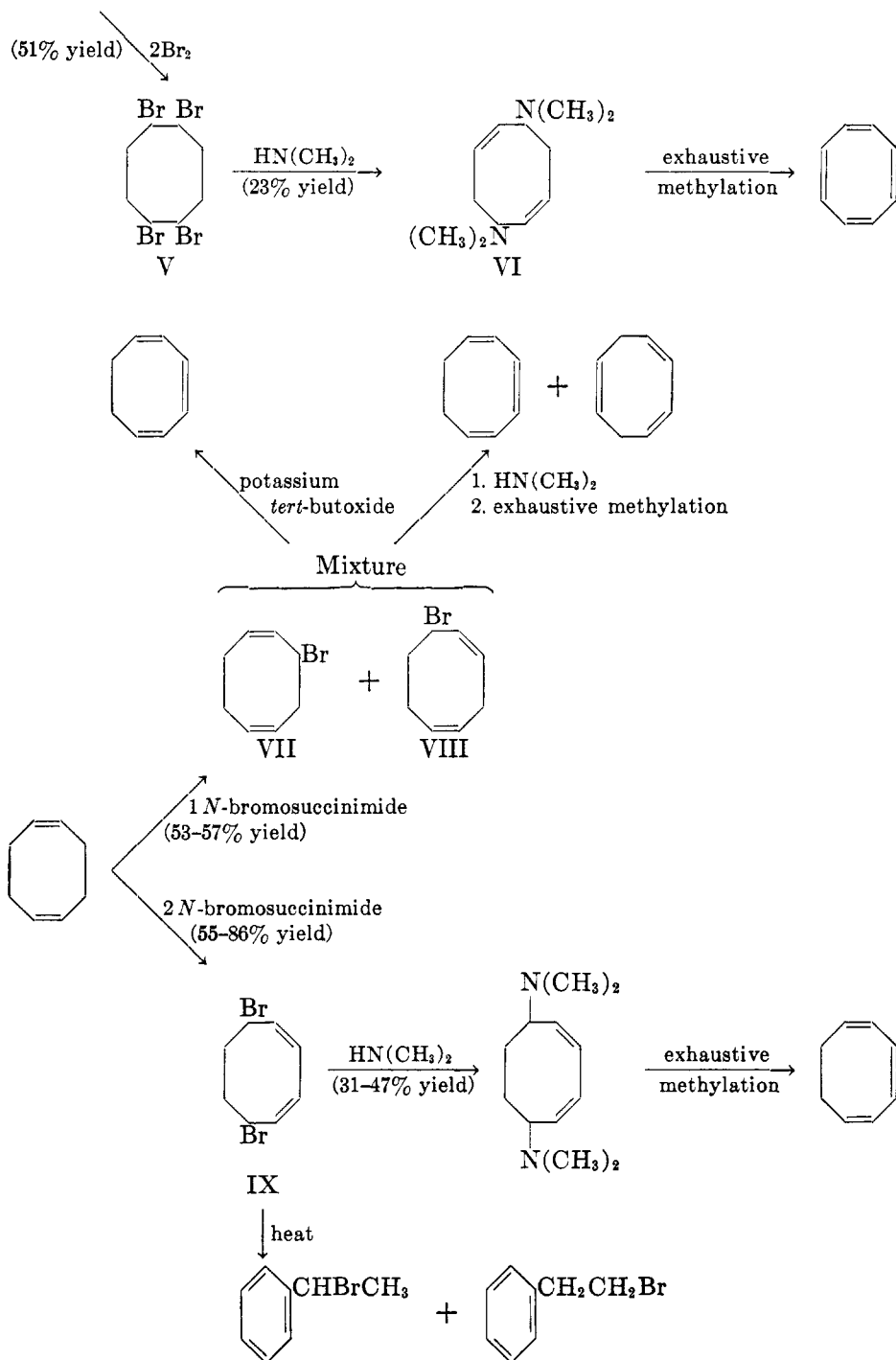
The 1,5-diene prepared in this manner is stable and presumably has a *cis-cis* configuration; this indicates that I probably has the *cis-cis* configuration also.

Of the three possible *cis-cis* forms—"chair," "skew," and "boat"—which compound I could have, Roberts (121) concluded from dipole moment measurements that at least 85 per cent of the molecules of I are in the "boat" form, a conclusion which is unexpected in view of the fact that calculation of strain energies involved in interconversions from one form to another shows that they should be easily interconvertible.



The reactions of 1,5-cyclooctadiene which follow are those of the stable *cis-cis* diene. 1,5-Cyclooctadiene forms a crystalline silver nitrate addition product (37) and is readily hydrogenated to cyclooctane (24, 160, 163, 173, 174). It adds stepwise one or two molar equivalents of bromine (161, 174) or hydrogen bromide (163, 174). The mono hydrogen bromide addition product, 5-bromocyclooctene (II), is converted to the carboxylic acid (III) by carbonation of the Grignard reagent or to *N,N*-dimethyl-4-cycloocten-1-ylamine (IV), along with some 1,5- and 1,4-cyclooctadiene, by treatment with dimethylamine (174). Treatment of the completely brominated diene (V) with methylamine results in the formation of *N,N,N',N'*-tetramethyl-2,6-cyclooctadiene-1,5-diamine (VI), which upon exhaustive methylation gives cyclooctatetraene (174).

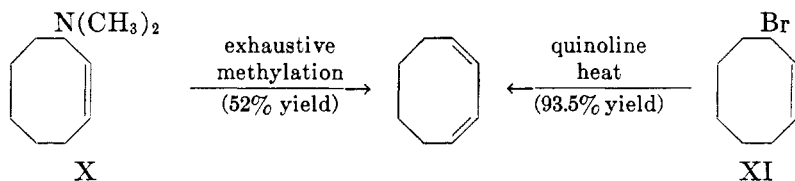




Treatment of 1,5-cyclooctadiene with one molar equivalent of *N*-bromosuccinimide (24, 37) results in a mixture of 3-bromo-1,5-cyclooctadiene (VII) and 6-bromo-1,4-cyclooctadiene (VIII), which were shown to undergo a reversible isomerism. With two molar equivalents, 5,8-dibromo-1,3-cyclooctadiene (IX) results. The bromine atoms of all three of these compounds are very reactive; all three compounds are readily hydrogenated to cyclooctane and converted to the corresponding dimethylamino compounds by reaction with dimethylamine. Heating a mixture of VII and VIII with potassium *tert*-butoxide in butanol gives essentially pure 1,3,5-cyclooctatriene, while treatment with dimethylamine followed by exhaustive methylation gives a mixture of 1,3,5- and 1,3,6-cyclooctatrienes. The reaction of IX and dimethylamine followed by exhaustive methylation gives cyclooctatetraene. Atmospheric distillation of IX leads to the elimination of one mole of hydrogen bromide with the formation of a mixture of  $C_8H_9Br$  isomers, which was shown to contain approximately 50 per cent  $\alpha$ -phenethyl bromide and 25 per cent  $\beta$ -phenethyl bromide. (See page 140.)

1,4-Cyclooctadiene was obtained as a by-product along with 1,5-cyclooctadiene by treatment of II with dimethylamine (174). It was obtained in pure form by fractional distillation and its structure proved by ozonolysis. The 1,4-cyclooctadiene ring system is also present in VIII.

1,3-Cyclooctadiene is prepared by decomposition of the quaternary base *N,N*-dimethyl-2-cycloocten-1-ylamine (X) (25) and by dehydrobromination of 3-bromocyclooctene (XI) (25, 174). It was also reported to be formed by treatment of 1-bromo-2-chlorocyclooctene with sodium (43) and by heating 2-chlorocyclooctanol with dilute ethanol (65, 97).



The products obtained from X and XI as shown above were found to have slightly different refractive indexes and infrared absorption curves (25). After purification of the product from X through the silver nitrate adduct, the two products were found to be identical. It was suggested that a small amount of a less stable isomer, perhaps a *cis-trans* isomer, was removed in the purification to give the pure *cis-cis* isomer.

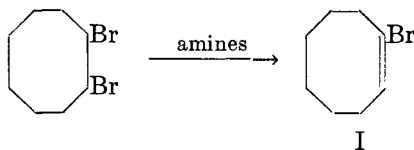
1,3-Cyclooctadiene is readily hydrogenated catalytically to cyclooctane (25) and reduced with lithium in methylaniline to cyclooctene (174). It forms an unstable silver nitrate addition product and adds one molar equivalent of bromine in the 1,4-positions (25). Surprisingly, it does not form a Diels-Alder addition product with maleic anhydride, but rather forms a heteropolymer (25, 174). It does not add phenyl azide spontaneously (174).

## D. CYCLOOCTENE

Cyclooctene is prepared by the dehydration of cyclooctanol (58, 83, 123, 173, 174), the degradation of trimethylcyclooctylammonium hydroxide (164, 173, 174), the hydrogenation of cyclooctatetraene (see page 120), and the reduction of 1,3-cyclooctadiene with lithium in methylaniline (174).

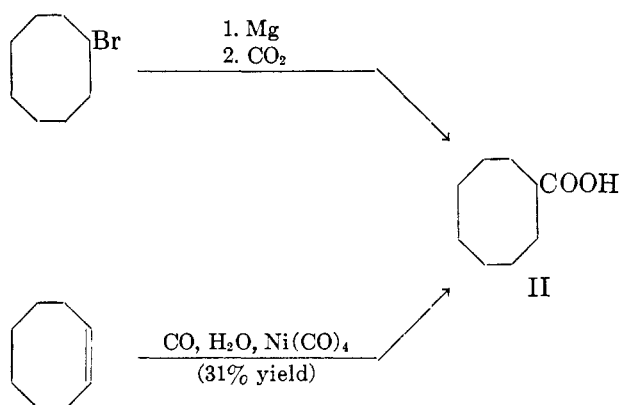
Ziegler and Wilms (173, 174) showed that the cyclooctenes obtained by degradation of trimethylcyclooctylammonium hydroxide and by dehydration of cyclooctanol had different refractive indexes and melting points. It was shown that the olefin from the quaternary base reacts completely with phenyl azide in a few hours, while the cyclooctene from dehydration of cyclooctanol requires several weeks. Furthermore, the two cyclooctenes with perbenzoic acid give epoxides with different melting points. The more reactive cyclooctene was believed to have a *trans* configuration, which imparts some strain to the molecule, and the less reactive, a strain-free *cis* configuration. It was shown that the *trans* isomer can be converted to the *cis* isomer by heating in the presence of an acid. The Raman spectra (57, 67) of the two cyclooctenes show lines in agreement with those known for *cis* and *trans* double bonds. Determinations of the heats of hydrogenation (22) and bromination (90) of cyclic olefins of the series cyclopentene to cyclooctene indicate that cyclooctene (*cis* isomer) is the least reactive of the series. The results of these experiments were explained on the basis of repulsion energy between the carbon atoms of the rings, and the statement was made (90) that these interactions probably exceed the carbon-hydrogen and hydrogen-hydrogen interaction. An examination of Fisher-Hirschfelder models shows, however, that there might be a considerable amount of hydrogen interference in the case of cyclooctane but little or none in the case of cyclooctene. This could contribute to the decreased reactivity of the double bond in cyclooctene.

The properties of cyclooctene obtained by hydrogenation of cyclooctatetraene resemble those reported for the *cis* isomer, and the subsequent discussion concerns this stable isomer. Cyclooctene is hydrogenated readily to cyclooctane and adds the usual reagents which add to a double bond, such as chlorine (83), bromine (38, 71, 76, 83, 115, 116, 119, 164, 174), hydrogen bromide (164), hypochlorous acid (65, 97), and nitrosyl chloride (58). Treatment of the dibromo- or dichlorocyclooctane with amines results in the formation of 1-halocyclooctene (I) rather than a diene (83). The Grignard reagent of bromocyclooctane gives cyclooctanecarboxylic acid (II) on carbonation. II is also prepared by the

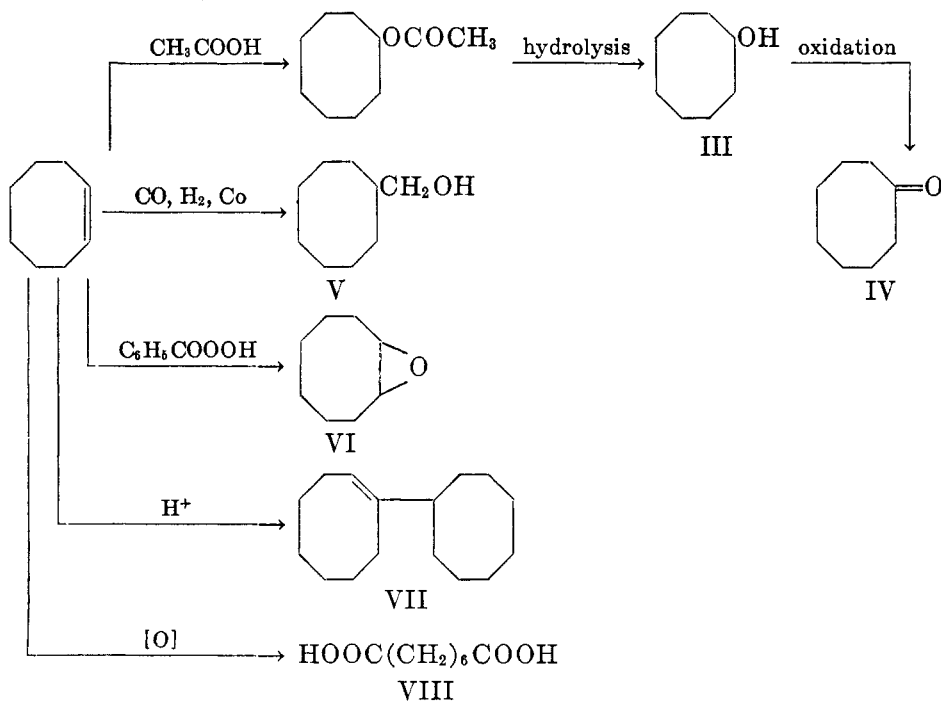


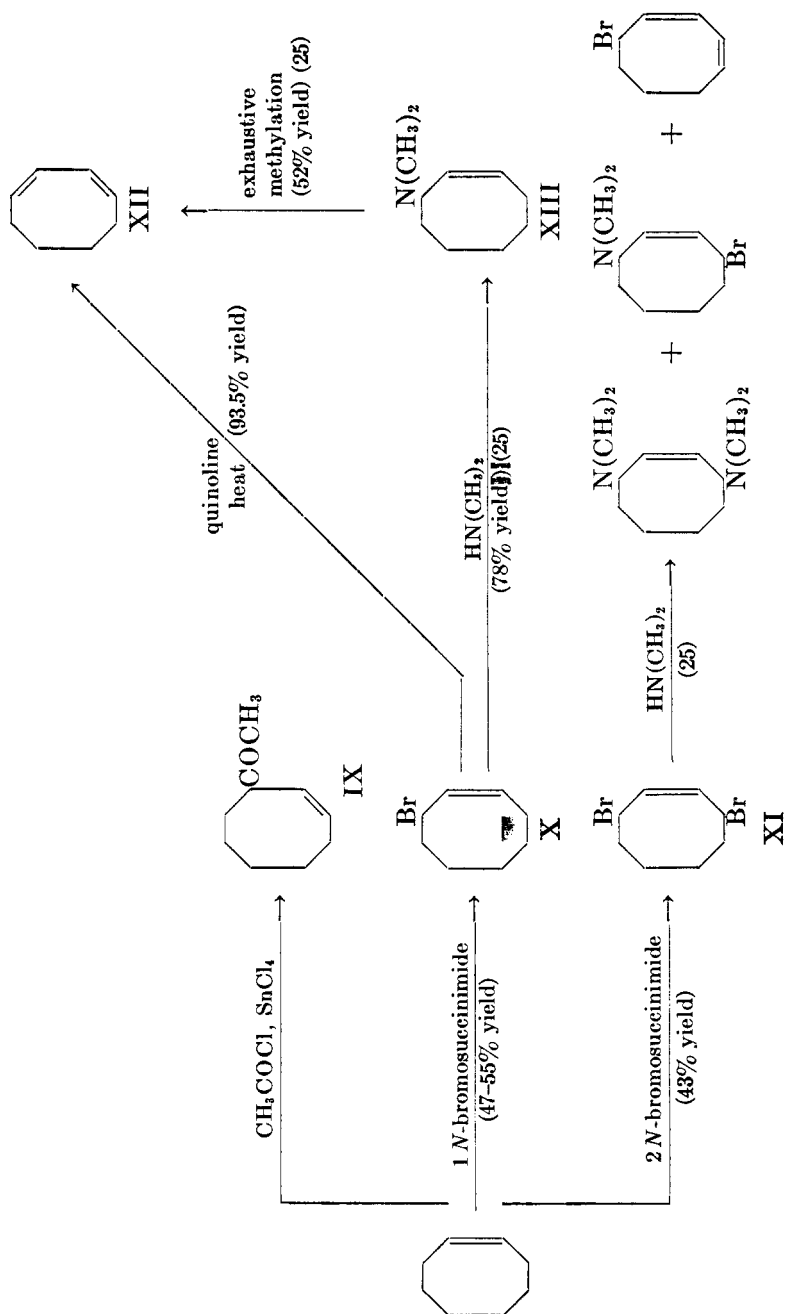
reaction of cyclooctene with carbon monoxide and water in the presence of nickel carbonyl (38, 71, 116, 117, 119).



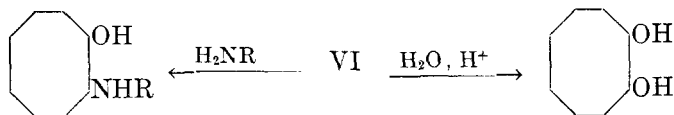


The investigations carried out in Germany under the direction of J. W. Reppe (38, 71, 76, 115, 116, 117, 119, 142) showed that cyclooctene is readily converted to various other functional derivatives. It is converted to cyclooctanol (III) by the addition of acetic acid to the double bond, followed by hydrolysis. As cyclooctanol can be oxidized to cyclooctanone (IV), this offers a method for the preparation of IV from cyclooctene, and hence from cyclooctatetraene. Cyclooctene is converted to cyclooctanemethanol (V) by the oxo reaction. It is converted to the 1,2-epoxide (VI) by treatment with perbenzoic acid. Cyclooctene dimerizes readily to give cyclooctenylcyclooctane (VII) and is oxidized readily to suberic acid (VIII).



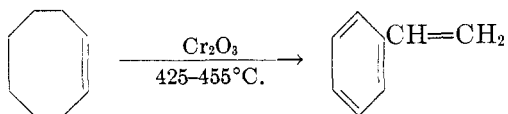


VI undergoes the usual reactions of epoxy compounds. It adds ammonia and amines (64, 96) and is converted to the glycol upon treatment with dilute acids (59, 174).



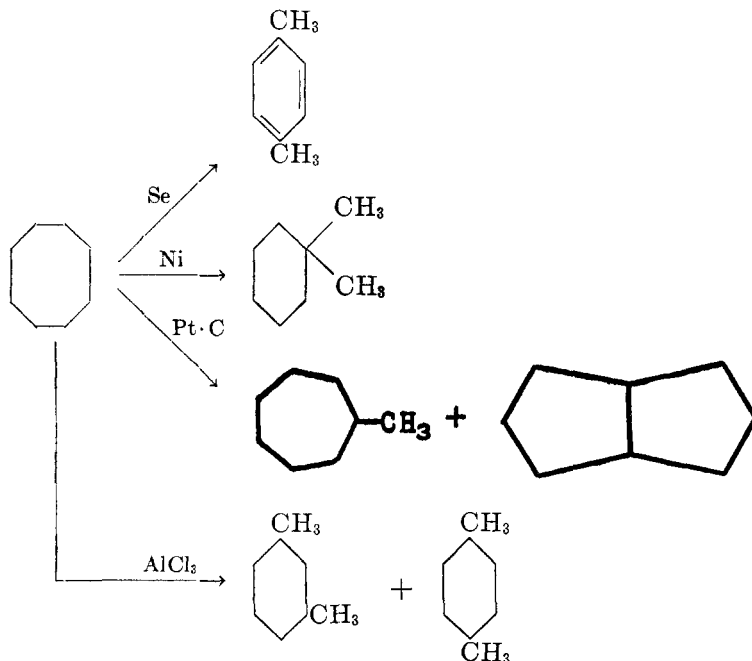
Cyclooctene is acetylated with acetyl chloride in the presence of stannic chloride (123) to give 3-acetylcyclooctene (IX) (see page 144). It reacts with one or two equivalents of *N*-bromosuccinimide (25, 174) to give 3-bromocyclooctene (X) or 3,8-dibromocyclooctene (XI). Since the bromines are in the allyl position, they are reactive and can be replaced by amines, although in the case of XI, some dehydrohalogenation occurs. X is dehydrohalogenated directly by heating with quinoline to give 1,3-cyclooctadiene (XII) or it can be converted to *N,N*-dimethyl-2-cycloocten-1-ylamine (XIII), which on exhaustive methylation gives XII (see page 141).

Cyclooctane is dehydrogenated over chromic oxide to give styrene in 93 per cent yield (66).



#### E. CYCLOOCTANE

Cyclooctane has been prepared many times by hydrogenation of various cyclic olefins as proof of the existence of the eight-membered ring. It was included in the studies made on homologous series of cyclic paraffins in terms of melting point (134), parachor and compressibility (124), infrared and Raman spectra (67, 80), and heats of combustion (135, 146).

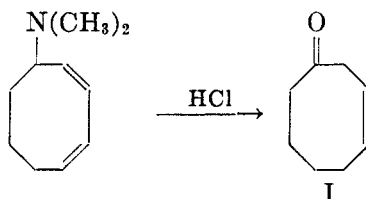


Heats of combustion measurements of the series cyclopentane to cyclooctane (146) showed that cyclooctane is of about the same stability as cyclopentane and cycloheptane but 9.6 kcal./mole less stable than cyclohexane. The instability was attributed to angular or torsional strain in the molecule. Examination of Fisher-Hirschfelder models shows that freedom of rotation of the  $\text{CH}_2$  groups about the carbon-carbon bond is possibly restricted by hydrogen interference.

Cyclooctane can be oxidized to suberic acid (76, 119) and isomerized to various hydrocarbons. At 390–400°C. over selenium, cyclooctane is converted to *p*-xylene (136). With nickel at 205–210°C., a mixture of hydrocarbons containing mainly 1,2-dimethylcyclohexane is produced (160). With platinized carbon at 300°C. (166), equal parts of methylcycloheptane and bicyclo[3.3.0]octane are produced, while with aluminum chloride (150), a mixture of 1,3- and 1,4-dimethylcyclohexanes is produced. (For equations see page 145.)

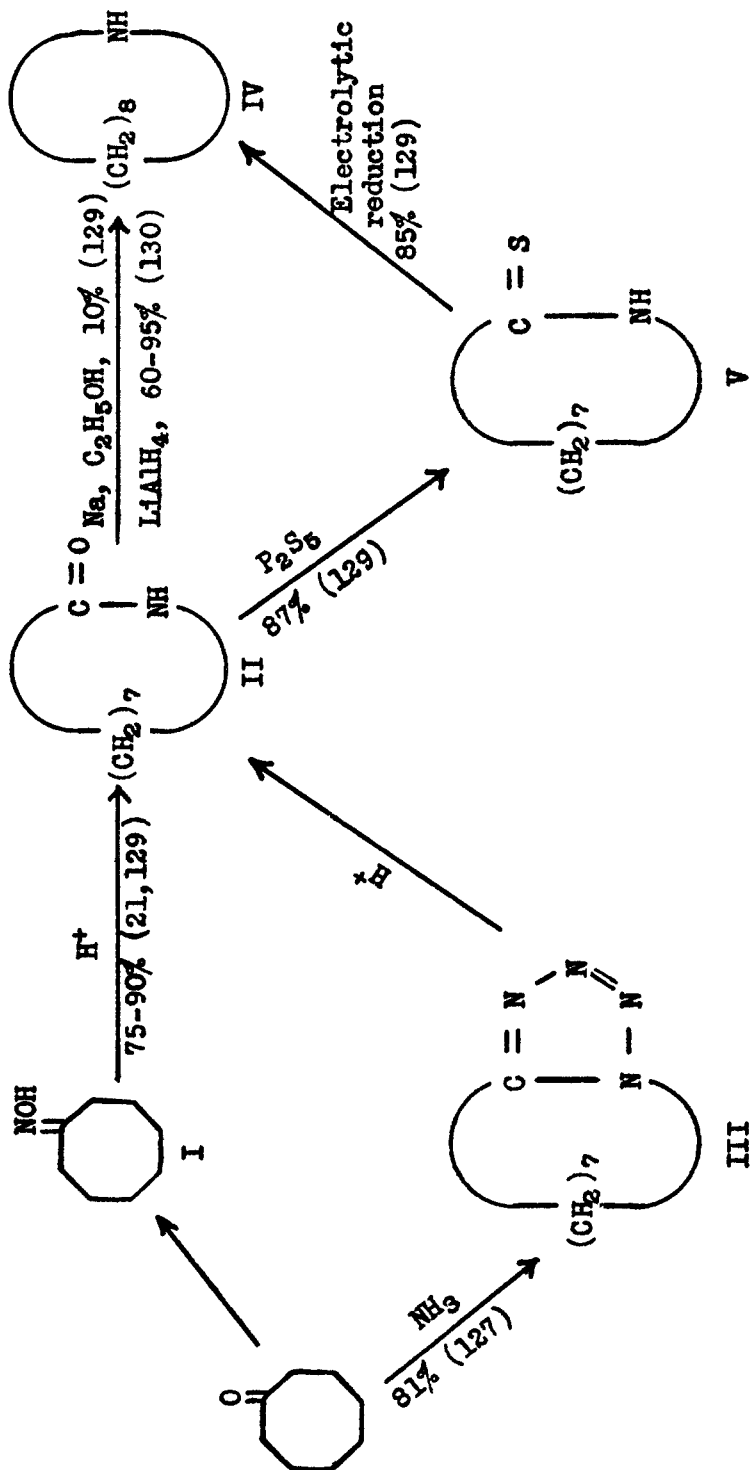
#### F. CYCLOOCTANONE

Cyclooctanones are prepared by intramolecular ring-closures of dicarboxylic acids and dinitriles, by ring-enlargement of cyclohexanones and cycloheptanones, by cleavage of ethylene bridges of bicyclic compounds (see Section II), and by oxidation of cyclooctanols (76, 115, 156). Ciamician and Silber (19, 20) treated *N,N*-dimethyl-2,4-cyclooctadien-1-ylamine ( $\alpha$ -des-dimethylgranatnine) with hydrochloric acid and obtained a product, granatal, which was later shown to be cycloocten-4-one (I).



Cyclooctanone was included in studies of homologous series of cyclic ketones in terms of infrared and Raman spectra (14, 17, 18, 62, 84), parachor and compressibility (124), heats of combustion (135), and dissociation of the cyanohydrins (106, 133). As the heat of combustion per  $\text{CH}_2$  group of cyclooctanone is not significantly different from larger cyclic ketones, no strain appears to be present in the cyclooctanone molecule, in contrast to cyclooctane, which does show some strain according to similar measurements.

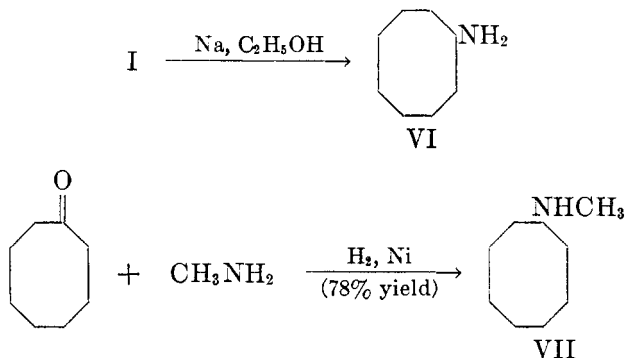
Comparison of the cyanohydrins of the homologous series of five- to twenty-membered cyclic ketones showed that the dissociation constants of the eight- to eleven-membered ketones are much higher than those of smaller and larger ketones. The dissociation constant of the cyanohydrin of cyclooctanone is almost one thousand times larger than that of cyclohexanone; hence the formation of the cyanohydrin is greatly hindered. These high dissociation constants of the eight- to eleven-membered ketones were considered (106) to indicate a configuration in which the oxygen of the carbonyl is turned toward the center of the ring rather than away from the ring.



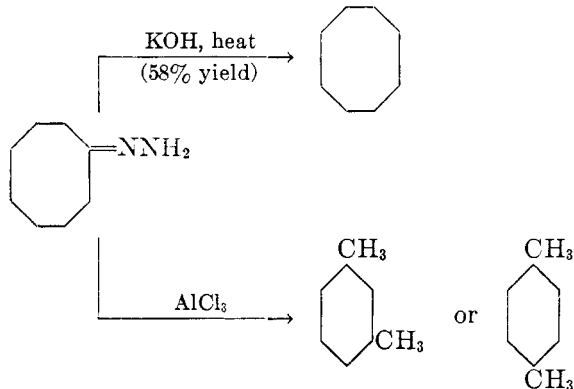
Cyclooctanone is oxidized to suberic acid with chromic acid (58, 125, 156). It is reduced to cyclooctanol with aluminum isopropoxide (58, 59, 100), by sodium in aqueous sodium bicarbonate (123), and catalytically with Raney nickel (82, 132).

Cyclooctanone undergoes the typical carbonyl addition reactions. It forms an oxime (59, 76, 122, 128), a hydrazone (152, 166), a semicarbazone (58, 83, 93, 122, 125, 156, 171), a 2,4-dinitrophenylhydrazone (15), and an anil (2). The oxime (I) rearranges to the lactam (II) smoothly upon treatment with strong acids (21, 76, 129, 130). II is also prepared by treating cyclooctanone with hydrazoic acid to give a tetrazole (III) which decomposes in the presence of mineral acids (127, 129). II can be converted to a polymeric amide (21) or reduced to the nine-membered cyclic imine, azacyclononane (IV), which is physiologically active (129). IV is also obtained by conversion of II to the thiolactam (V), followed by electrolytic reduction. (For equations see page 147.)

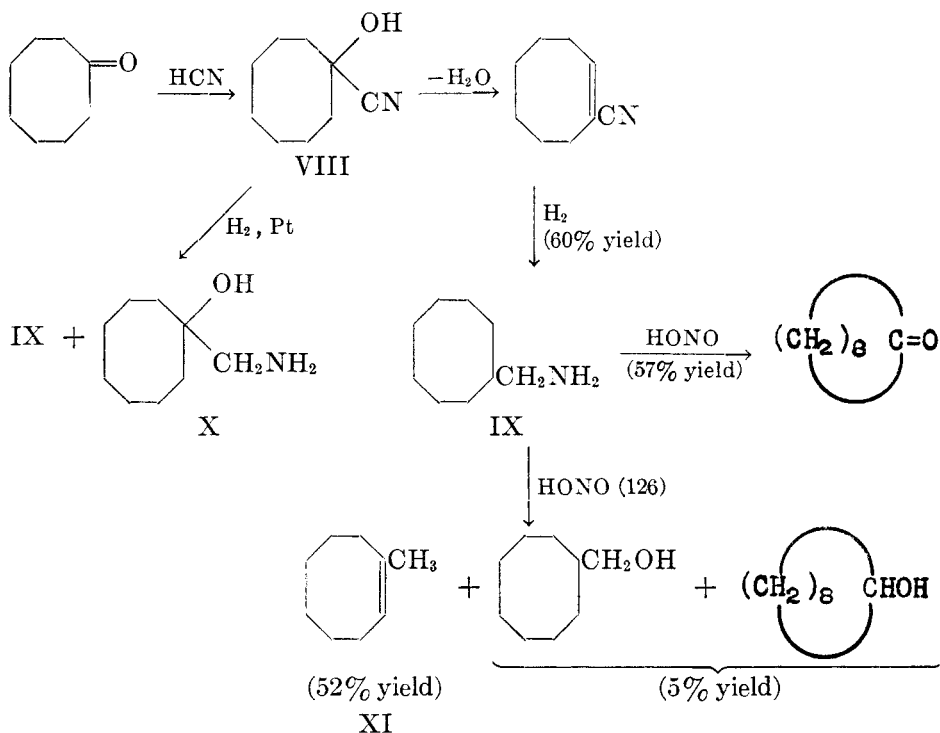
Cyclooctylamine (VI) is conveniently prepared by reduction of I (128). *N*-Methylcyclooctylamine (VII) is obtained by the reductive alkylation of methylamine with cyclooctanone, a method presumably applicable to the preparation of cyclooctylamines in general (174).



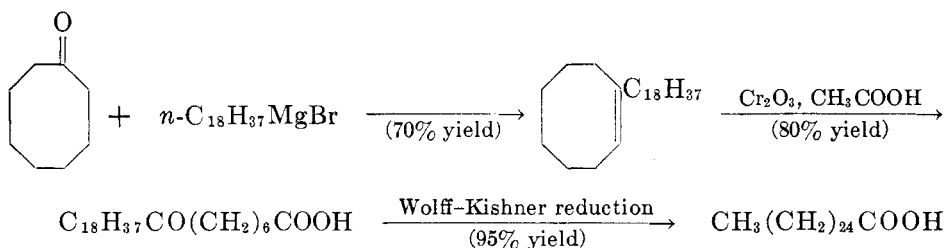
The hydrazone of cyclooctanone is converted to cyclooctane upon heating in the presence of alkali (152, 166) and to either 1,3- or 1,4-cyclohexane upon treatment with aluminum chloride (152).



Cycloöctanone forms a cyanohydrin (VIII), which is best converted to aminomethylcycloöctane (IX) by dehydration of the cyanohydrin before reduction (126). Hydrogenation of VIII leads to the formation of appreciable quantities of 1-aminomethylcycloöctanol (X) along with IX (131). Treatment of IX with nitrous acid was reported to lead to ring-enlargement in one case (131) and to the formation of 1-methylcycloöctene (XI) as the main product in another (126).

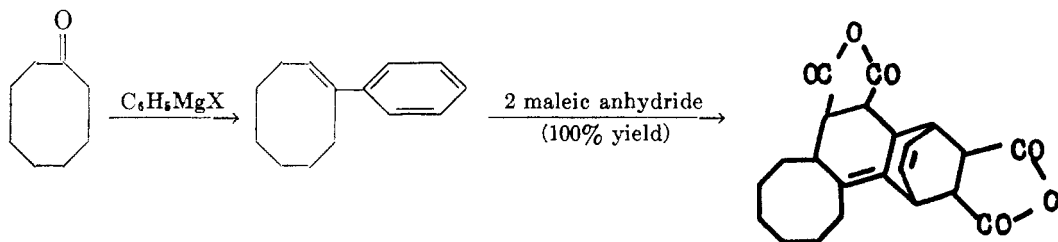


Cycloöctanone reacts with Grignard reagents in the usual manner (27, 40, 53, 58), the cycloöctanol formed as the primary product being readily dehydrated to the substituted cycloöctene. The Grignard reaction with cycloöctanone was used (53) in the synthesis of *n*-keto acids and long-chain fatty acids as illustrated by the following reactions:

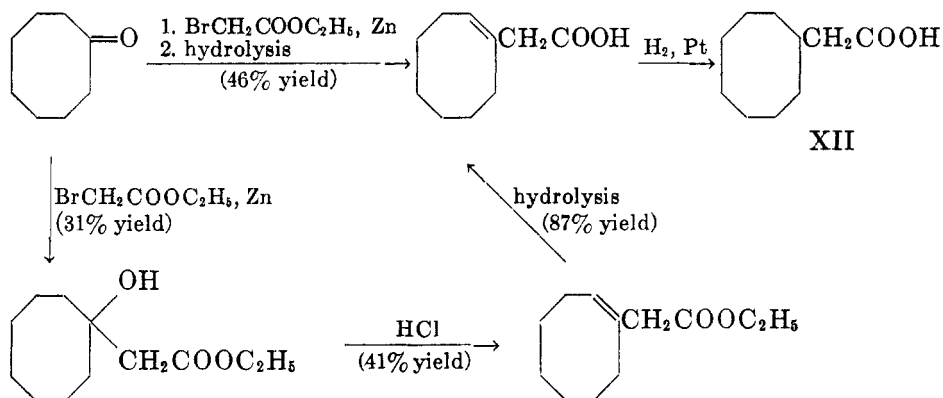


1-Phenylcycloöctene, prepared from cycloöctanone by the Grignard reaction,

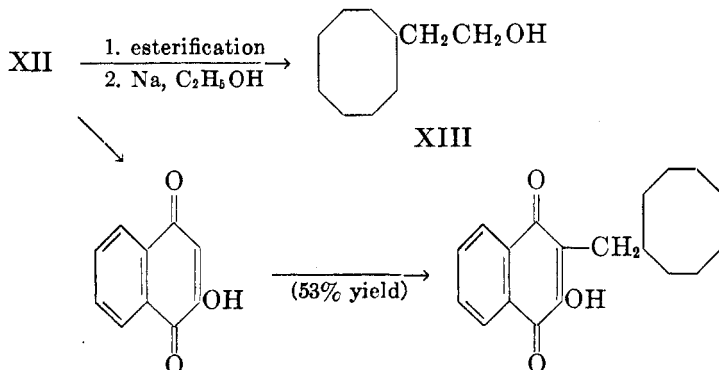
adds two molar equivalents of maleic anhydride quantitatively in the Diels-Alder reaction according to the following scheme (148):



Cyclooctanone undergoes the Reformatsky reaction (51, 123). The products which have been isolated in this reaction are indicated in the following scheme:



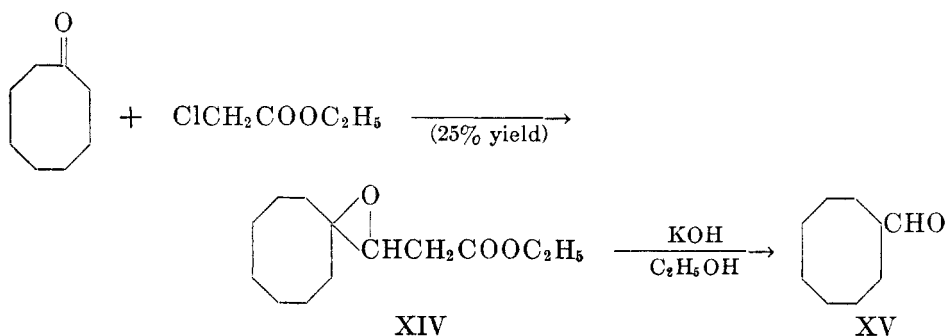
The cyclooctaneacetic acid (XII) can be esterified and reduced to  $\beta$ -cyclooctaneethanol (XIII) (123) and can be used in the peroxide alkylation of 2-hydroxy-1,4-naphthoquinone (51).



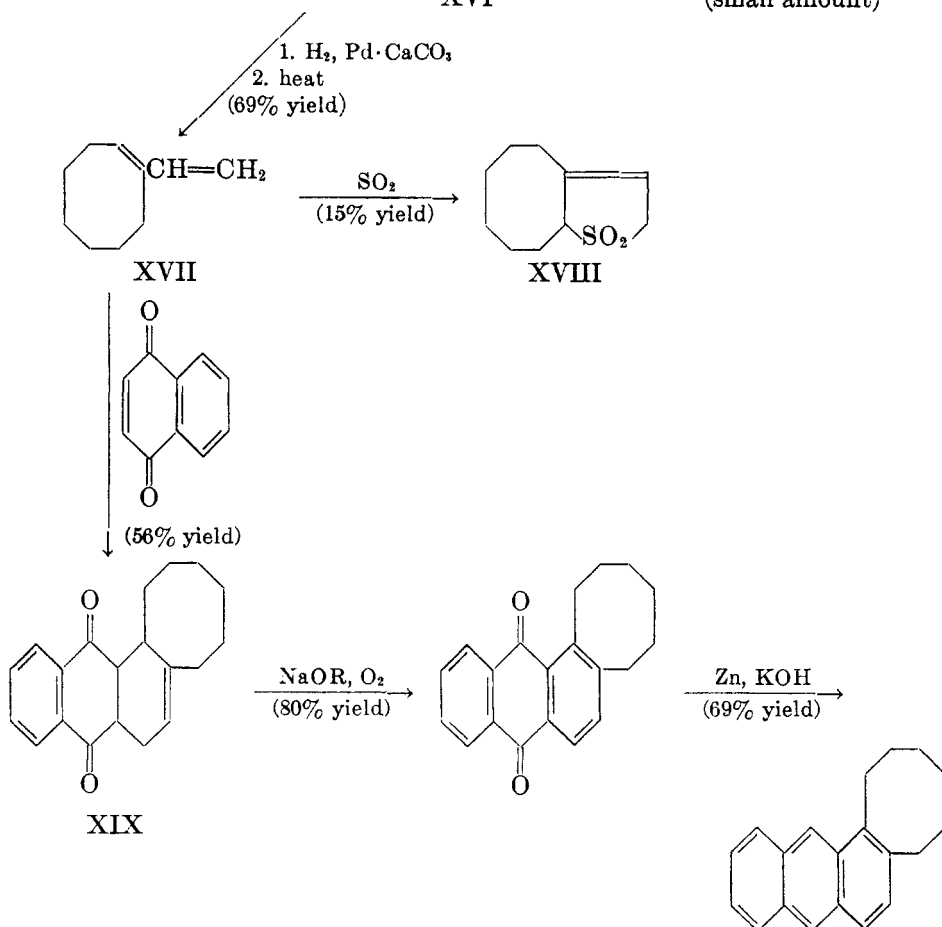
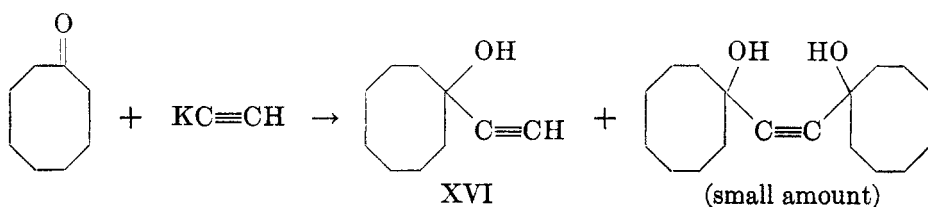
Cyclooctanone forms a glycid ester (XIV) which with alcoholic potassium hydroxide gives cyclooctanecarboxaldehyde (XV) (123) (see page 151).

Acetylene adds to the carbonyl group of cyclooctanone to produce 1-ethanylethynylcyclooctanol (XVI) as the main product (5). XVI can be hydrogenated to the vinyl compound and dehydrated to give 2-vinylcyclooctene (XVII), which adds sulfur dioxide to form the cyclic sulfone (XVIII) and undergoes typical diene reactions with maleic anhydride, quinone, and naphthoquinone. The adducts

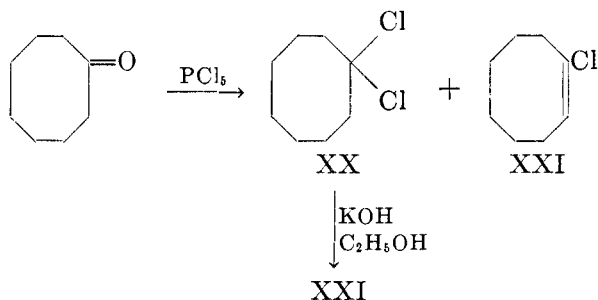




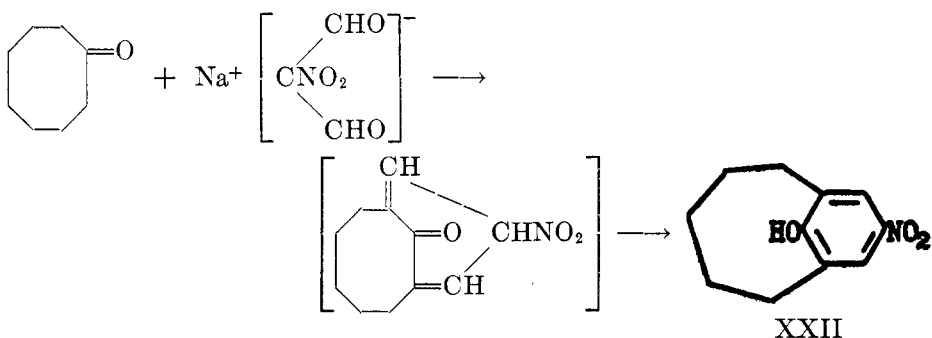
have been reduced and oxidized to give various products, as typified in the equations below by the naphthoquinone adduct (XIX):



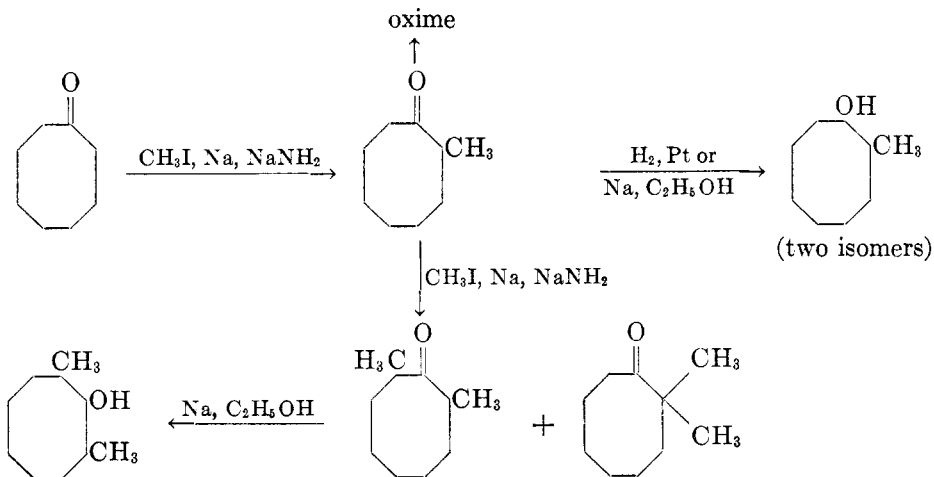
Treatment of cycloöctanone with phosphorus pentachloride results in the formation of a mixture of 1,2-dichlorocycloöctane (XX) and 1-chlorocycloöctene (XXI). XX is converted to XXI by treatment with alcoholic potassium hydroxide (42).



Cycloöctanone undergoes the usual reactions associated with methylene groups in the  $\alpha$ -position to a carbonyl group. It forms a dibenzylidene derivative (39, 59) with benzaldehyde and reacts with the sodium salt of nitromalonaldehyde

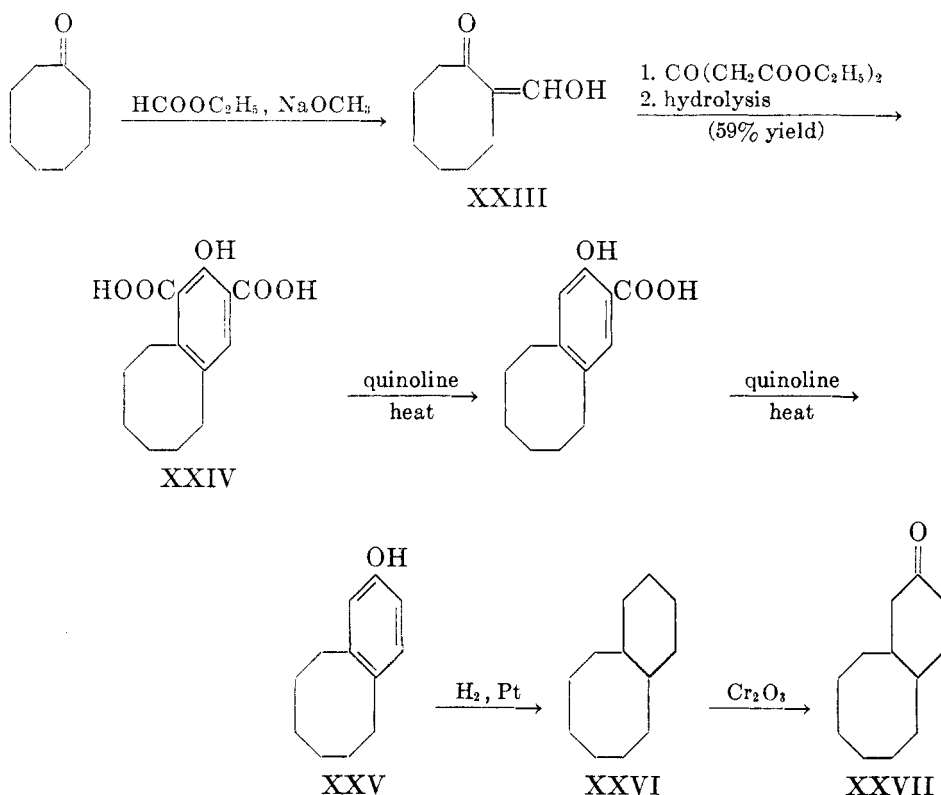


(109, 110) to give a pentamethylenenitrophenol (XXII), presumably by way of an intermediate formed from condensation of the dialdehyde with the two  $\alpha$ -methylene groups.



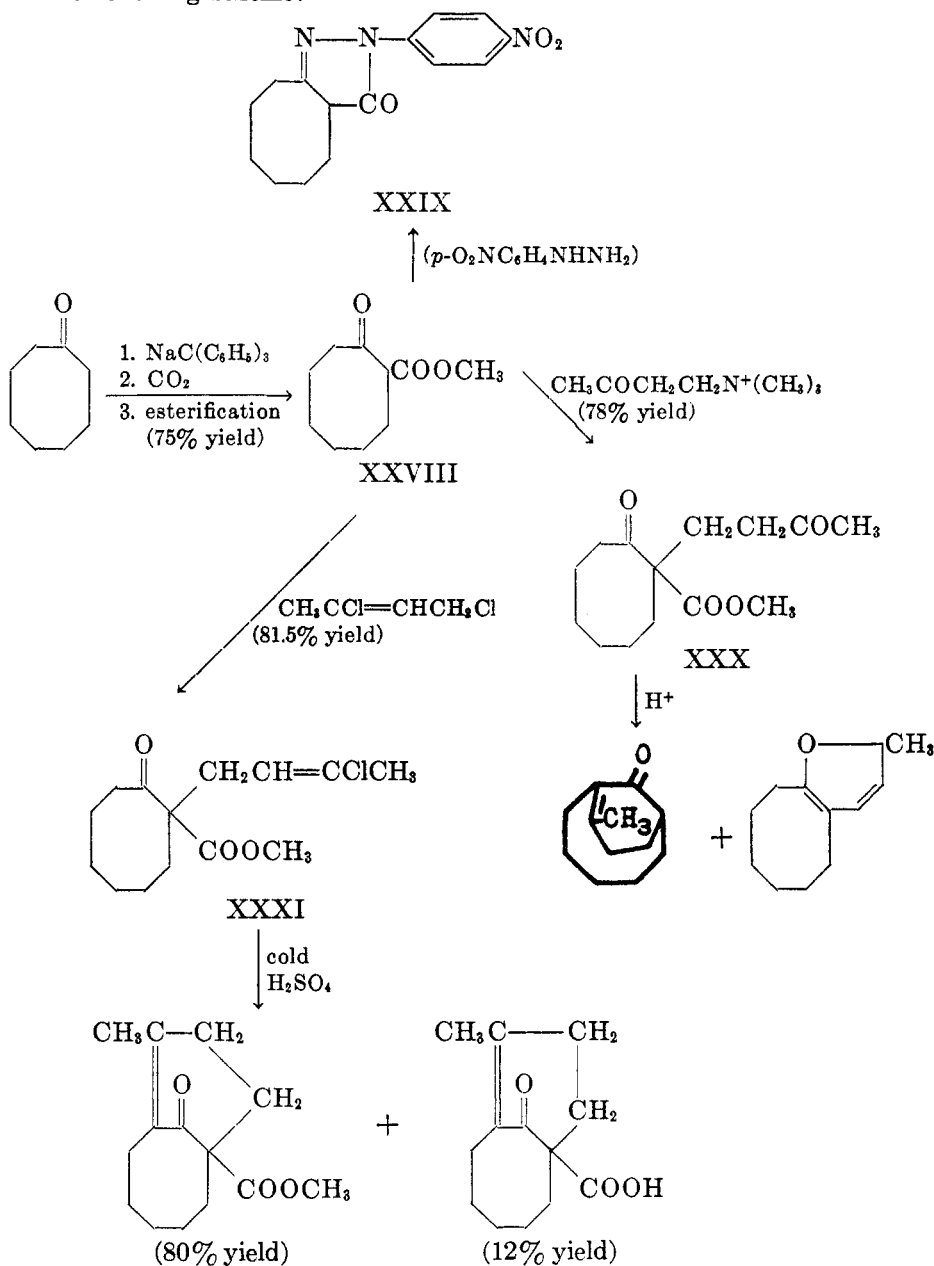
With methyl iodide in the presence of sodium and sodium amide, one or two methyl groups can be introduced in the  $\alpha$ -positions (59). The resulting methylcycloöctanones form carbonyl addition compounds and can be oxidized and reduced in the same manner as cycloöctanone (59, 60). (See page 152.)

2-(Hydroxymethylene)cycloöctanone (XXIII) is prepared by treating cycloöctanone with ethyl formate and sodium methoxide (108). Reaction of XXIII with diethyl acetonedicarboxylate, followed by hydrolysis, results in the formation of 3,4-hexamethylenephenol-2,6-dicarboxylic acid (XXIV), which can be decarboxylated stepwise to 3,4-hexamethylenephenol (XXV). XXV can be hydrogenated to bicyclo[6.4.0]dodecane (XXVI), which in turn can be oxidized to *cis*-3,4-hexamethylenecyclohexanone (XXVII).

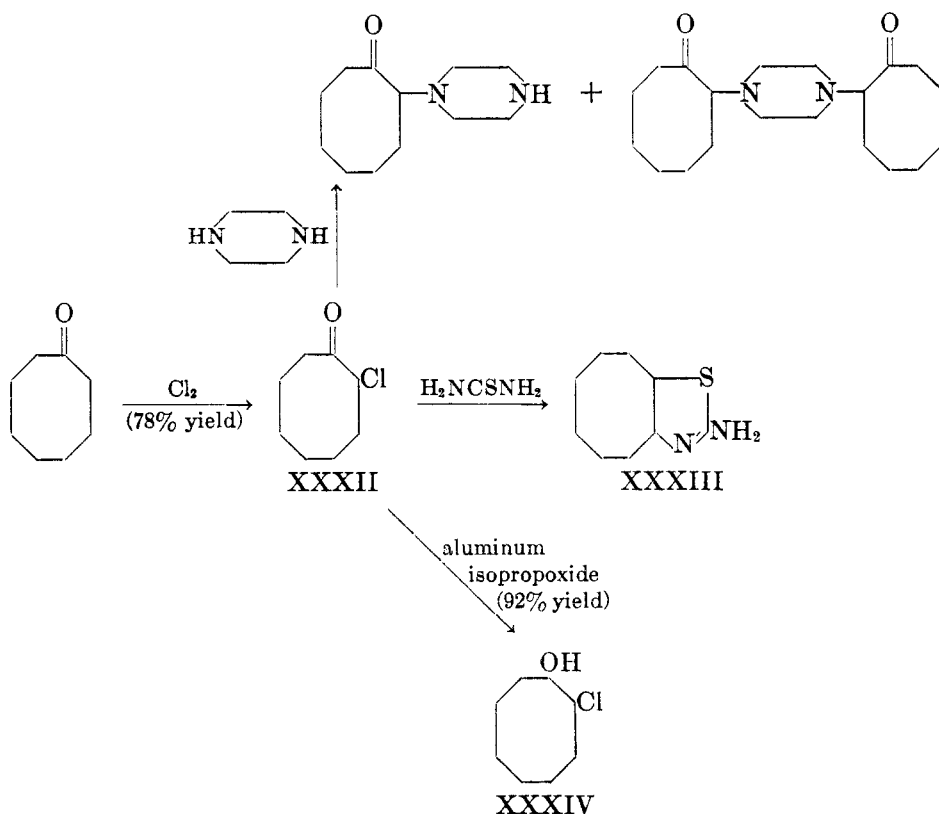


Cycloöctanone is converted to its sodium salt by sodium triphenylmethane. Carbonation and esterification give methyl cycloöctanone-2-carboxylate (XXVIII) (107), which reacts with *p*-nitrophenylhydrazine to give a pyrazolone (XXIX). XXVIII can be further alkylated with  $\beta$ -acetyethyltrimethylammonium iodide (which decomposes to methyl vinyl ketone) (107) or with  $\gamma$ -chlorocrotyl chloride (105). The resulting compounds, XXX and XXXI, undergo

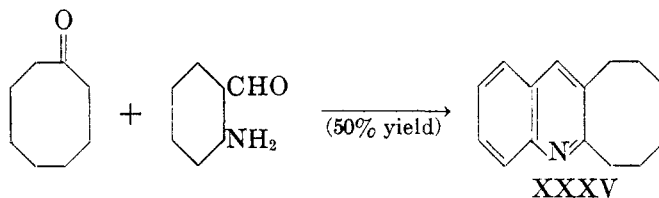
ring-closure in the presence of acids to give the bicyclic compounds indicated in the following scheme:



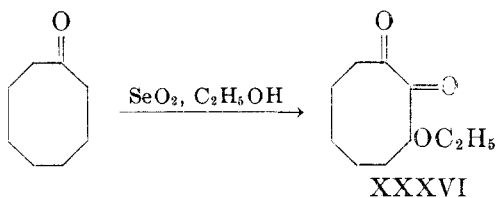
2-Chlorocyclooctanone (XXXII), conveniently prepared by chlorination of cyclooctanone (49, 63), reacts with piperazine to give replacement of the active chlorine (95) and with thiourea to give a thiazole (XXXIII) (49). Reduction of XXXII with aluminum isopropoxide gives 2-chlorocyclooctanol (XXXIV) with only 7 per cent of the chlorine being removed (100).



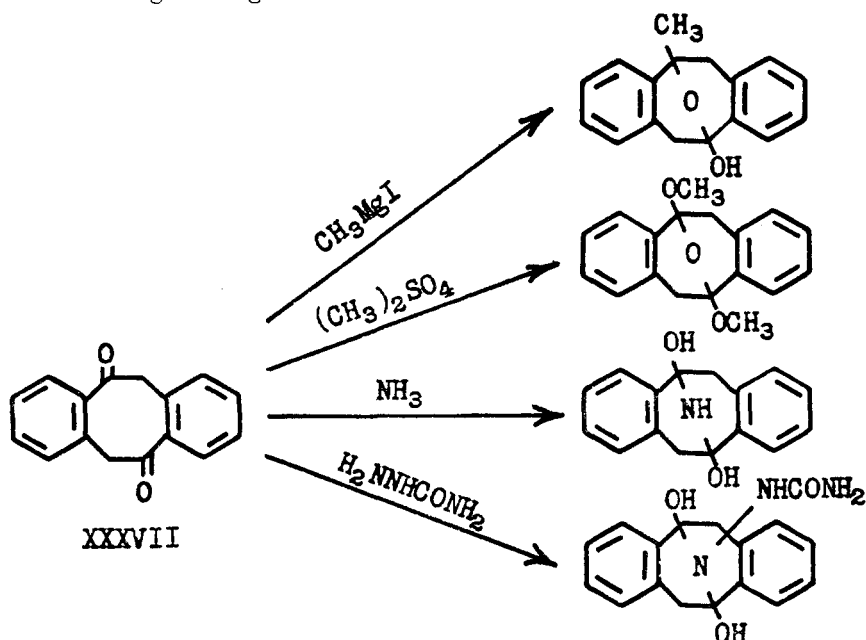
A reaction involving both the addition to the carbonyl and the  $\alpha$ -methylene group is the formation of 2,3-hexamethylenequinoline (**XXXV**) by reaction with 2-aminobenzaldehyde (127).



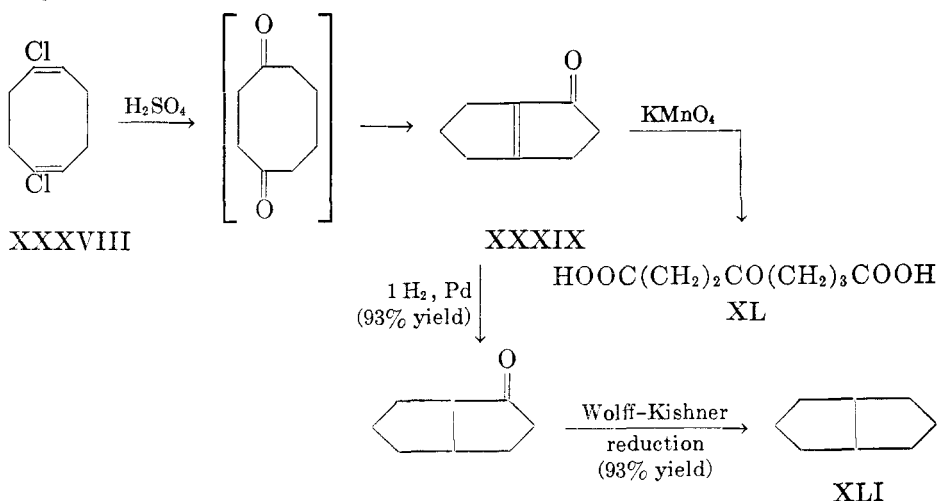
Certain substituted cyclooctanediones have been prepared (see pages 105, 106, and 110 for 1,5-cyclooctanediones). The reaction of cyclooctanone with selenium dioxide in ethanol was found to give 3-ethoxy-1,2-cyclooctanedione (**XXXVI**) (61).



Some interesting reactions of 1,5-cyclooctanediones have been reported. It was found (157) that many reactions of the diketone XXXVII lead to the formation of bridges between the two carbons of the carbonyl groups. An oxygen bridge is introduced when XXXVII is treated with methylmagnesium iodide and with dimethyl sulfate. Ammonia and semicarbazide are added with formation of a nitrogen bridge.

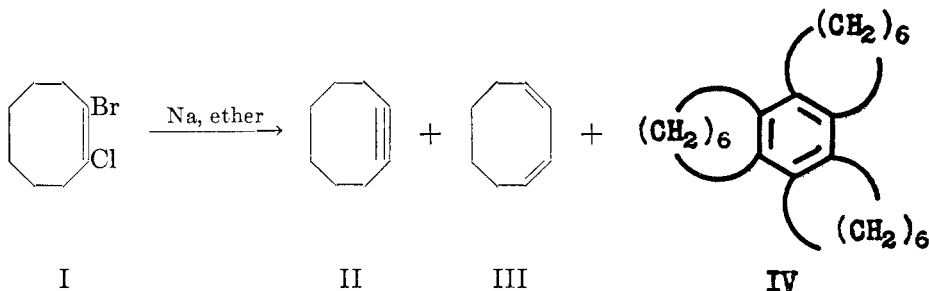


Treatment of the eight-membered cyclic chloroprene dimer (XXXVIII) with sulfuric acid gives a bicyclic ketone (XXXIX), and 1,5-cyclooctanedione was postulated as an intermediate (36). The structure of XXXIX was proved by oxidation to a ketodicarboxylic acid (XL) and hydrogenation to the known bicyclo[3.3.0]octane (XLI).

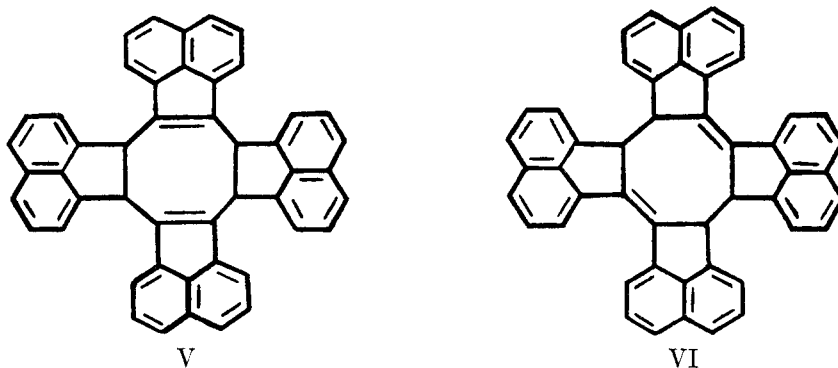


## G. MISCELLANEOUS EIGHT-MEMBERED CARBOCYCLES

The reaction of 1-bromo-2-chlorocyclooctene (I) and sodium was reported (42, 43) to give cyclooctyne (II) along with 1,3-cyclooctadiene (III) and trihexamethylenebenzene (IV). The evidence for the structure of II rests in the oxidation to suberic acid.



The product, fluorocyclene, formed by heating acenaphthene with lead oxides was believed to be a cyclooctadiene derivative, either V or VI.



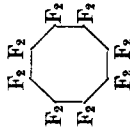

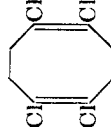
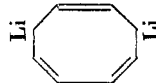
Fluorocyclene adds bromine to give a dibromo and a tetrabromo derivative and can be nitrated to give dinitro and tetranitro compounds and sulfonated to give a tetrasulfonic acid (47). With sodium and alcohol, tetrahydro, octahydro, and dodecahydro derivatives are produced (44). All compounds of this series, except the bromine addition products, exhibit a blue or violet fluorescence. The fluorescence spectra of fluorocyclene and its partially hydrogenated derivatives have been examined thoroughly (12, 75, 92, 102, 153, 154).

## IV. TABLES

Table 1 contains the eight-membered carbocycles which have been reported in the literature. The tabulation is believed to represent complete coverage of the literature with the exception that many derivatives made solely for identification purposes have not been included. Table 2 contains the compounds with condensed polycyclic ring systems which have been prepared from eight-membered carbocycles. This tabulation was included in this review since many of these compounds would be very difficult to prepare by other methods.

The compounds are numbered consecutively and are listed in order of increas-

TABLE 1  
*Eight-membered carbocycles*

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
1.....	C <sub>8</sub> F <sub>16</sub>		From C <sub>2</sub> F <sub>4</sub> at 420–450°C. over activated carbon	(69)
2.....	C <sub>8</sub> H <sub>8</sub>		70–95% from acetylene with nickel catalysts 87–98% by degradation of compound 173 By degradation of compound 174 See compounds 4, 5, 6, 7, 31, 43, 67, 74, 154, 187, 260, 261, 262, 265, 266, 267, 269, 287, 294, 318, 338, and 359	(13, 38, 68, 71, 76, 114, 115, 116, 117, 118, 119, 120, 142) (24, 34, 35, 37, 159, 165) (174)
3.....	C <sub>8</sub> H <sub>8</sub> Cl <sub>4</sub>		12.5% by dimerization of CH <sub>2</sub> =CClCCl=CH <sub>2</sub> See compound 43	(54)
4.....	C <sub>8</sub> H <sub>8</sub> Li <sub>2</sub>		By addition of lithium to compound 2 See compounds 6, 7, and 75	(38, 71, 76, 115, 116, 117, 119, 142)



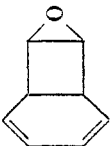
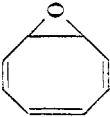
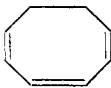

5. ....	$C_8H_8O$	 or 	45-52% from compound 2 with $C_6H_5CO_3H$ See compounds 24, 46, 296, and 322	(38, 55, 71, 76, 115, 116, 117, 119, 142)
6. ....	$C_8H_{10}$		62-66% by degradation of compound 106 71% from compounds 11 and 12 with $KOC(CH_3)_3$ 53% from compound 8 and Mg 20-30% along with compound 7 from compound 4 and $CH_3OH$ 78% by degradation of compound 107 Along with compound 7 from compound 2 and sodium in liquid ammonia From compound 2 and sodium in $C_6H_5NHCH_3$ Along with compound 7 and compound 154 from compound 2 and $C_6H_5Li$ By isomerization of compound 7 with $KOC(CH_3)_3$ See compounds 8, 43, and 116	(33, 34, 35, 165) (37) (37) (31) (24) (31) (174)
7. ....	$C_8H_{10}$		Along with compounds 6 and 154 from compound 2 and $C_6H_5Li$ Along with compound 6 from compound 2 and sodium in liquid ammonia Along with compound 6 from compound 4 and $CH_3OH$ Along with compound 6 from the degradation of compound 107 See compounds 6 and 43	(32) (31) (31) (24)

TABLE I—Continued

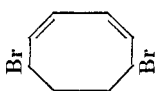
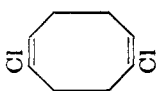
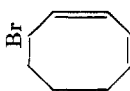
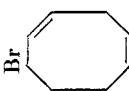
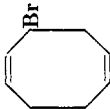

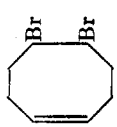
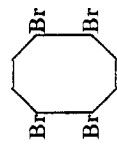
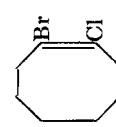
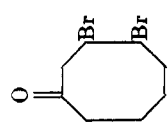
COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
8.....	$C_8H_{10}Br_2$		47% from compound 6 and bromine 55-86% from compound 15 and <i>N</i> -bromosuccinimide See compounds 6, 43, and 131	(34, 35, 37, 165) (24, 37)
9.....	$C_8H_{10}Cl_2$		10-22% by dimerization of chloroprene See compounds 15, 43, and 272	(16, 24, 36, 54)
10.....	$C_8H_{11}Br$		Along with compounds 89 and 136 from compound 18 and $HN(CH_3)_2$	(25)
11.....	$C_8H_{11}Br$		53-57% along with compound 12 from compound 15 and <i>N</i> -bromosuccinimide See compounds 6, 12, 43, and 86	(24, 37)
12.....	$C_8H_{11}Br$		53-57% along with compound 11 from 15 and <i>N</i> -bromosuccinimide By isomerization of compound 11 See compounds 6, 15, 43, and 86	(24, 37) (37)



TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
18.....	$C_8H_{12}Br_2$		78% from compound 13 and bromine 43% from compound 31 and <i>N</i> -bromosuccinimide See compounds 10, 89, and 136	(25) (25)
19.....	$C_8H_{12}Br_3$		From compound 15 and bromine	(161)
20.....	$C_8H_{12}Br_4$		51% from compound 15 and bromine See compound 132	(174)
21.....	$C_8H_{12}BrCl$		Along with compound 17 from compound 29 and alcoholic KOH See compounds 13, 16, and 245	(42)
22.....	$C_8H_{12}Br_2O$		From compound 23 and bromine	(19)

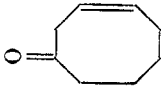
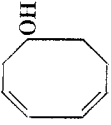
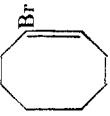

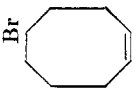
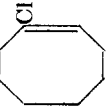
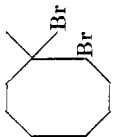
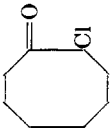

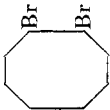
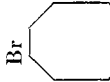
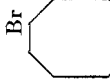
23. ....	$C_8H_{12}O$		From compound 85 and aqueous HCl See compound 22	(19, 165)
24. ....	$C_8H_{12}O$		31% by hydrogenation of compound 5 over Pd.CaCO <sub>3</sub>	(55)
25. ....	$C_8H_{13}Br$		70% from compound 32 and HN(CH <sub>3</sub> ) <sub>2</sub>	(83)
26. ....	$C_8H_{13}Br$		47-55% from compound 31 and <i>N</i> -bromo- succinimide See compounds 13, 96, and 191	(25, 174)
27. ....	$C_8H_{13}Br$		76% from compound 15 and HBr See compounds 14, 15, 54, and 97	(174)
28. ....	$C_8H_{13}Cl$		From compound 34 or 35 and HN(CH <sub>3</sub> ) <sub>2</sub> or alcoholic KOH Along with compound 34 from com- pound 37 and PCl <sub>5</sub> See compound 29	(42, 83) (42)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
29.....	$C_8H_{13}ClBr_2$		From compound 28 and bromine See compounds 17 and 21	(42)
30.....	$C_8H_{13}ClO$		78% by chlorination of compound 37 From $\alpha$ -chlorocycloheptanone and diazomethane See compounds 40 and 65	(49, 63) (147)
31.....	$C_8H_{14}$		93% by dehydration of compound 46 62% by degradation of compound 111 83–86% by hydrogenation of compound 2 over $Pd \cdot CaCO_3$ 93% from compound 13 and lithium and $C_6H_5NHCH_3$ See compounds 18, 26, 32, 35, 36, 38, 39, 40, 43, 62, 67, 79, 93, 165, and 195	(58, 83, 123, 173, 174) (164, 173, 174) (13, 38, 71, 76, 115, 116, 117, 118, 119, 142) (174)
32.....	$C_8H_{14}Br_2$		30–91% from compound 31 and bromine See compound 25	(38, 71, 76, 83, 90, 115, 116, 119, 164, 174)
33.....	$C_8H_{14}Br_2$	 or 	From compound 15 and HBr See compound 15	(163)

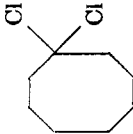
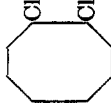
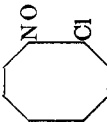
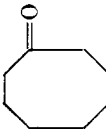
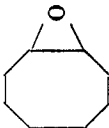
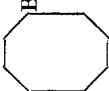
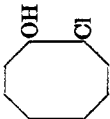
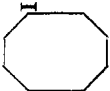
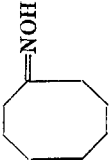
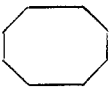
34.....	$C_8H_{14}Cl_2$		Along with compound 28 from compound 37 and $PCl_5$	(42)
35.....	$C_8H_{14}Cl_2$		90% from compound 31 and chlorine See compound 28	(83)
36.....	$C_8H_{14}ClNO$		From compound 31 and $NOCl$	(58)
37.....	$C_8H_{14}O$		20% by dry distillation of thorium azelate 50-85% by hydrolysis of compound 52 or 53 By treatment of cyclohexanone or cycloheptanone with diazomethane By treatment of 1-aminomethylcycloheptanol with $HNO_2$ By oxidation of compound 46 By oxidation and pyrolysis of ricinoleic acid See compounds 28, 30, 34, 42, 45, 46, 51, 55, 57, 60, 64, 69, 70, 72, 80, 82, 83, 88, 102, 103, 129, 135, 157, 160, 161, 164, 176, 197, 207, 233, 235, and 250	(42, 58, 63, 122, 125, 166, 167) (138, 169, 170, 171) (1, 5, 83, 94) (149) (76, 115, 156) (99)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
38.....	$C_8H_{14}O$		65% from compound 31 and $C_8H_5CO_2H$ See compounds 47, 49, and 71	(38, 59, 71, 76, 115, 116, 117, 119, 174)
39.....	$C_8H_{13}Br$		From compound 31 and HBr See compound 62	(164)
40.....	$C_8H_{13}ClO$		92% from compound 30 and $Al[OCH(CH_3)_2]_3$ From compound 31 and HOCl See compounds 13, 137, and 226	(100) (65, 97)
41.....	$C_8H_{13}I$		From compound 46 and HI	(132)
42.....	$C_8H_{13}NO$		From compound 37 and $H_2NOH$ See compound 48	(122, 128)
43.....	$C_8H_{16}$		By catalytic hydrogenation of: Compound 2 (80%) Compound 3 (80%) Compounds 6 and 7	(35, 38, 71, 76, 115-119, 134, 159, 165) (54) (31, 33, 35, 37, 119)



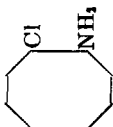
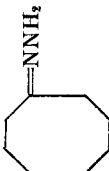
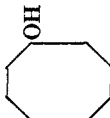
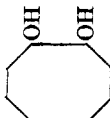
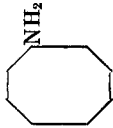
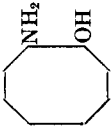
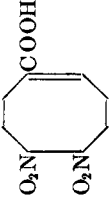
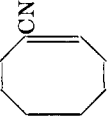
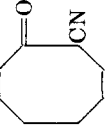
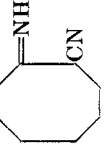
44.....	$C_8H_{16}ClN$		Compound 8 (19%) Compound 9 (59%) Compounds 11 and 12 (25-37%) Compound 15 Compound 31 By heating compound 45 with KOH and Pt·C	(37) (16, 24, 54) (37) (24, 160, 163, 172, 174) (22, 119, 123, 164) (152, 166)
45.....	$C_8H_{14}N_2$		From compound 37 and $H_2NNH_2$ See compound 43	(152, 166)
46.....	$C_8H_{16}O$		85-98% by reduction of compound 37 67% by hydrogenation of compound 5 By hydrolysis of compound 93 By treatment of aminomethylcycloheptane with $HNO_2$ See compounds 31, 37, 41, and 93	(58, 59, 82, 83, 100, 123, 132) (38, 71, 76, 115, 116, 117, 119) (38, 71, 76, 115, 116, 117, 119, 142) (156)
47.....	$C_8H_{16}O_2$		From compound 38 and dilute acids	(59, 174)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
48.....	$C_8H_{17}N$		By reduction of compound 42 See compound 66	(128)
49.....	$C_8H_{17}NO$		From compound 38 and $NH_3$ See compound 44	(64, 96)
50.....	$C_9H_{12}N_2O_6$		From caoutchouc and $HNO_3$ or $Pb(NO_3)_2$	(3)
51.....	$C_8H_{13}N$		From compound 37 and HCN See compound 70	(126)
52.....	$C_8H_{12}NO$		By hydrolysis of compound 53 See compound 37	(138, 168, 169, 171)
53.....	$C_9H_{14}N_2$		90% from azelanitrile and $LiNR_2$ See compounds 37 and 52	(167, 168, 170)

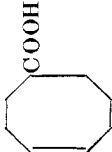
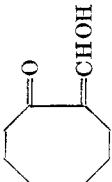
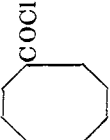
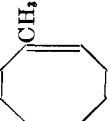
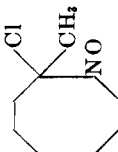
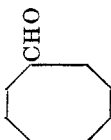
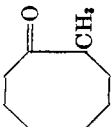
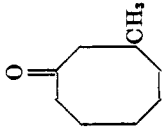
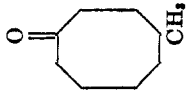
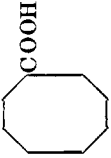
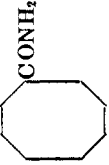
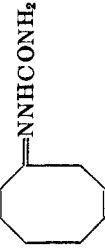
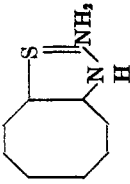
54.....	$C_8H_{14}O_2$		31% from compound 27 by carbonation of the Grignard reagent	(174)
55.....	$C_8H_{14}O_2$		81% from compound 37 and $HCOOC_2H_5$ in the presence of $NaOC_2H_5$ See compound 178	(108)
56.....	$C_8H_{15}ClO$		From compound 62 See compound 63	(60)
57.....	$C_8H_{16}$		From compound 37 and $CH_3MgI$ From compound 70 and $HONO$ See compound 58	(58) (126)
58.....	$C_8H_{16}ClNO$		From compound 57 and $NOCl$	(58)
59.....	$C_8H_{16}O$		By alkaline hydrolysis of compound 129	(123)
60.....	$C_8H_{16}O$		From compound 37 and $CH_3I$ in the presence of $Na$ and $NaNH_2$ See compounds 68, 91, and 92	(59)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
61.....	$C_9H_{16}O$	 or 	By treatment of 3-methylcycloheptanone with $CH_2N_2$	(98)
62.....	$C_9H_{16}O_2$		31% from compound 31 by the oxo process By carbonation of the Grignard reagent of compound 39 See compound 56	(38, 71, 117, 119) (60, 164)
63.....	$C_9H_{17}NO$		From compound 56 and $NH_3$	(60)
64.....	$C_9H_{17}N_3O$		From compound 37 and $H_2NNHCONH_2$ See compound 73	(58, 83, 93, 122, 125, 156, 171)
65.....	$C_9H_{17}N_3S$		From compound 30 and $H_2NCSNH_2$	(49)

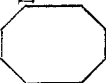

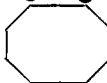
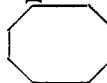
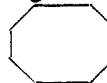

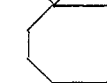

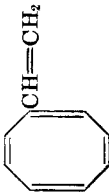
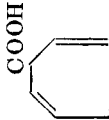
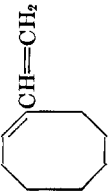
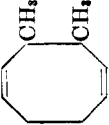
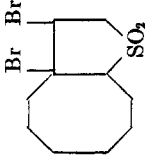
66.....	$C_8H_{15}N_2O$			From compound 48 and KCNO	(128)
67.....	$C_8H_{16}O$			From compound 2 or 31 by the oxo process From compound 70 and $HNO_2$	(38, 71, 76, 115, 116, 117, 142) (126)
68.....	$C_8H_{16}O$			By reduction of compound 60 with Na and $C_2H_5OH$ or catalytically	(60)
69.....	$C_8H_{15}N$			78% from compound 37 and $H_2NCH_3$ by reductive alkylation See compound 111	(174)
70.....	$C_8H_{15}N$			60% by reduction of compound 51 Along with compound 72 by reduction of the cyanohydrin of compound 37 See compounds 57 and 67	(126) (131)
71.....	$C_8H_{15}NO$			From compound 38 and $CH_3NH_2$	(64, 96)
72.....	$C_8H_{15}NO$			Along with compound 70 by reduction of the cyanohydrin of compound 37	(131)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
73. ....	$C_9H_{10}N_2O$		81% by catalytic hydrogenation of compound 64	(93)
74. ....	$C_{10}H_{10}$		Isolated from the $C_{10}H_{10}$ fraction from the preparation of compound 2 See compounds 88 and 98	(27, 40)
75. ....	$C_{10}H_{10}O_4$		Suggested structure for product from compound 4 and $CO_2$	(38, 71, 76, 115, 116, 117, 119, 142)
76. ....	$C_{10}H_{16}$		By hydrogenation of compound 80 over $Pd \cdot CaCO_3$ followed by dehydration See compounds 84, 162, 189, 219, and 249	(5)
77. ....	$C_{10}H_{16}$		74% by dimerization of $CH_3CH=CHCH=CHCOOH$ along with compound 180	(41)
78. ....	$C_{10}H_{14}Br_2O_3S$		From compound 84 and bromine	(5)

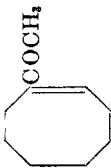
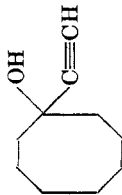
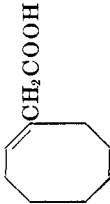
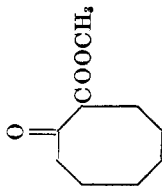
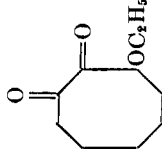
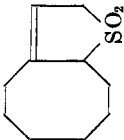
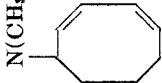

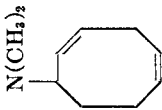

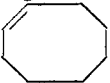


79. ....	$C_{10}H_{16}O$		From compound 31 and $CH_3COCl$ in the presence of $SnCl_4$ . See compound 90	(123)
80. ....	$C_{10}H_{16}O$		Along with a small amount of compound 207 from compound 37 and $KC\equiv CH$ . See compound 76	(5)
81. ....	$C_{10}H_{16}O_2$		87% by hydrolysis of compound 128. See compounds 87 and 94	(51, 123)
82. ....	$C_{10}H_{16}O_3$		75% by carbonation of the sodium salt of compound 37, followed by esterification. See compounds 170 and 177	(107)
83. ....	$C_{10}H_{16}O_3$		From compound 37 and $SeO_2$ in $C_2H_5OH$	(61)
84. ....	$C_{10}H_{16}O_2S$		From compound 76 and $SO_2$ . See compound 78	(5)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
85.....	$C_{10}H_{17}N$		77-85% by degradation of <i>N</i> -methylgranatene methiodide See compounds 23, 101, and 106	(33, 34, 35, 165)
86.....	$C_{10}H_{17}N$	 and 	61% from a mixture of compounds 11 and 12 and $HN(CH_3)_2$ See compounds 101 and 107	(24)
87.....	$C_{10}H_{17}NO$		From compound 81 and $NH_3$	(51)
88.....	$C_{10}H_{18}$		46-57% from compound 37 and $C_2H_5MgI$ Along with compound 98 on hydrogenation of compound 74 over $Pd \cdot CaCO_3$ See compound 98	(27, 40) (40)
89.....	$C_{10}H_{18}BrN$		Along with compounds 10 and 136 from compound 18 and $HN(CH_3)_2$ See compound 101	(25)
90.....	$C_{10}H_{18}O$		By hydrogenation of compound 79	(123)



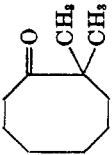
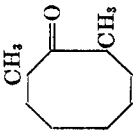
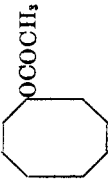
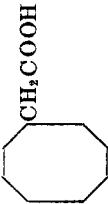
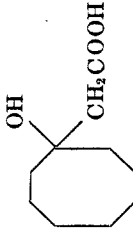
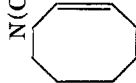

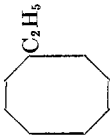
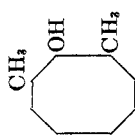
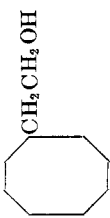
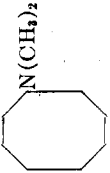
91. ....	$C_{10}H_{18}O$		Along with compound 92 from compound 60 and $CH_3I$ in the presence of Na and $NaNH_2$	(59)
92. ....	$C_{10}H_{18}O$		Along with compound 91 from compound 60 and $CH_3I$ in the presence of Na and $NaNH_2$ See compound 99	(59)
93. ....	$C_{10}H_{18}O_2$		31% by the addition of $CH_3COOH$ to compound 31 in the presence of acids By acetylation of compound 46 See compound 46	(38, 71, 76, 115, 116, 117, 119, 142) (82)
94. ....	$C_{10}H_{18}O_2$		By hydrogenation of compound 81 See compounds 134 and 208	(51, 123)
95. ....	$C_{10}H_{18}O_3$		79% by hydrolysis of compound 135	(51)
96. ....	$C_{10}H_{19}N$		78% from compound 26 and $HN(CH_3)_2$ See compounds 101 and 109	(25)

TABLE 1—Continued

COMPOUND No.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
97.....	$C_{10}H_{19}N$		By degradation of <i>N</i> -methylgranatnine methiodide 22% from compound 27 and HN(CH <sub>3</sub> ) <sub>2</sub> See compounds 101 and 110	(162) (174)
98.....	$C_{10}H_{20}$		64% on hydrogenation of compound 74 over platinum Along with compound 88 on hydrogenation of compound 74 over Pd·CaCO <sub>3</sub> 60–99% on hydrogenation of compound 88 over platinum	(27) (40) (27) (40)
99.....	$C_{10}H_{19}O$		By reduction of compound 92 with Na and C <sub>2</sub> H <sub>5</sub> OH	(60)
100.....	$C_{10}H_{19}O_2$		By reduction of compound 134 with Na and C <sub>2</sub> H <sub>5</sub> OH	(123)
101.....	$C_{10}H_{21}N$		85% on hydrogenation of compound 85 over platinum By hydrogenation of compounds 86, 89, 96, and 97 over platinum See compound 111	(24, 33, 35) (24, 25, 164)


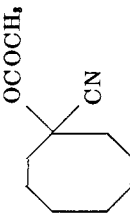
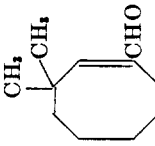
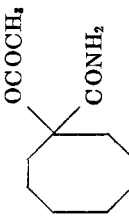
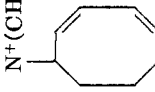

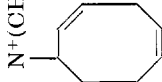
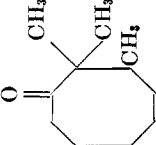

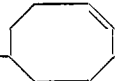
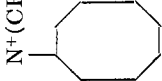
102. ....	$C_{11}H_{12}NO_2$		11% from compound 37 and $NaC(CHO)_2NO_2$	(109, 110)
103. ....	$C_{11}H_{17}NO_2$		By the addition of HCN to compound 37 in $(CH_3CO)_2O$ and $CH_3COCl$ See compound 105	(131)
104. ....	$C_{10}H_{18}O$		Source unknown	(145a)
105. ....	$C_{11}H_{19}NO_2$		By partial hydrolysis of compound 103	(131)
106. ....	$C_{11}H_{20}IN$		95-97% from compound 85 and $CH_3I$ See compound 6	(34, 35)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
107.....	$C_{11}H_{20}IN$	 $N^+(CH_3)_3 I^-$ and  $N^+(CH_3)_3 I^-$	91% from compound 86 and $CH_3I$ See compounds 6 and 7	(24)
108.....	$C_{11}H_{20}O$		By distillation of the thorium salt of alkylazelaic acid	(144, 145)
109.....	$C_{11}H_{22}IN$	$N^+(CH_3)_3 I^-$ 	94.5% from compound 96 and $CH_3I$ See compound 13	(25)
110.....	$C_{11}H_{22}IN$	$N^+(CH_3)_3 I^-$ 	From compound 97 and $CH_3I$ See compound 15	(162)
111.....	$C_{11}H_{24}IN$	$N^+(CH_3)_3 I^-$ 	100% from compound 69 and $CH_3I$ From compound 101 and $CH_3I$ See compound 31	(174) (24, 25, 33, 35, 164)

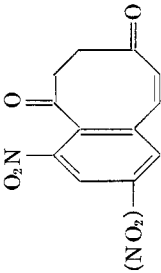
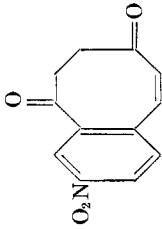
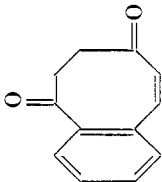
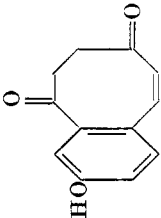
112.....	$C_{12}H_9NO_4$	 <p>(Structure probably incorrect; see page 105)</p>	By treatment of $\delta$ -( <i>m</i> -nitrobenzylidene)-levulinic acid with $(CH_3CO)_2O$	(140)
113.....	$C_{12}H_9NO_4$	 <p>(Structure probably incorrect; see page 105)</p>	By treatment of $\delta$ -( <i>p</i> -nitrobenzylidene)-levulinic acid with $(CH_3CO)_2O$	(140)
114.....	$C_{12}H_{10}O_2$	 <p>(Structure probably incorrect; see page 105)</p>	40% yield by treatment of $\delta$ -benzylidene-levulinic acid with $(CH_3CO)_2O$ See compound 246	(140)
115.....	$C_{12}H_{10}O_3$	 <p>(Structure probably incorrect; see page 105)</p>	By treatment of $\delta$ -( <i>p</i> -hydroxybenzylidene)levulinic acid with $(CH_3CO)_2O$	(140)

TABLE 1—Continued

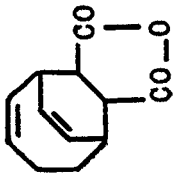
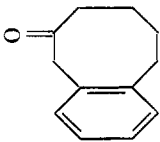



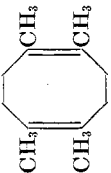
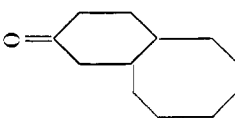
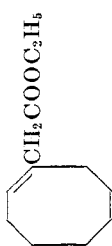
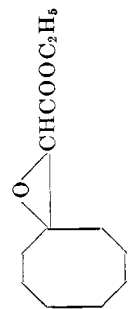
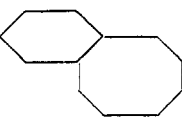
COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
116. ....	$C_{12}H_{12}O_3$		Possible structure of the maleic anhydride adduct of compound 6 (64%)	(33, 174)
117. ....	$C_{12}H_{14}O$		6-7% from $\alpha$ -tetralone and $CH_2N_2$	(150)
118. ....	$C_{12}H_{14}O$		85% by hydrolysis and decarboxylation of compound 140 or 141 74% by oxidation of compound 121 See compound 121	(56) (52)
119. ....	$C_{12}H_{12}Br$		From compound 121 and $PBr_3$ See compound 148	(56)
120. ....	$C_{12}H_{16}$		Along with compound 15 by dimerization of $CH_2=CHCH=CHCOOH$	(41)



TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
126.....	C <sub>12</sub> H <sub>20</sub>		5.2% by dimerization of $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CH}_2$	(174)
127.....	C <sub>12</sub> H <sub>20</sub> O		By oxidation of compound 133	(108)
128.....	C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>		41% by dehydration of compound 135 See compound 81	(51)
129.....	C <sub>12</sub> H <sub>20</sub> O <sub>3</sub>		25% from compound 37 and ClCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub> See compound 59	(123)
130.....	C <sub>12</sub> H <sub>22</sub>		97% by hydrogenation of compound 122 over platinum, along with a small amount of compound 133 See compound 133	(108)



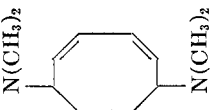
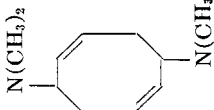
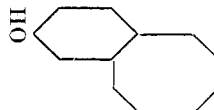
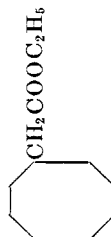
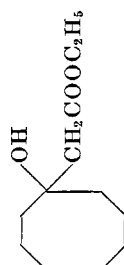
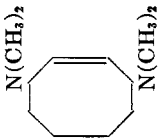
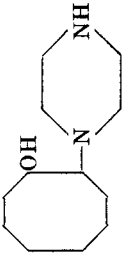
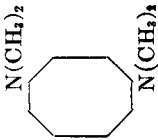
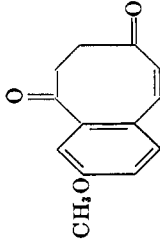
131 .....	$C_{12}H_{22}N_2$		31-47% from compound 8 and $HN(CH_3)_2$ See compounds 138, 172, and 173	(24, 34, 35, 37, 165)
132 .....	$C_{12}H_{22}N_2$		23% from compound 20 and $HN(CH_3)_2$ See compound 174	(174)
133 .....	$C_{12}H_{22}O$		Small amount along with compound 130 by hydrogenation of compound 122 over platinum 77% from compound 122 by hydrogenation over nickel See compound 127	(108) (108)
134 .....	$C_{12}H_{22}O_2$		By esterification of compound 94 See compound 100	(123)
135 .....	$C_{12}H_{22}O_3$		31% from compound 37 by the Reformatsky reaction See compounds 95 and 128	(51)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
136.....	$C_{12}H_{24}N_2$		Along with compounds 10 and 89 from compound 18 and $HN(CH_3)_2$ See compound 138	(25)
137.....	$C_{12}H_{24}N_2O$		Along with compound 226 from compound 40 and piperazine	(95)
138.....	$C_{12}H_{24}N_2$		By hydrogenation of compound 136 100% by hydrogenation of compound 131 See compound 175	(25) (24, 35, 165)
139.....	$C_{13}H_{12}O_2$	 <p>(Structure probably incorrect; see page 105)</p>	By treatment of $\delta$ -( <i>p</i> -methoxybenzylidene)levulinic acid with $(CH_3CO)_2O$	(140)

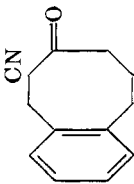
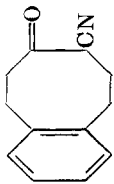
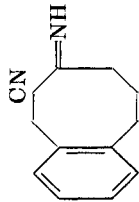

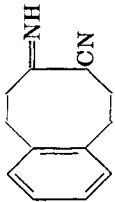
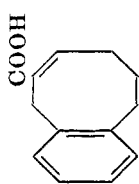
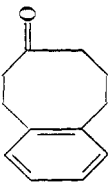
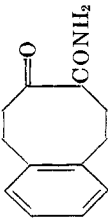
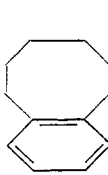
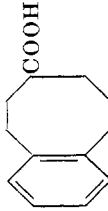
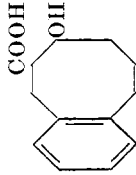
140.....	$C_{13}H_{13}NO$		By partial hydrolysis of compound 142 See compound 118	(56)
141.....	$C_{13}H_{13}NO$		By partial hydrolysis of compound 143 See compound 118	(56)
142.....	$C_{13}H_{14}N_2$		Along with compound 143 from  and $NaN(CH_3)C_6H_5$	(56)
143.....	$C_{13}H_{14}N_2$		See compounds 140 and 145 Along with compound 142 ( <i>q.v.</i> ) See compounds 141 and 146	(56)
144.....	$C_{13}H_{14}O_2$		By dehydration of compound 149 See compound 147	(56)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
145 . . . . .	$C_{13}H_{16}NO_2$		By partial hydrolysis of compound 142 See compound 151	(56)
146 . . . . .	$C_{13}H_{16}NO_2$		By partial hydrolysis of compound 143 See compound 152	(56)
147 . . . . .	$C_{13}H_{16}O_2$		56% by hydrogenation of compound 144 over platinum	(56)
148 . . . . .	$C_{13}H_{16}O_2$		30% by carbonation of the Grignard reagent of compound 119	(56)
149 . . . . .	$C_{13}H_{16}O_3$		By hydrolysis of compound 151 See compound 144	(56)

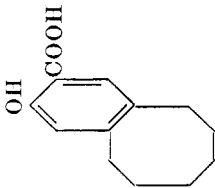
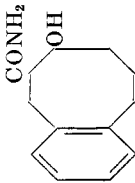
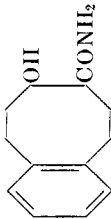
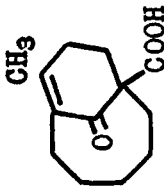
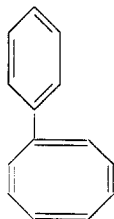
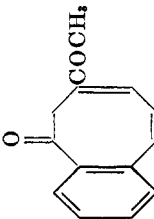
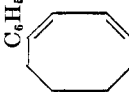
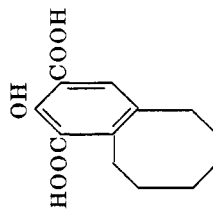
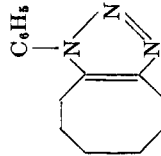
150. ....	$C_{13}H_{16}O_3$		By partial decarboxylation of compound 157 See compound 122	(108)
151. ....	$C_{13}H_{17}NO_2$		By hydrogenation of compound 145 over platinum See compound 149	(56)
152. ....	$C_{13}H_{17}NO_2$		By hydrogenation of compound 146 over platinum	(56)
153. ....	$C_{13}H_{18}O_3$		12% along with 80% of compound 169 from compound 170 and concentrated $H_2SO_4$	(105)
154. ....	$C_{14}H_{12}$		14-19% along with compounds 6 and 7 from compound 2 and $C_6H_5Li$ See compound 167	(32)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
155.....	$C_{14}H_{12}O_2$	 <p>(Structure probably incorrect; see page 105)</p>	From $\beta$ -cinnamyllevulinic acid and $(CH_3CO)_2O$	(140)
156.....	$C_{14}H_{16}$		56% from degradation of compound 200 See compound 167	(30)
157.....	$C_{14}H_{16}O_5$		59% from compound 37 and diethyl acetonedicarboxylate, followed by hydrolysis See compound 150	(108)
158.....	$C_{14}H_{17}N_3$		From compound 164 and $C_6H_5N_3$	(2)

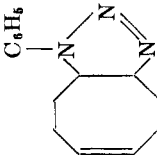
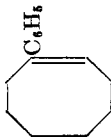
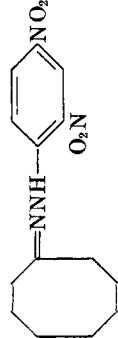
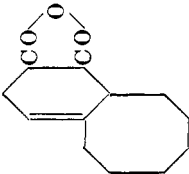
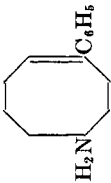
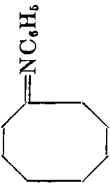
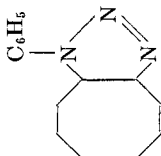
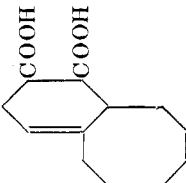
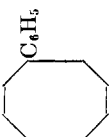
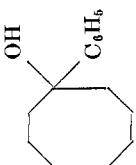
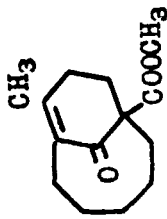
159. ....	$C_{14}H_{17}N_3$		From compound 15 and $C_6H_5N_3$	(173, 174)
160. ....	$C_{14}H_{18}$		Along with compound 168 from compound 37 and $C_6H_5MgBr$ See compound 236	(53)
161. ....	$C_{14}H_{18}N_4O_4$		From compound 37 and 2, 4-dinitrophenylhydrazine	(15)
162. ....	$C_{14}H_{18}O_2$		From compound 76 and maleic anhydride See compound 166	(5)
163. ....	$C_{14}H_{19}N$		47-54% from the oxime of 2-phenylbicyclo[3.3.1]non-2-en-9-one by Beckmann rearrangement and hydrolysis See compounds 192 and 227	(30)
164. ....	$C_{14}H_{19}N$		From compound 37 and aniline See compound 158	(2)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
165.....	$C_{14}H_{19}N_3$		65% from <i>trans</i> form of compound 31 and $C_6H_5N_3$	(2, 173, 174)
166.....	$C_{14}H_{19}O_4$		By hydrolysis of compound 162	(5)
167.....	$C_{14}H_{20}$		78% by hydrogenation of compound 156 over palladium From compound 154 by hydrogenation over palladium	(30) (32)
168.....	$C_{14}H_{20}O$		Along with compound 160 from compound 37 and $C_6H_5MgBr$	(53)
169.....	$C_{14}H_{20}O_3$		80% along with 20% of compound 153 from compound 170 and concentrated $H_2SO_4$	(105)



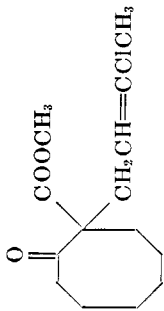
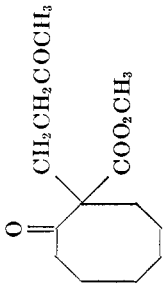
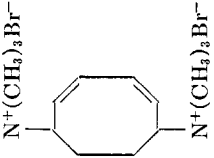
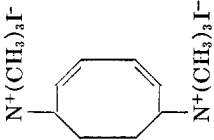
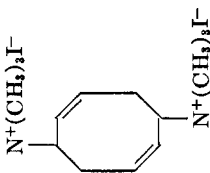
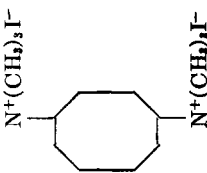
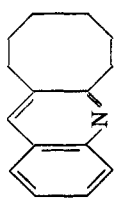
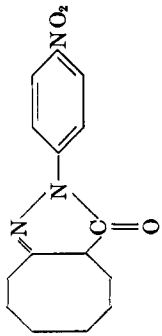
170.....	$C_{14}H_{21}ClO_3$		81.5% from compound 82 and $CH_3CCl=CHCH_2Cl$ See compounds 153 and 169	(105)
171.....	$C_{14}H_{22}O_4$		78% from compound 82 and $CH_3COCH_2CH_2N^+(CH_3)_3$ See compounds 124 and 125	(107)
172.....	$C_{14}H_{23}Br_2N_2$		From compound 131 and $CH_3Br$	(165)
173.....	$C_{14}H_{23}I_2N_2$		87-97.5% from compound 131 and $CH_3I$ See compound 2	(24, 34, 35, 37, 159, 165)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
174. ....	$C_{14}H_{23}I_2N_2$		From compound 132 and $CH_3I$ See compound 2	(174)
175. ....	$C_{14}H_{22}I_2N_2$		96% from compound 138 and $CH_3I$	(24, 35)
176. ....	$C_{13}H_{17}N$		From compound 37 and <i>o</i> -aminobenzaldehyde	(127)
177. ....	$C_{14}H_{17}N_3O_3$		From compound 82 and <i>p</i> -nitrophenylhydrazine	(107)

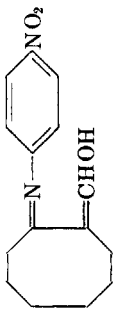
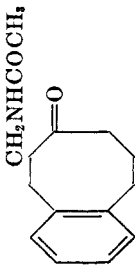
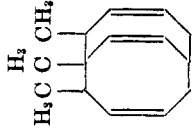
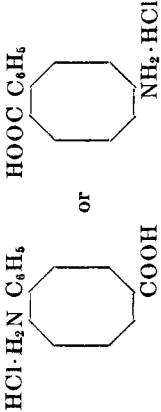
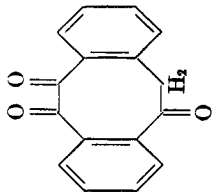
178.....	$C_{16}H_{18}N_2O_2$		From compound 55 and <i>p</i> -nitroaniline (108)
179.....	$C_{16}H_{16}NO_2$		By hydrogenation of compound 140 over platinum in $(CH_3CO)_2O$ (56)
180.....	$C_{16}H_{22}$		Along with compound 77 by dimerization of $CH_3CH=CHCH=CHCOOH$ (41)
181.....	$C_{16}H_{22}ClNO_2$		79% by hydrolysis of the lactam formed by Beckmann rearrangement of the oxime of 2-phenylbicyclo[3.3.1]nonan-9-one (30)
181a.....	$C_{16}H_{16}O_2$		19% from compound 203, $Br_2$ , and concentrated $NH_4OH$ (157)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
182.....	$C_{16}H_{12}$		70% by pyrolysis of compound 221 19% by decarboxylation of compound 202 See compound 185	(28) (52)
183.....	$C_{16}H_{12}O_2$		36% by ozonolysis and reduction of the ozonide of compound 335 60% from compound 335a and $Pb(OCOCH_3)_4$ See compounds 188, 198, 199, 204, 206, 213, 243, 251, and 335a	(157) (157)
184.....	$C_{16}H_{14}Br_2$		97% from compound 185 and <i>N</i> -bromo- succinimide See compound 221	(28)
185.....	$C_{16}H_{16}$		6-30% from $\omega, \omega'$ -dibromo- <i>o</i> -xylene and sodium 65% by hydrogenation of compound 182 over platinum See compound 184	(7, 28) (52)
186.....	$C_{16}H_{16}O_2$		By hydrolysis of compound 221	(28)

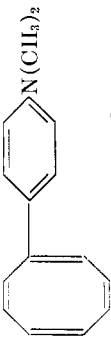
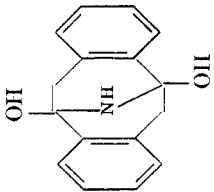
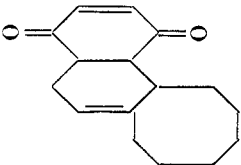
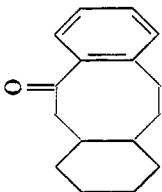
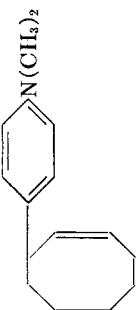
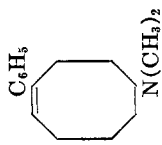
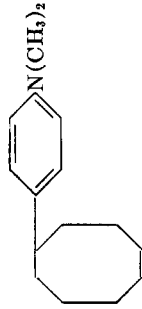
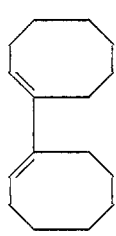
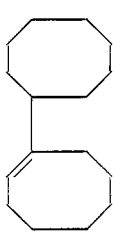
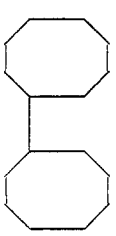
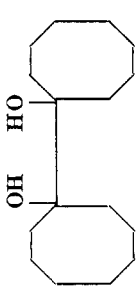
187. ....	$C_{16}H_{17}N$		13-25% along with compounds 6 and 7 from compound 2 and <i>p</i> -dimethylaminophenyllithium See compound 193	(32)
188. ....	$C_{16}H_{17}NO_2$		47% from compound 183 and $NH_3$	(157)
189. ....	$C_{16}H_{19}O_2$		From compound 76 and naphthoquinone	(5)
190. ....	$C_{16}H_{20}O$		Small yield from 2-( $\beta$ -phenethyl)cyclohexylacetyl chloride and $AlCl_3$	(23)
191. ....	$C_{16}H_{23}N$		34% from compound 26 and <i>p</i> -dimethylaminophenyllithium See compound 193	(32)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
192.....	$C_{16}H_{23}N$		77% from compound 163 and HCHO and HCOOH See compound 200	(30)
193.....	$C_{16}H_{25}N$		By hydrogenation of compounds 187 and 191 over palladium	(32)
194.....	$C_{16}H_{26}$		By dehydration of compound 197 See compound 196	(123)
195.....	$C_{16}H_{28}$		70% from compound 31 and dilute acids See compound 196	(38, 71, 76, 115, 116, 117, 119, 142)
196.....	$C_{16}H_{30}$		By hydrogenation of compound 194 over platinum By hydrogenation of compound 195 over palladium	(123)
197.....	$C_{16}H_{30}O_2$		As a by-product in the reduction of compound 37 to compound 46 with Na in NaHCO <sub>3</sub> solution See compound 194	(38, 71, 76, 115, 116, 117, 119, 142) (123)

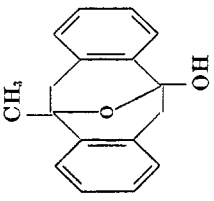
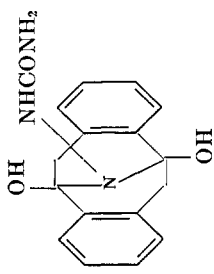
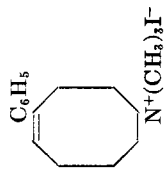
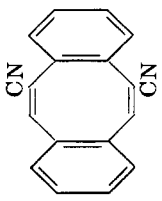
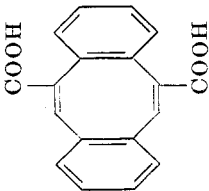
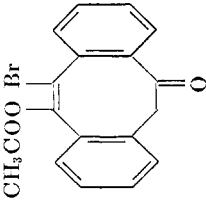
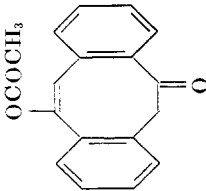
198 .....	$C_{17}H_{17}O_2$		From compound 183 and $CH_3MgI$	(157)
199 .....	$C_{17}H_{14}N_4O_2$		From compound 183 and semicarbazide	(157)
200 .....	$C_{17}H_{26}IN$		100% from compound 192 and $CH_3I$ See compound 156	(30)
201 .....	$C_{18}H_{16}N_2$		47% from <i>o</i> -phthalaldehyde and <i>o</i> -phenylenediacetonitrile See compound 232	(52)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
202.....	$C_{18}H_{12}O_4$		92% by hydrolysis of compound 232 See compounds 182 and 335	(52)
203.....	$C_{18}H_{13}BrO_2$		68% from compound 204 and bromine See compound 181a	(157)
204.....	$C_{18}H_{14}O_3$		61% from compound 183 and $(CH_3CO)_2O$ See compound 203	(157)



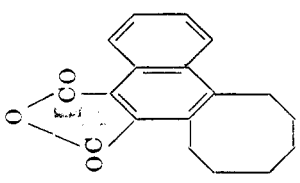
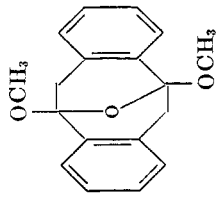
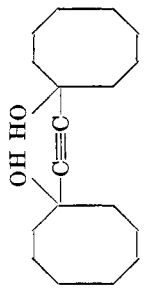
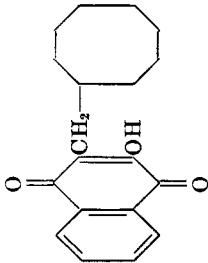
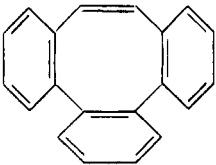
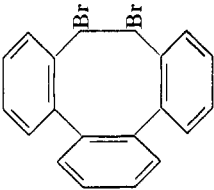
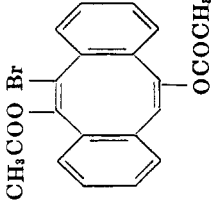
205..... $C_{18}H_{16}O_3$		By heating compound 235 and sulfur (148)
206..... $C_{18}H_{20}O_3$		84% from compound 183, $(CH_3)_2SO_4$ , and $NaOH$ (157)
207..... $C_{18}H_{30}O_2$		Small amount along with compound 80 from compound 37 and $KC\equiv CH$ (5)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
208.....	$C_{19}H_{22}O_2$		53% by peroxide alkylation of 2-hydroxy-1,4-naphthoquinone with compound 94	(51)
209.....	$C_{20}H_{14}$		32% by decarboxylation of compound 231 See compounds 210 and 212	(141)
210.....	$C_{20}H_{14}Br_2$		61% from compound 209 and bromine	(141)
211.....	$C_{20}H_{14}BrO_4$		From compound 213 and bromine	(157)

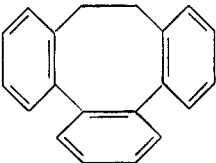
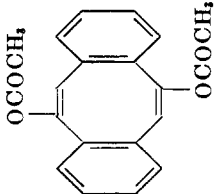
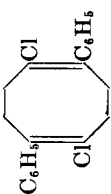
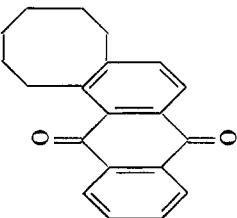
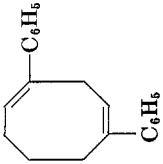
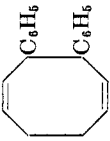
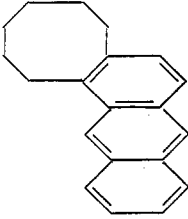
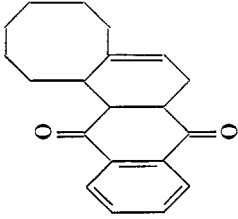
212.....	$C_{20}H_{16}$			By hydrogenation of compound 209 over platinum	(141)
213.....	$C_{20}H_{16}O_4$			34% by acetylation of compound 183 See compound 211	(157)
214.....	$C_{20}H_{18}Cl_2$			24% from compound 220 and $PCl_5$	(158)
215.....	$C_{20}H_{18}O_2$			By heating compound 219 with oxygen and $NaOC_2H_5$ See compound 218	(5)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
216. ....	$C_{20}H_{20}$		78% by exhaustive methylation of compound 237 See compound 225	(26)
217. ....	$C_{20}H_{20}$		66% by dimerization of $C_6H_5CH=CHCOOH$	(41)
218. ....	$C_{20}H_{20}$		69% by reduction of compound 215 with Zn and KOH	(5)
219. ....	$C_{20}H_{20}O_2$		From compound 76 and naphthoquinone See compound 215	(5)

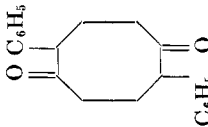
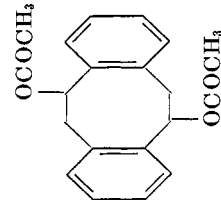
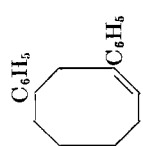
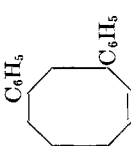
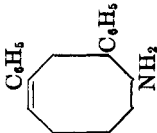
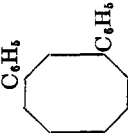

220.....	$C_{20}H_{20}O_2$		62% from 1,4-diphenyl-1,2,3,4,5,6-hexahydrotetralene by ozonolysis and hydrogenation of the ozonide 16% with cleavage of compound 353 with $Pb(OCOCH_3)_4$ See compounds 214, 234, and 353	(158)
221.....	$C_{20}H_{20}O_4$		78% from compound 184 and $AgOCOCH_3$ See compounds 182 and 186	(28)
222.....	$C_{20}H_{22}$		92% by degradation of compound 240 See compound 225	(26)
223.....	$C_{20}H_{22}$		By pyrolysis of compound 240 See compound 225	(26)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
224. ....	$C_{10}H_{21}N$		80% from the oxime of 2,4-diphenylbicyclo[3.3.1]non-2-en-9-one by Beckmann rearrangement and hydrolysis See compound 237	(26)
225. ....	$C_{10}H_{14}$		90-96% by hydrogenation of compounds 216, 222, or 223 over palladium From compound 222 and HI	(26) (26)
226. ....	$C_{20}H_{24}N_2O_2$		Along with compound 137 from compound 40 and piperazine	(95)

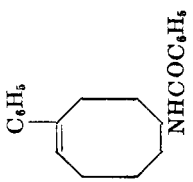
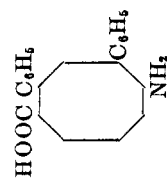
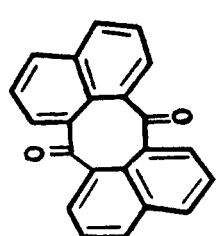
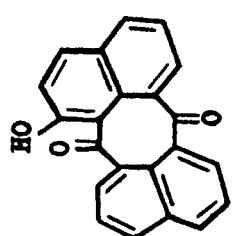
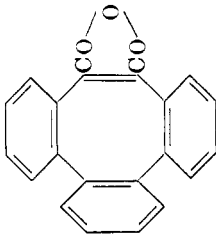
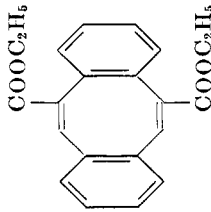
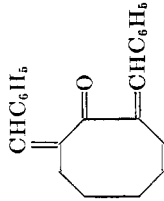
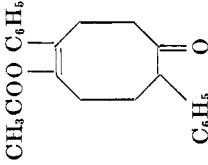
227.....	$C_{21}H_{21}NO$	 <p>Chemical structure of 1-(cyclooct-1-en-1-yl)pyrrolidine: A cyclooctene ring with a pyrrolidine ring attached at the 1-position.</p>	38% from compound 163 and $C_6H_5COCl$	(30)
228.....	$C_{21}H_{23}NO_2$	 <p>Chemical structure of 1-(cyclooct-1-en-1-yl)pyrrolidine-2-carboxylic acid: A cyclooctene ring with a pyrrolidine ring attached at the 1-position, and a carboxylic acid group at the 2-position.</p>	By hydrolysis of the lactam formed by the Beckmann rearrangement of 2,4-diphenylbicyclo[3.3.1]nonan-9-one	(26)
229.....	$C_{22}H_{12}O_2$	 <p>Chemical structure of 1,4-diphenyl-1,4-dihydro-2H-benzo[1,2-b:4,5-b']dipyrrolo[3,2-a:3',2'-d]phthalazine-2,5-dione: A complex polycyclic aromatic system with two phenyl groups and two carbonyl groups.</p>	10% by cyclodehydration of 8-(1'-naphthoyl)-1-naphthoic acid	(81)
230.....	$C_{22}H_{12}O_2$	 <p>Chemical structure of 1,4-diphenyl-1,4-dihydro-2H-benzo[1,2-b:4,5-b']dipyrrolo[3,2-a:3',2'-d]phthalazine-2,5-dione: A complex polycyclic aromatic system with two phenyl groups and two carbonyl groups.</p>	5% from $\beta$ -naphthol, naphthoic anhydride, and $AlCl_3$	(81)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
231 .....	$C_{22}H_{12}O_3$		24% by oxidation of compound 244 with $Cr_2O_3$ See compound 209	(141)
232 .....	$C_{22}H_{20}O_4$		73% by alcoholysis of compound 201 See compound 202	(52)
233 .....	$C_{22}H_{22}O$		From compound 37 and $C_6H_5CHO$	(39, 59)
234 ....	$C_{22}H_{22}O_3$		28% by acetylation of compound 220	(158)



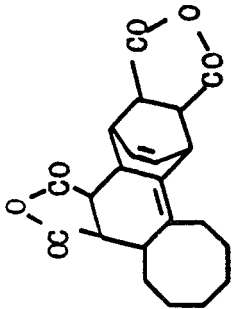
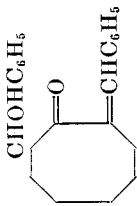
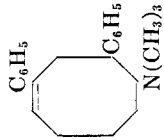
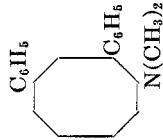
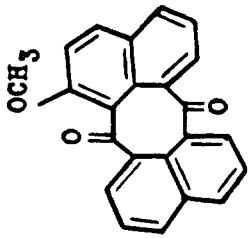
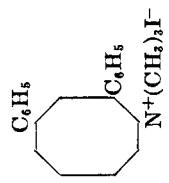
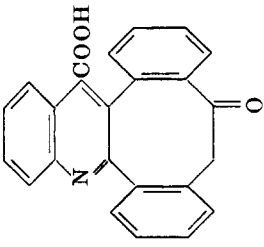
235.....	$C_{22}H_{22}O_6$		From compound 160 and maleic anhydride See compound 205	(148)
236.....	$C_{22}H_{24}O_2$		From compound 37 and $C_6H_5CHO$	(39)
237.....	$C_{22}H_{27}N$		78% from compound 224, $HCHO$ , and $HCOOH$ See compounds 216 and 238	(26)
238.....	$C_{22}H_{29}N$		99% by hydrogenation of compound 237 over palladium See compound 240	(26)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
239 .....	$C_{24}H_{14}O_3$		20% by cyclodehydration of 2-methoxynaphthalenenaphthaloylic acid	(81)
240 .....	$C_{24}H_{22}IN$		100% from compound 238 and $CH_3I$ See compounds 222 and 223	(26)
241 .....	$C_{24}H_{12}N_2O_3$	Tetranitrotetraphenylene	By nitration of compound 244	(113)
242 .....	$C_{24}H_{12}Br$	Monobromotetraphenylene	By bromination of compound 244	(113)
243 .....	$C_{24}H_{16}NO_2$		31% from compound 183 and isatin	(157)

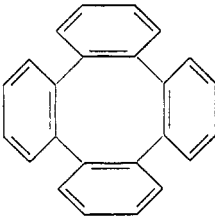
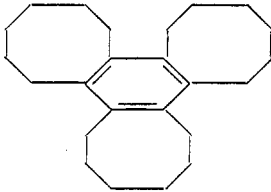
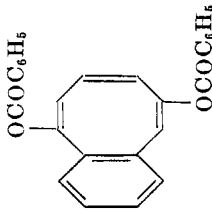
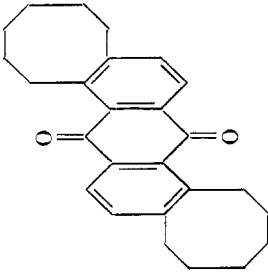
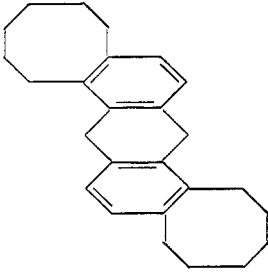
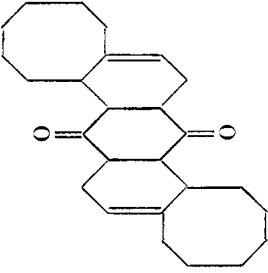
244.....	$C_{24}H_{16}$		16% from 1,1'-dibromobiphenyl and magnesium See compounds 231, 241, and 242	(113)
245.....	$C_{24}H_{16}$		Along with compounds 13 and 16 from compound 21 and sodium	(43)
246.....	$C_{26}H_{18}O_4$		From compound 114 and $C_6H_5COCl$	(140)

TABLE 1—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
247 . . . . .	$C_{26}H_{38}O_2$		By heating compound 249 with oxygen and $NaOC_2H_5$ See compound 248	(5)
248 . . . . .	$C_{26}H_{32}$		By reducing compound 247 with amalgamated Zn and HCl	(5)
249 . . . . .	$C_{26}H_{36}O_2$		From compound 76 and quinone See compound 247	(5)

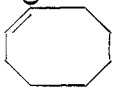

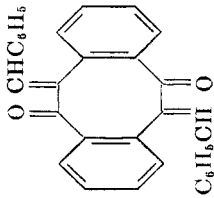
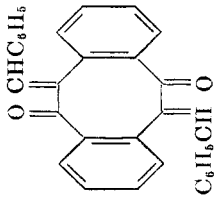
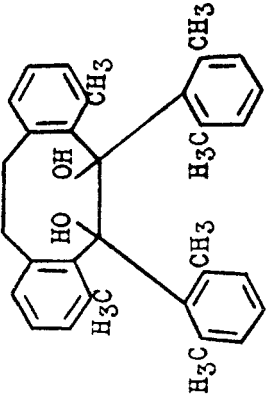
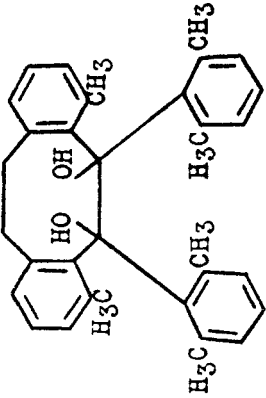
250. ....	$C_{26}H_{50}$			70% from compound 37 and $C_{18}H_{37}MgBr$	(53)
251. ....	$C_{30}H_{20}O_2$			21% from compound 183 and $C_6H_5CHO$	(157)
252. ....	$C_{34}H_{38}O_2$			From bis(2,6-dimethylphenyl) ketone and 2,6-dimethylphenyllithium	(50)

TABLE 1—*Concluded*

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	PREPARATION AND REACTION PRODUCTS	REFERENCES
253. ....	$C_{38}H_{16}O_2$		From mesityl ketone and mesityllithium	(50)
254. ....	$C_{48}H_{22}Br_2$		Along with compound 255 from compound 256 and bromine	(47)
255. ....	$C_{48}H_{27}Br_2$		Along with compound 254 from compound 256 and bromine	(47)

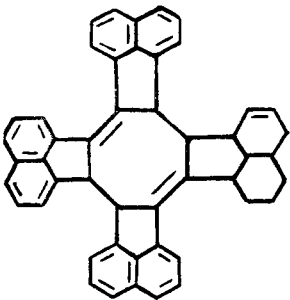
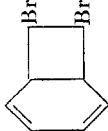
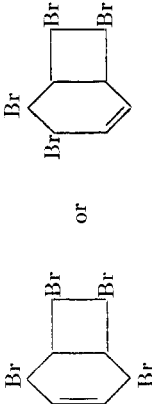
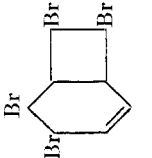
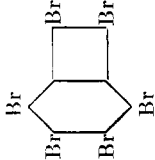
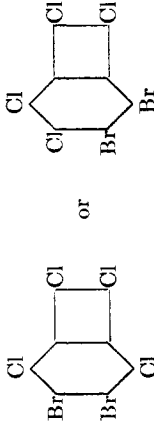
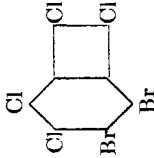
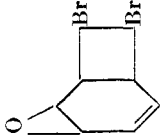
256. ....	$C_{48}H_{28}$		4-5% by pyrolysis of acenaphthene 25-37.5% by pyrolysis of acenaphthene in the presence of $PbO$ or $PbO_2$ See compounds 254, 255, 257, 258, and 259	(45) (44, 46, 47)
257. ....	$C_{48}H_{32}$	Tetrahydrofluorocyclene	Reduction of compound 256 with Na and $C_2H_5OH$	(44)
258. ....	$C_{48}H_{36}$	Octahydrofluorocyclene	Reduction of compound 256 with Na and $C_2H_5OH$	(44)
259. ....	$C_{48}H_{40}$	Dodecahydrofluorocyclene	Reduction of compound 256 with Na and $C_2H_5OH$	(44)

TABLE 2  
*Polycyclic compounds prepared from eight-membered carbocycles*

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
260.....	$C_8H_3Br_2$		100% from compound 2 and bromine; see compounds 264, 273, 290, 311, 320, and 343	(38, 55, 71, 76, 115, 116, 117, 119, 142, 159)
261.....	$C_8H_3Br_4$	 or 	27-56% from compound 2 and bromine	(38, 71, 76, 115, 116, 117, 119, 142, 159)
262.....	$C_8H_3Br_6$		55% from compound 2 and bromine	(38, 71, 76, 115, 116, 117, 119, 142)
263.....	$C_8H_3Br_2Cl_4$	 or 	95% from compound 266 and bromine	(38, 71, 116, 117, 119)
264.....	$C_8H_3Br_2O$		From compound 260 and $C_6H_5CO_2H$	(38, 71, 116, 117)



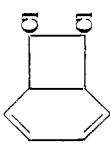
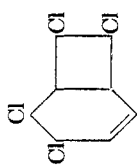
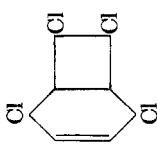
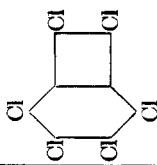
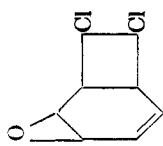
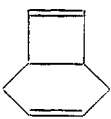
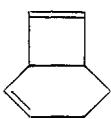
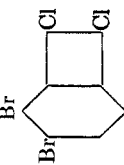
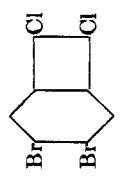
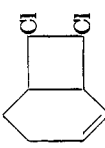
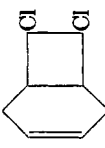
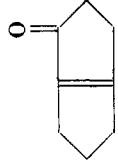

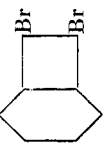
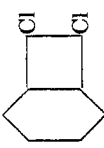
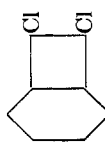


265. ....	$C_8H_8Cl_2$		 or 	63–69% from compound 2 and $Cl_2$ or $SO_2Cl_2$ See compounds 268, 271, 274, 280, 283, 293, 308, 317, 321, and 348	(38, 71, 76, 115, 116, 117, 119, 142)
266. ....	$C_8H_8Cl_4$			99% from compound 2 and $Cl_2$ ; see compounds 263 and 274	(38, 71, 76, 115, 116, 117, 119, 142)
267. ....	$C_8H_8Cl_6$			19% from compound 2 and $Cl_2$	(38, 71, 76, 115, 116, 117, 119, 142)
268. ....	$C_8H_8Cl_2O$			From compound 265 and $C_6H_5CO_2H$ ; see compounds 275 and 281	(38, 71, 116, 117, 119)
269. ....	$C_8H_{10}$	 or 		Suggested product from compound 2, Na, and $C_6H_5NHCH_3$ in the cold; see compound 277	(174)
270. ....	$C_8H_8Br_2Cl_2$	 or 		29% from compound 271 and $Br_2$	(38, 71, 115, 116, 117, 119)

TABLE 2—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
271.....	$C_8H_{10}Cl_2$	 or 	By hydrogenation of compound 265 over Pd·CaCO <sub>3</sub> ; see compounds 270 and 274	(38, 71, 115, 116, 117, 119)
272.....	$C_8H_{10}O$	 or 	70–77% from compound 9 and H <sub>2</sub> SO <sub>4</sub> See compound 276	(36)
273.....	$C_8H_{12}Br_2$		65% by hydrogenation of compound 260 over Pd·CaCO <sub>2</sub>	(38, 71, 116, 117, 119)
274.....	$C_8H_{12}Cl_2$		84–88% by hydrogenation of compound 265 over Pd·CaCO <sub>3</sub> or nickel By hydrogenation of compound 271 over Pd·CaCO <sub>3</sub> 99% by hydrogenation of compound 266 over Pd·CaCO <sub>3</sub> ; see compound 277	(38, 71, 76, 115, 116, 117, 119, 142) (119)
275.....	$C_8H_{12}Cl_2O$	 or 	76% by hydrogenation of compound 268 over palladium	(38, 71, 116, 117, 119)
276.....	$C_8H_{12}O$		93% by hydrogenation of compound 272 over palladium; see compound 278	(36)

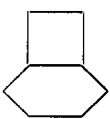
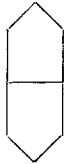
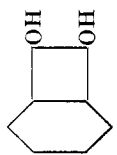
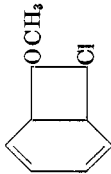
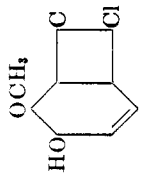

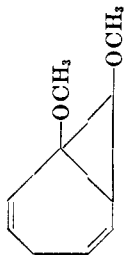
277.....	$C_8H_{14}$		By hydrogenation of compound 269; 27% by hydrogenation of compound 274 with KOH over nickel	(174) (38, 71, 76, 115, 116, 117, 119, 142)
278.....	$C_8H_{14}$		93% from compound 276 by Wolff- Kishner reduction	(36)
279.....	$C_8H_{14}O_2$		93% by hydrolysis of compound 312	(38, 71, 76, 115, 116, 117, 119, 142)
280.....	$C_8H_{11}ClO$		From compound 265 and $NaOCH_3$	(38, 71, 116, 117)
281.....	$C_9H_{12}Cl_2O_2$		From compound 268 and $CH_3OH$	(38, 71, 116, 117, 119)
282.....	$C_{10}H_{14}$		43% by heating compound 286 with $H_3PO_4$ See compound 284	(38, 71, 76, 115, 116, 117, 119, 142)
283.....	$C_{10}H_{14}O_2$		96% from compound 265 and $NaOCH_3$	(38, 71, 76, 115, 116, 117, 119, 142)

TABLE 2—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
284.....	$C_{10}H_{16}$		79% by hydrogenation of compound 282 over Pd·C	(38, 71, 76, 115, 116, 117, 119, 142)
285.....	$C_{10}H_{16}O$		50% from compound 286 and $HNO_2$	(38, 71, 116, 117, 119)
286.....	$C_{10}N_{17}N$		75% from compound 288 and $HN_3$ See compounds 282, 285, and 344	(38, 71, 76, 115, 116, 117, 119, 142)
287.....	$C_{11}H_{12}O_2$		25% from compound 2 and acrylic acid See compounds 288 and 305	(38, 71, 76, 115, 116, 117, 119, 142)
288.....	$C_{11}H_{16}O_2$		91% by hydrogenation of compound 287 over Pd·C See compound 286	(38, 71, 76, 115, 116, 117, 119, 142)
289.....	$C_{12}H_8O_3$		By heating compound 295 with $(CH_3CO)_2O$	(38, 71, 116, 117, 119)





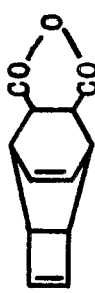



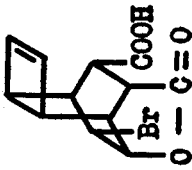
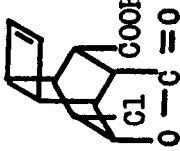
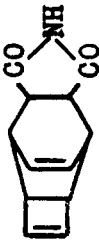

290.....	$C_{12}H_{10}Br_2O_3$		93% from compound 260 and maleic anhydride	(38, 71, 116, 117, 119)
291.....	$C_{12}H_{10}Br_2O_3$		28% from compound 323 by hydrolysis	(38, 71, 116, 117, 119)
292.....	$C_{12}H_{10}Br_2O_4$		By hydrolysis of compound 320	(38, 71, 116, 117, 119)
293.....	$C_{12}H_{10}Cl_2O_3$		80% from compound 265 and maleic anhydride See compound 324	(38, 71, 116, 117, 119)
294.....	$C_{12}H_{10}O_3$		88-97% from compound 2 and maleic anhydride See compounds 298, 299, 300, 303, 306, 307, 310, 327, 340, 354, 355, and 361	(35, 38, 71, 76, 115, 116, 117, 118, 119, 142)
295.....	$C_{12}H_{10}O_4$		By hydrolysis of compound 338 See compound 289	(38, 71, 116, 117, 142)
296.....	$C_{12}H_{10}O_4$		24-53% from compound 5 and maleic anhydride See compounds 297 and 304	(38, 55, 71, 116, 117, 119)

TABLE 2—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
297. ....	$C_{12}H_{10}O_5$		From compound 296 and $C_6H_5CO_2H$	(55)
298. ....	$C_{12}H_{11}BrO_4$		86% by the action of bromine on the potassium salt of compound 294 By hydrolysis of compounds 313 and 323 with methanolic KOH; see compound 313	(38, 71, 76, 115, 116, 117, 119, 142) (119)
299. ....	$C_{12}H_{11}ClO_4$		77.5% by the action of chlorine on the potassium salt of compound 294; see compound 314	(119)
300. ....	$C_{12}H_{11}NO_2$		61% from compound 294 and $NH_3$	(38, 71, 116, 117, 119)
301. ....	$C_{12}H_{12}Br_2O_4$		By hydrolysis of compound 323	(38, 71, 116, 117, 119)




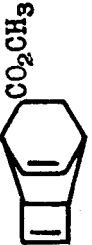
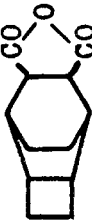

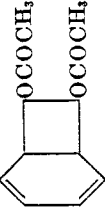
302.....	$C_{12}H_{12}O_3$		By distillation of the <i>cis</i> isomer of 307 See compounds 331 and 341	(38, 71, 116, 117, 119)
303.....	$C_{12}H_{12}O_4$		<i>Cis</i> form by hydrolysis of the <i>cis</i> forms of compounds 327 and 294; <i>trans</i> form by hydrolysis of <i>trans</i> form of compound 327; see compounds 307, 310, 313, and 327	(38, 71, 116, 117, 119)
304.....	$C_{12}H_{12}O_4$		By hydrogenation of compound 296 over $Pd \cdot CaCO_3$	(38, 55, 71, 116, 117, 119)
305.....	$C_{12}H_{14}O_2$		By esterification of compound 287	(38, 71, 116, 117, 119)
306.....	$C_{12}H_{14}O_2$		88% by distillation of the <i>cis</i> form of compound 310 and by hydrogenation of compound 294 over palladium; see compounds 309, 315, 333, and 342	(38, 71, 116, 117, 119)
307.....	$C_{12}H_{14}O_4$		<i>Cis</i> form (84%) by hydrogenation of compound 294 over nickel in the presence of KOH <i>Trans</i> form (90%) by hydrogenation of <i>trans</i> form of compound 303 over $Pd \cdot CaCO_3$ See compounds 302, 331, 341, and 356	(38, 71, 116, 117, 119)
308.....	$C_{12}H_{14}O_4$		64% from compound 265 and $KOCOC_2H_5$ See compounds 312, 337, 351, and 360	(38, 71, 76, 115, 116, 117, 119, 142)

TABLE 2—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
309.....	$C_{12}H_{18}NO_2$		82% from compound 306 and $NH_3$	(38, 71, 116, 117, 119)
310.....	$C_{12}H_{18}O_4$		<i>Cis</i> form (89%) by hydrogenation of compound 294 over Pd-C or nickel in the presence of KOH <i>Trans</i> form by hydrolysis of compound 333 after heating with $NaOCH_3$ and by hydrogenation of <i>trans</i> form of compound 303 See compounds 306, 333, 342, and 357	(38, 71, 115, 116, 119)
311.....	$C_{12}H_{18}O_4$		From compound 260 and $NaOC_2H_5$	(38, 71, 116, 117),
312.....	$C_{12}H_{18}O_4$		98% by hydrogenation of compound 308 over Pd- $CaCO_3$ ; see compound 279	(38, 71, 76, 115, 116, 117, 119, 142)
313.....	$C_{12}H_{15}BrO_4$		By esterification of compound 298 and the action of bromine in $CH_3OH$ on the <i>cis</i> form of compound 303 By action of bromine in $CH_3OH$ on the <i>cis</i> form of compound 327; see compound 298	(119) (38, 71, 115, 116, 117, 119)



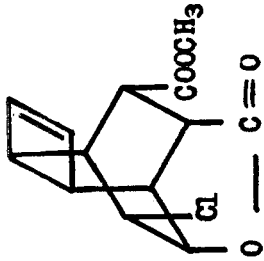

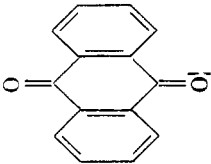
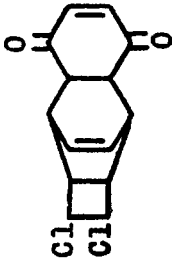
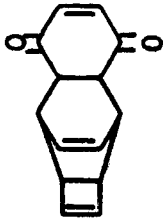
314.....	$C_{12}H_{13}ClO_4$		By esterification of compound 299	(119)
315.....	$C_{13}H_{15}O_4$		63% from compound 306 and $CH_3OH$	(38, 71, 116, 117, 119)
316.....	$C_{14}H_{15}O_4$		By pyrolysis of compounds 346 (98%), 347 (63%), and 360	(38, 71, 116, 117, 119)
317.....	$C_{14}H_{12}Cl_2O_2$		41% from compound 265 and quinone	(38, 71, 116, 117)
318.....	$C_{14}H_{12}O_2$		From compound 2 and quinone; see compounds 319, 325, 330, and 334	(38, 71, 76, 115, 116, 117, 119, 142)

TABLE 2—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
319 .....	$C_{14}H_{12}O_2$		80% by heating compound 318; see compounds 326, 336, and 350	(38, 71, 76, 115, 116, 117, 119, 142)
320 .....	$C_{14}H_{14}Br_2O_4$		58% from compound 260 and $CH_3OOC\equiv CCOOCH_3$ See compounds 292 and 329	(38, 71, 116, 117, 119)
321 .....	$C_{14}H_{14}Cl_2O_4$		54% from compound 265 and $CH_3OOC\equiv CCOOCH_3$	(13, 38, 71, 76, 115, 116, 117, 119, 142)
322 .....	$C_{14}H_{14}O_5$		28% from compound 5 and $CH_3OOC\equiv CCOOCH_3$ See compound 332	(38, 71, 116, 117, 119)
323 .....	$C_{14}H_{16}Br_2O_4$		30% from the <i>cis</i> form of compound 327 and bromine See compounds 291, 298, and 301	(38, 71, 116, 117, 119)
324 .....	$C_{14}H_{16}Cl_2O_4$		76-85% by esterification of compound 293	(38, 71, 116, 117, 119)

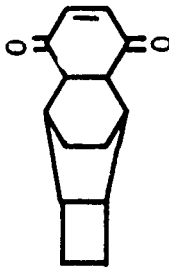
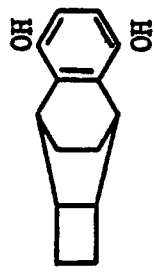
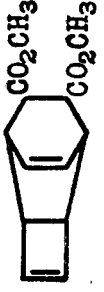


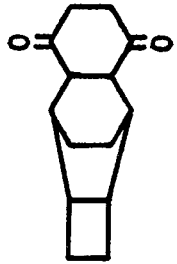



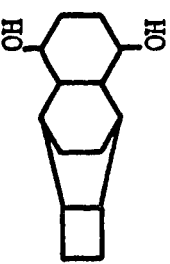
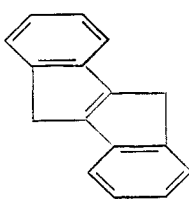
325.....	$C_{14}H_{16}O_2$		By hydrogenation of compound 318	(38, 71, 116, 117)
326.....	$C_{14}H_{16}O_2$		87% by hydrogenation of compound 319 over Pd.C	(38, 71, 116, 117, 119, 142)
327.....	$C_{14}H_{16}O_4$		<i>Cis</i> form by esterification of compound 294 (86-98%) or of the <i>cis</i> form of compound 303 <i>Trans</i> form by heating the <i>cis</i> form with $NaOCH_3$ or esterification of the <i>trans</i> form of compound 303; see compounds 303, 313, 323, and 328	(38, 71, 116, 117, 119)
328.....	$C_{14}H_{16}O_6$		64% from the <i>cis</i> form of compound 327 and $C_6H_5CO_2H$	(38, 71, 116, 117, 119)
329.....	$C_{14}H_{18}Br_2O_4$		60% by hydrogenation of compound 320 over Pd.C	(38, 71, 116, 117, 119)
330.....	$C_{14}H_{18}O_2$		By hydrogenation of compound 318 over Pd.C	(38, 71, 116, 117, 119)

TABLE 2—Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
331 . . . . .	$C_{14}H_{18}O_4$		By esterification of the <i>cis</i> form of compound 307 (92%) or of compound 302	(38, 71, 116, 117, 119)
332 . . . . .	$C_{14}H_{18}O_5$		By hydrogenation of compound 322	(38, 71, 116, 117, 119)
333 . . . . .	$C_{14}H_{20}O_4$		By esterification of the <i>cis</i> form of compound 310 (89%) or of compound 306; see compound 310	(38, 71, 116, 117, 119)
334 . . . . .	$C_{14}H_{22}O_2$		By hydrogenation of compound 318 over nickel	(38, 71)
335 . . . . .	$C_{16}H_{12}$		Along with compound 182 by decarboxylation of compound 202; see compound 183	(52)

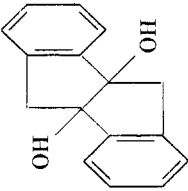
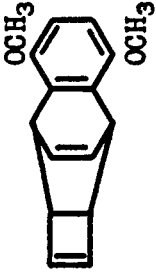


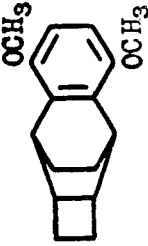



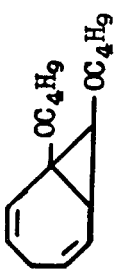

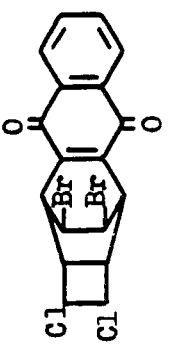
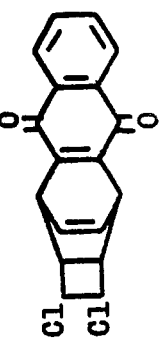
335a.....	$C_{16}H_{14}O_2$		52% from compound 183 with amalgamated zinc and acid See compound 183	(157)
336.....	$C_{16}H_{16}O_2$		81% from compound 319 and $(CH_3)_2SO_4$ See compound 339	(38, 71, 116, 117, 119, 142)
337.....	$C_{16}H_{16}O_7$		100% from compound 308 and maleic anhydride	(38, 71, 116, 117, 119)
338.....	$C_{16}H_{18}O_4$		From compound 2 and $C_2H_5OOC\equiv CCOOC_2H_5$ See compound 295	(38, 71, 116, 117, 119)
339.....	$C_{16}H_{20}O_2$		74% by hydrogenation of compound 336 over Pd-C	(38, 71, 116, 117, 119)
340.....	$C_{16}H_{20}O_4$		93% by esterification of compound 294	(38, 71, 116, 117, 119)

TABLE 2--Continued

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
341.....	$C_{16}H_{22}O_4$		By esterification of compound 302 or of the <i>cis</i> form of compound 307	(38, 71, 116, 117, 119)
342	$C_{16}H_{24}O_4$		By esterification of the <i>cis</i> form of compound 310 (84%) or of compound 306	(38, 71, 116, 117, 119)
343.....	$C_{16}H_{26}O$		From compound 260 and $NaOC_4H_9$	(38, 71, 116, 117)
344.....	$C_{17}H_{21}NO$		From compound 286 and $C_6H_5COCl$	(38, 71, 116, 117, 119)
345.....	$C_{18}H_{12}Br_2Cl_2O_2$		42% from compound 346 and $Br_2$	(38, 71, 116, 117, 119)
346.....	$C_{18}H_{12}Cl_2O_2$		96% by heating compound 348 in air in the presence of alkali; see compounds 316 and 345	(38, 71, 76, 115, 116, 117, 119, 142)

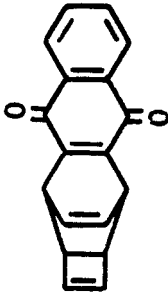
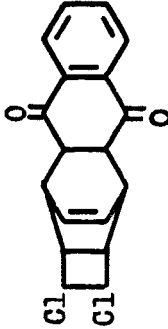
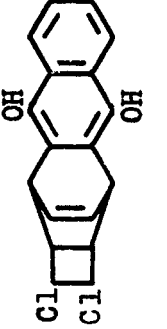
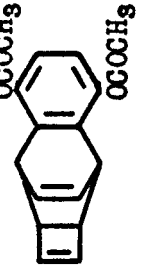


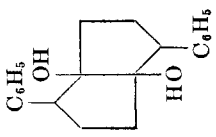




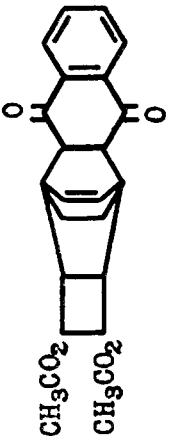
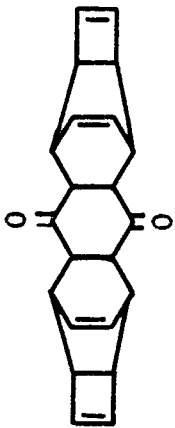
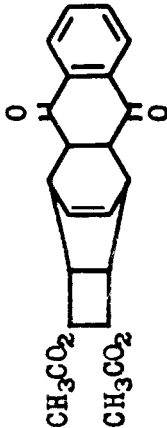

347 . . . . .	$C_{13}H_{12}O_2$		16% from compound 2 and naphthoquinone, followed by heating with air and alkali; see compound 316	(38, 71, 76, 115, 116, 117, 119, 142)
348 . . . . .	$C_{13}H_{14}Cl_2O_2$		97% from compound 265 and naphthoquinone See compounds 346 and 349	(38, 71, 76, 115, 116, 117, 119, 142)
349 . . . . .	$C_{16}H_{14}Cl_2O_2$		From compound 348 and NaOH	(71, 116, 117)
350 . . . . .	$C_{18}H_{16}O_4$		By acetylation of compound 319	(38, 71, 116, 117, 119)
351 . . . . .	$C_{18}H_{20}O_8$		54% from compound 308 and $CH_3OOC\equiv CCOOCH_3$ See compound 352	(38, 71, 115, 116, 117, 119)
352 . . . . .	$C_{18}H_{24}O_8$		99% by hydrogenation of compound 351 over Pd·CaCO <sub>3</sub> .	(119)

TABLE 2—Concluded

COMPOUND NO.	EMPIRICAL FORMULA	STRUCTURE	SOURCE	REFERENCES
353	$C_{20}H_{22}O_2$		70% by reduction of compound 220 with Zn and $CH_3COOH$ ; see compound 220	(158)
354	$C_{20}H_{28}O_4$		By esterification of compound 294	(38, 71, 116, 117, 119)
355	$C_{20}H_{28}O_4$		98% by esterification of compound 294	(71, 116, 117, 119)
356	$C_{20}H_{28}O_4$		91% by esterification of the <i>cis</i> form of compound 307	(38, 71, 116, 117, 119)
357	$C_{20}H_{28}O_4$		By esterification of the <i>cis</i> form of compound 310	(38, 71, 116, 117, 119)



358. ....	$C_{22}H_{18}O_6$		By heating compound 360 in air in the presence of $NaOCH_3$	(38, 71, 116, 117, 119)
359. ....	$C_{22}H_{20}O_8$		From two moles of compound 2 and quinone	(38, 71, 116, 117, 119)
360. ....	$C_{22}H_{20}O_6$		84% from compound 308 and naphthoquinone See compounds 316 and 358	(38, 71, 115, 116, 117, 119)
361. ....	$C_{22}H_{32}O_4$		By esterification of compound 294	(38, 71, 116, 117, 119)

ing complexity of empirical formula according to the convention used by *Chemical Abstracts*. Structures which may or may not have been proved conclusively are included. No attempt was made to include the name of the compound because of the complexity of naming certain of the compounds, particularly those with polycyclic ring systems. The method of preparation and yield, when they were reported or could be calculated, as well as materials to which the compound in question has been converted are indicated by numbers in the fourth column.

The author would like to express his appreciation to Dr. H. B. Hass for his interest in this work and to Dr. S. R. Buc and Mrs. I. L. Ressa for their assistance in the preparation of the manuscript.

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