in 10 ml. of xylene. The mixture was filtered and the filtrate was taken to dryness, giving 90 mg. of material. This material melted at 255–260° alone, at 256–261° when mixed with the iodide and at 208–240° when mixed with triptycene.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XXX. Reactions of Cycloöctatrienone; Ethoxycycloöctatetraene

BY ARTHUR C. COPE, SIDNEY F. SCHAEREN AND ELMER R. TRUMBULL[1]

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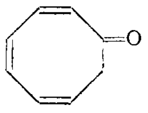
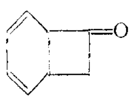
2,4,6-Cycloöctatrien-1-one (I) has been isolated as a yellow crystalline solid, m.p. 13.5–14.5°. The ketone I shows little tendency to form an enolate with bases, even though the enolate would be completely conjugated. Condensation of the ketone with ethyl cyanoacetate formed an alkylidene ester III with an exocyclic double bond. Diels–Alder adducts of the ketone I with maleic anhydride, dimethyl acetylenedicarboxylate and 1,4-naphthoquinone were prepared, and evidence is presented indicating that all of them are derived from the valence tautomer of I (formula II) containing a cyclobutanone ring. The diethyl ketal of I (formula XIV) on heating in the presence of *p*-toluenesulfonic acid or aluminum *t*-butoxide forms ethanol and ethoxycycloöctatetraene (XVI), which was characterized by hydrolysis to the ketone I and by hydrogenation to cycloöctyl ethyl ether.

This paper reports an investigation of some of the reactions of 2,4,6-cycloöctatrien-1-one (I), prepared by the base-catalyzed isomerization of cyclooctatetraene oxide.[2] The ketone was isolated as a pure liquid in 80–90% yield by distillation of the product obtained by rearrangement of cyclooctatetraene oxide. It solidified on cooling, and after recrystallization from pentane melted at 13.5–14.5°. The crystalline ketone immediately after melting had an infrared spectrum with a strong carbonyl band at 6.0μ and a weaker band at 5.63μ as previously reported, probably indicating the presence of the bridged isomer II with the carbonyl group in a four-membered ring.[2] The infrared spectrum of a single crystal of the ketone in the 5–6μ region was determined by the microspectrometric method described by Blout and Bird.[3] Both carbonyl bands present in the spectrum of the liquid ketone were present in the spectrum of the crystal, which accordingly may contain both molecular species I and II.



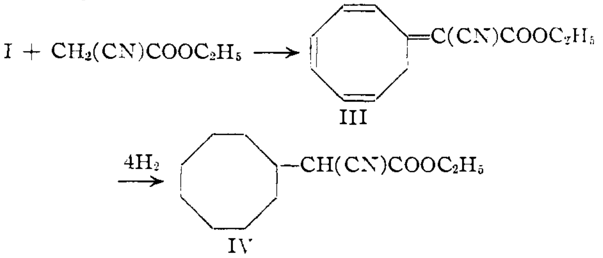
I



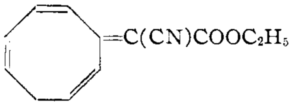
II

The ketone I does not appear to form an enolate readily. It is soluble to the extent of at least 1% in 3 *N* sodium hydroxide, but is somewhat soluble in water, and can be recovered unchanged from alkaline solution by extraction with ether. Treatment of I with sodium ethoxide in ethanol and with potassium *t*-butoxide in *t*-butyl alcohol led to decomposition, and preliminary attempts to alkylate the ketone with diethyl sulfate or ethyl iodide in the presence of these bases or sodamide in benzene were unsuccessful.

Condensation of the ketone I with ethyl cyanoacetate in the presence of ammonium acetate formed a mixture from which a yellow crystalline solid, $C_{13}H_{13}NO_2$ (III), m.p. 75–76°, was isolated in 10% yield. Quantitative hydrogenation of III in the presence of palladium on Norit resulted in absorption of four molar equivalents of hydrogen and formed a liquid octahydro derivative, $C_{13}H_{21}NO_2$ (IV). A crystalline amide prepared from IV and ammonium hydroxide proved to be identical with an authentic sample of cycloöctylcyanoacetamide, derived from ethyl cycloöctylcyanoacetate (obtained by hydrogenating ethyl cycloöctylidenecyanoacetate, prepared from cycloöctanone and ethyl cyanoacetate).



Evidence that one double bond in III is exocyclic was furnished by the ultraviolet absorption spectrum which has two strong maxima at 258 mμ (log ϵ 4.21) and 350 mμ (log ϵ 4.03) in cyclohexane, instead of the low absorption in this region characteristic of cycloöctatetraene derivatives.[4] This evidence does not exclude a cross-conjugated structure V rather than III for the ester.



V

Cycloöctatrienone reacted readily with maleic anhydride, forming a crystalline adduct VI, which was converted into the corresponding dibasic acid VII by saponification, and subsequently into the dimethyl ester VIII with diazomethane. The infrared spectrum of the dimethyl ester VIII (Fig. 1) has a strong absorption band at 5.63μ indicating that the ketonic carbonyl group is located in a four-membered ring.[5] Bridging in the

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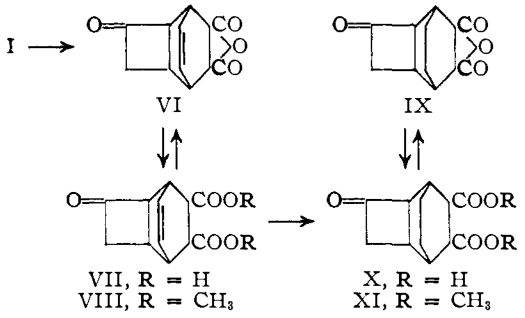
(1) du Pont Postdoctorate Fellow.

(2) A. C. Cope and B. D. Tiffany, THIS JOURNAL, **73**, 4158 (1951).

(3) E. R. Blout and G. R. Bird, *J. Opt. Soc. Am.*, **41**, 547 (1951). We are indebted to Mr. Mario Abbate and Dr. Blout for determination of the spectrum.

(4) A. C. Cope and D. F. Rugen, *ibid.*, **75**, 3215 (1953).

(5) See J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949), for the infrared spectrum of cyclobutanone.



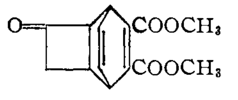
VI IX

VII, R = H
VIII, R = CH_3

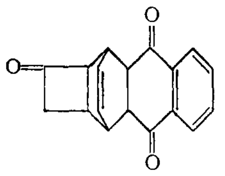
X, R = H
XI, R = CH_3

formation of the adduct VI is analogous to the bridging that occurs in formation of Diels–Alder adducts from 1,3,5-cycloöctatriene[6] or cycloöctatetraene.[7] Catalytic hydrogenation of the potassium salt of VII or of the dimethyl ester VIII in the presence of palladium formed dihydro derivatives; the dihydro acid X was isolated as the anhydride IX formed on sublimation. The infrared spectrum of the dihydro ester XI (Fig. 1) contained a carbonyl band at 5.63μ, indicating that the cyclobutanone structure remained intact in the reduction. The absorption of hydrogen did not stop at one molar equivalent in these reductions, and continued hydrogenation resulted in slow absorption of a total of three molar equivalents. On reduction of the dihydro ester XI two molar equivalents of hydrogen were absorbed and a product that failed to crystallize was formed which had an infrared spectrum indicating the presence of an hydroxyl group (band at 2.9μ). It is uncertain whether the absorption of the third molar equivalent of hydrogen in these reductions was caused by opening of the fused ring system or some other structural change.

Diels–Alder adducts also were obtained from cycloöctatrienone and dimethyl acetylenedicarboxylate (XII) and α-naphthoquinone (XIII).



XII



XIII

Pyrolysis of XII formed dimethyl phthalate (70%) and a very small amount of a volatile liquid (7% calculated as cyclobutenone or an isomer thereof) which was not obtained in sufficient quantity for further study. Oxidation of XIII with air in alkaline solution also resulted in elimination of the four-membered ring and formed anthraquinone.

The diethyl ketal (XIV) of cycloöctatrienone was prepared in 69% yield by treatment with ethyl orthoformate in the presence of ferric chloride. The ketal formed an adduct with maleic anhydride that was hydrolyzed by dilute acid to the adduct VI obtained from cycloöctatrienone and maleic anhydride, and therefore has the bridged ring structure XV.

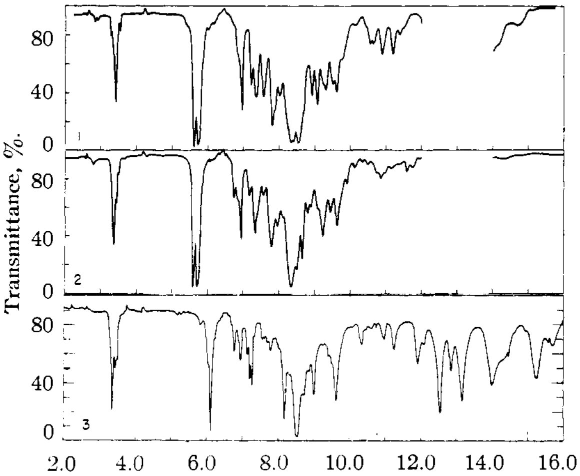
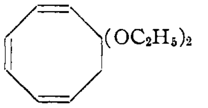
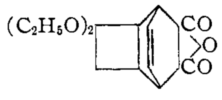


FIG. 1.—Infrared absorption spectra: curve 1, unsaturated dimethyl ester VIII; curve 2, saturated dimethyl ester XI, both as solutions (100 mg./ml.) in carbon tetrachloride. Absorption in the 12–14 μ region was obscured by the strong absorption of carbon tetrachloride. Curve 3, ethoxycyclooctatetraene (XVI) as a solution (100 mg./ml.) in carbon tetrachloride in the region 2–7.4 μ and in carbon disulfide in the region 7.4–16 μ.



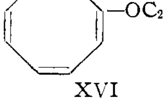
XIV



XV

The ketal XIV was readily hydrolyzed to the ketone I with dilute acid. There is no positive evidence distinguishing between structure XIV for the ketal and a bridged-ring structure analogous to II, for quantitative hydrogenations of the ketal were inconclusive.

It was possible to convert the ketal XIV into ethoxycycloöctatetraene (XVI) by elimination of ethanol. This reaction occurred on heating XIII with *p*-toluenesulfonic acid[8] or aluminum *t*-butoxide,[9] although yields were poor by both procedures. The ultraviolet spectrum of ethoxycyclooctatetraene shows weak absorption beginning in the visible region, becoming strong at about 230 mμ, while the infrared spectrum (Fig. 1) contains the bands previously noted as characteristic of monosubstituted cycloöctatetraenes.[4] Chemical evidence for the structure of ethoxycycloöctatetraene was obtained by its rapid hydrolysis as a vinyl ether by dilute acid, forming cycloöctatrienone (isolated as the 2,4-dinitrophenylhydrazone).



XVI

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[6] A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *J. Opt. Soc. Am.*, **74**, 4867 (1952).

[7] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[8] Conditions used for the conversion of acetals to vinyl ethers by A. Johannissian and E. Akunian, *Bull. univ. état R.S.S.-Arménie, No.* **5**, 245 (1930); *C. A.*, **25**, 921 (1931).

[9] Used as a catalyst for conversion of ortho esters to ketene acetals by S. M. McElvain and W. R. Davie, THIS JOURNAL, **73**, 1400 (1951).

Quantitative hydrogenation gave cycloöctyl ethyl ether, which was proved to be identical with an authentic sample prepared from the sodium salt of cycloöctanol and ethyl iodide by comparison of physical properties and infrared spectra.

Experimental[10]

2,4,6-Cycloöctatrien-1-one (I).—The procedure described previously[2] for preparation of I was followed, except that the product was fractionated carefully through a semi-micro column rather than converted into the semicarbazone. The pure yellow liquid ketone that was obtained in yields of 80–90% crystallized slowly on cooling with Dry Ice. Samples that were recrystallized from pentane melted at 13.5–14.5°.

A sample (1.20 g.) of I was shaken vigorously with 100 ml. of 3 *N* sodium hydroxide for 5 minutes. A deep yellow-orange solution was obtained. Although the aqueous solution retained this color after extraction with four 30-ml. portions of ether, concentration of the extracts yielded 1.18 g. of the unchanged ketone I.

Addition of the ketone I to alcoholic sodium ethoxide or potassium *t*-butoxide in *t*-butyl alcohol at room temperature gave brown solutions that turned violet after a few minutes. No pure compound was isolated after attempted alkylation with diethyl sulfate or addition of dilute sulfuric acid (attempted regeneration of I). Addition of I to sodium amide in benzene followed by treatment with ethyl iodide under reflux resulted in no reaction and recovery of most of the original ketone.

Ethyl Cycloöcta-2,4,6-trienylidenecyanoacetate (III).—A solution of 22.6 g. of ethyl cyanoacetate, 26.4 g. of the ketone I and 1.0 g. of ammonium acetate in 12.0 g. of glacial acetic acid and 50 ml. of benzene was heated for 6 hours under reflux in a bath at 140°, and the water that formed was removed continuously with a modified Dean and Stark separator.[11] The mixture was cooled, diluted with 500 ml. of ether, washed with four 50-ml. portions of water and dried over magnesium sulfate. The solution was concentrated and the residue was fractionated through a semimicro column. Of the six fractions that were separated, the last five (24.1 g., 56%) were collected at 119–125° (0.35 mm.), n^{25}_D 1.5535–1.6000. Fraction 3 (4.25 g., b.p. 121–122° at 0.35 mm., n^{25}_D 1.5570) obviously was a mixture but its analysis was in satisfactory agreement (C, H and N) with the formula $C_{13}H_{13}NO_2$. Fraction 6 partially solidified and recrystallization of the solid from a mixture of benzene and cyclohexane yielded 4.6 g. (9.7%) of III as bright yellow crystals, m.p. 75–76°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.52; H, 6.09; N, 6.50. Found: C, 72.81; H, 6.15; N, 6.49.

Quantitative hydrogenation of a solution of 0.158 g. of III in 10 ml. of absolute ethanol in the presence of 0.5 g. of 10% palladium on Norit was complete in 1 hour and 106% of four molar equivalents of hydrogen was absorbed. The reduction product was isolated by a short-path distillation and converted into cycloöctylcyanoacetamide by shaking overnight with concentrated ammonium hydroxide; m.p. and mixed m.p. with an authentic sample described below, 123–124°.

Ethyl cycloöctylidenecyanoacetate was prepared by heating 2.77 g. of cycloöctanone, 2.26 g. of ethyl cyanoacetate, 0.2 g. of ammonium acetate, 1.2 g. of acetic acid and 20 ml. of benzene under reflux for 6 hours with continuous separation of the water formed.[11] The product was isolated in the same manner as III, and amounted to 3.05 g. (63%) of ethyl cycloöctylidenecyanoacetate, a colorless liquid, b.p. 135° (1.2 mm.), n^{25}_D 1.5041.

Anal. Calcd. for $C_{13}H_{19}NO_2$: C, 70.54; H, 8.66; N, 6.33. Found: C, 70.39; H, 8.67; N, 6.38.

Cycloöctylcyanoacetamide was prepared from ethyl cyclooctylcyanoacetate, obtained by hydrogenating ethyl cyclooctylidenecyanoacetate in ethanol in the presence of Adams platinum catalyst. The ester IV was shaken overnight with concentrated ammonium hydroxide, and the crystalline cycloöctylcyanoacetamide that was formed was purified by two sublimations at 0.5 mm. with a heating block temperature of 130°; m.p. 123–124°.

Anal. Calcd. for $C_{11}H_{18}N_2O$: C, 67.98; H, 9.35; N, 14.42. Found: C, 67.82; H, 9.12; N, 14.41.

Maleic Anhydride Adduct of Cycloöctatrienone (VI).—Finely ground maleic anhydride (17.1 g.) was added to a solution of 21.0 g. of the ketone I in 75 ml. of benzene and the solution was warmed in an oil-bath at 60° in an atmosphere of nitrogen. After a few minutes the mixture boiled from the heat of reaction, and the rate of reflux was moderated by cooling with an ice-bath. After 5 minutes the contents of the flask solidified and ebullition ceased. The mixture was heated under reflux for 1.5 hours, cooled, and the solid was collected on a filter and washed with 30 ml. of benzene. The crude product (33 g.) was recrystallized from 700 ml. of ethyl acetate, yielding 23.7 g. (62%) of VI, m.p. 209–210.5°. An additional 8.5 g. (22%), m.p. 206–208°, was obtained from the mother liquor.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.00; H, 4.62. Found: C, 65.92; H, 4.68.

Unsaturated Dicarboxylic Acid VII.—A suspension of 1.60 g. of the anhydride VI in 10 ml. of water was warmed on a steam-bath, and 10% sodium hydroxide was added dropwise until a clear solution was obtained. The solution was cooled in ice, acidified to congo red with dilute sulfuric acid, and the acid VII that separated was recrystallized from hot water; yield 1.30 g. (75%), m.p. 195–197° (dec., reforming the anhydride VI).

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found: C, 61.01; H, 5.27.

Unsaturated Dimethyl Ester VIII.—A solution of 4.0 g. of the dicarboxylic acid VII in 100 ml. of tetrahydrofuran was cooled and an ethereal solution of diazomethane was added until a yellow color persisted. The excess diazomethane was decomposed by adding acetic acid, the solution was concentrated, and the residue was distilled in a small alembic, yielding 2.95 g. (66%) of VIII as a pale yellow solid, b.p. 155° (0.5 mm.). Recrystallization from benzene–hexane yielded 2.4 g., m.p. 93–95°. An analytical sample of VIII that was recrystallized again and sublimed at 0.5 mm. with a heating block temperature of 90° melted at 95.5–97°.

Anal. Calcd. for $C_{14}H_{16}O_5$: C, 63.60; H, 6.10. Found: C, 63.55; H, 6.23.

Reduction of a solution of 0.213 g. of the unsaturated dimethyl ester VIII in 95% ethanol in the presence of 0 2 g. of prereduced 10% palladium on Norit resulted in absorption of one molar equivalent of hydrogen in approximately 20 minutes and a total of 95% of three molar equivalents in three days.

Saturated Dicarboxylic Acid Anhydride IX.—The maleic anhydride adduct VI (5.0 g., 0.0230 mole) was warmed with 20 ml. of water and 50% potassium hydroxide solution was added dropwise until the solid dissolved. The solution was added to a suspension of 1 g. of prereduced 10% palladium on Norit in 50 ml. of water and the mixture was shaken with hydrogen until 0.0232 mole had been absorbed (45 minutes). The catalyst was separated, and the filtrate was acidified to congo red with hydrochloric acid and extracted with ether in a continuous extractor for 12 hours. Concentration of the extract yielded a crude solid (4.2 g.) which was purified by recrystallization from ethyl acetate and then sublimed at 0.5 mm. with a heating block temperature of 160°, forming the anhydride IX. The analytical sample of IX melted at 242–244°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50. Found: C, 65.65; H. 5.79.

Reduction of a solution prepared from 0.286 g. of the anhydride VI and potassium hydroxide was conducted in the manner described above, except that the hydrogenation was allowed to proceed to completion, which required 3 days and resulted in absorption and 102% of three molar equivalents of hydrogen. Reduction of a solution prepared from 0.229 g. of the saturated dicarboxylic acid anhydride IX and potassium hydroxide under similar conditions was complete in 4 days and resulted in absorption of 96% of two molar equivalents of hydrogen.

Saturated Dimethyl Ester XI.—The saturated anhydride IX (1.4 g.) was suspended in 10 ml. of hot water and 50%

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(10) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Infrared spectra were determined with a Baird Double Beam Infrared Recording Spectrometer, Model B, fitted with a sodium chloride prism.

(11) A. C. Cope, C. M. Hofmann, C. Wyckoff and E. Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

aqueous potassium hydroxide was added dropwise until the solid dissolved. The solution was cooled and acidified to congo red with hydrochloric acid, and the dicarboxylic acid X that crystallized on standing was separated and dried under reduced pressure (1.0 g., m.p. 228–233° dec.). The crude acid X was dissolved in 15 ml. of tetrahydrofuran and converted to the dimethyl ester XI under conditions similar to those described for preparation of VIII from VII. The crude ester XI was crystallized from benzene–hexane and sublimed at 0.5 mm. with a heating block temperature of 95°; m.p. 105–107°.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.80. Found: C, 63.14; H, 6.98.

Adduct from Cycloöctatrienone and Dimethyl Acetylenedicarboxylate (XII).—A mixture of 4.0 g. of dimethyl acetylenedicarboxylate and 3.3 g. of the ketone I was heated at 50° for 4 hours, 70° for 2 hours, and finally at 90° for 4 hours. Preliminary experiments had shown that at 120° dimethyl phthalate was formed rather than the adduct XII, and that heating under the conditions described above resulted in gradual loss of the strong infrared carbonyl band at 6.0 μ due to the ketone I and increase in intensity of the carbonyl band of the adduct XII at 5.63 μ. The liquid product solidified on cooling, and amounted to 5.5 g. (76%) of XII as white needles which were recrystallized from benzene–cyclohexane; m.p. 69–71°.

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38. Found: C, 64.31; H, 5.56.

The adduct XII was first prepared and then decomposed thermally by heating 2.0 g. of I and 2.5 g. of dimethyl acetylenedicarboxylate at 160° for 1 hour. Distillation of the product through a semimicro column yielded 2.26 g. (70%) of dimethyl phthalate, b.p. 111° (0.7 mm.), n^{25}_{D} 1.5150 (identified by its infrared spectrum and by saponification to phthalic acid) and a small polymeric residue.

Pyrolysis of a 5.94-g. sample of XI in a nitrogen atmosphere at 100 mm. in a bath at 200° for 0.5 hour yielded 0.84 g. of a liquid that was collected in a receiver cooled with liquid nitrogen. Redistillation to separate low-boiling material from dimethyl phthalate yielded 0.08 g. of a low-boiling liquid with a sharp odor that had two carbonyl bands in the infrared spectrum at approximately 5.6 and 5.8 μ.

Adduct from Cycloöctatrienone and α-Naphthoquinone (XIII).—A solution of 2.4 g. of the ketone I and 3.2 g. of α-naphthoquinone in 30 ml. of benzene was heated under reflux on a steam-bath for 21 hours. A total of 4.34 g. (80%) of the adduct XIII, m.p. 186–188°, was obtained by cooling the benzene solution and concentrating the mother liquor. Recrystallization from benzene yielded XIII as thick white needles, m.p. 193–196°.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.76; H, 5.08. Found: C, 77.77; H, 5.21.

Addition of 1.45 g. of the adduct XIII to the sodium ethoxide prepared from 0.30 g. of sodium and 50 ml. of absolute ethanol formed a red solution that was heated under reflux on a steam-bath for 1 hour. After this treatment, designed to rearrange XIII to the corresponding hydroquinone, a stream of air was introduced, which caused the red color to disappear and the solution to turn brown. The mixture was allowed to stand at 5° overnight, and the solid that formed was separated and recrystallized from benzene, yielding 0.827 g. (73%) of anthraquinone, identified by m.p. and mixed m.p. with an authentic sample (283–285°) and the infrared spectrum.

2,4,6-Cycloöctatrienone Diethyl Ketal (XIV).—A solution of 9.4 g. of the ketone I, 25 ml. of ethyl orthoformate and 0.2 g. of anhydrous ferric chloride in 20 ml. of absolute ethanol was allowed to stand in a glass-stoppered flask at room temperature for 2 days. The solution was diluted with 150 ml. of ether and washed with four 20-ml. portions of a solution of 2.0 g. of the disodium salt of ethylenediaminetetraacetic acid ("disodium Versenate") in 80 ml. of water, to which enough 10% sodium hydroxide had been added to bring the *p*H to 9–10. The light red ether solution was dried over calcium sulfate and concentrated. Distillation of the residue through a short column yielded 10.35 g. (69%) of crude XIV, b.p. 50–52° (0.3 mm.). Redistillation through a semimicro column yielded pure XIV, b.p. 49–50° (0.3 mm), n^{25}_{D} 1.4783, d^{25}_{4} 0.9772.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.35. Found: C, 74.11; H, 9.45.

A solution of 0.158 g. of XIV in 10 ml. of 95% ethanol was acidified with a drop of 20% hydrochloric acid and heated under reflux for 30 minutes. After addition of 20 ml. of a 1% solution of 2,4-dinitrophenylhydrazine in ethanol containing 1% of hydrochloric acid the mixture was allowed to stand at 5° overnight. The 2,4-dinitrophenylhydrazone of I that separated (0.155 g., 63%) melted at 154–155°, and after two recrystallizations from benzene–cyclohexane had m.p. and mixed m.p. with an authentic sample of 160–161°.

A solution of 0.38 g. of the ketal XIV in 15 ml. of 95% ethanol that was acidified with 5 ml. of 36% hydrochloric acid immediately developed the odor of phenylacetaldehyde. Addition of 0.40 g. of 2,4-dinitrophenylhydrazine in 20 ml. of ethanol immediately precipitated 0.155 g. (27%) of a yellow 2,4-dinitrophenylhydrazone. After several recrystallizations from benzene–cyclohexane the derivative was identified as the 2,4-dinitrophenylhydrazone of phenylacetaldehyde, long yellow needles, m.p. and mixed m.p. with an authentic sample, 122–123°.

Maleic Anhydride Adduct of 2,4,6-Cycloöctatrien-1-one Diethyl Ketal (XV).—A mixture of 0.64 g. of the ketal XIV and 0.323 g. of freshly sublimed maleic anhydride was heated on a steam-bath for 30 minutes, protected from atmospheric moisture. A solution of the product in a mixture of benzene and cyclohexane was allowed to stand at 5°, and after 2 days large transparent prisms of XV were formed; yield 0.68 g. (70%), m.p. 92–94°. Recrystallization from benzene–cyclohexane did not raise the melting point.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.48; H, 7.01. Found: C, 65.71; H, 6.89.

It was possible to sublime the adduct XV at 0.5 mm. with a heating block temperature of 70°.

A solution of 0.15 g. of the maleic anhydride adduct XV in 25 ml. of 95% ethanol was acidified with 1 drop of 20% hydrochloric acid and heated under reflux on a steam-bath for 1 hour. The acid was neutralized with sodium bicarbonate and the solution was concentrated under reduced pressure. Sublimation of the residue at 0.5 mm. with a heating block temperature of 200° yielded 0.080 g. (86%) of the maleic anhydride adduct of cycloöctatrienone (VI), m.p. and mixed m.p. with a known sample 208–210°.

Ethoxycycloöctatetraene (XVI). (a).—A mixture of 15.5 g. of the diethyl ketal XIV and 22.0 g. of aluminum *t*-butoxide was heated in a bath at 180–190° in a flask attached to a semimicro column for 1 hour at atmospheric pressure and at 500 mm. for 0.5 hour, during which period 5.15 g. (87%) of *t*-butyl alcohol was collected. The flask was filled with dry glass wool before the contents solidified, and then was connected to a simple still head and all of the material that was volatile at 0.05 mm. with a bath temperature of 120° was distilled into a trap cooled with Dry Ice. The distillate was fractionated through a semimicro column, yielding 4.31 g. (37%) of crude XVI, b.p. 54–60° (1 mm.), n^{25}_{D} 1.51 to 1.52. Careful refractionation yielded 1.43 g. of pure XVI, a deep yellow liquid, b.p. 76° (2 mm.), n^{25}_{D} 1.5250. The higher boiling fractions contained the diethyl ketal XIV.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.00; H, 8.17; OC_2H_5, 30.40. Found: C, 80.88; H, 8.42; OC_2H_5, 30.22.

The ultraviolet spectrum of XVI in 95% ethanol showed weak absorption at long wave lengths, gradually increasing to log ϵ values of 2.94, 3.26, 3.52 and 3.94 at 260, 240, 230 and 220 mμ, respectively.

(b).—A solution of 1.0 g. of the diethyl ketal XIV in 20 ml. of dry benzene was heated under reflux with approximately 10 mg. of *p*-toluenesulfonic acid for 30 minutes. The solution was cooled, washed with aqueous sodium bicarbonate, dried over magnesium sulfate and concentrated. The residue was distilled through a semimicro column, and the fractions from two such preparations were combined and redistilled, yielding 0.12 g. of analytically pure XVI as a deep yellow liquid, b.p. 44–46° (0.4 mm.), n^{25}_{D} 1.5240.

A solution of 0.12 g. of ethoxycycloöctatetraene in 1 ml. of 95% ethanol was treated with 5 ml. of a 1% solution of 2,4-dinitrophenylhydrazine in ethanol containing 1% of hydrochloric acid. A red precipitate of the 2,4-dinitrophenylhydrazone of cycloöctatrienone formed in a few seconds; the yield was 0.10 g. (41%), m.p. and mixed m.p. with an authentic sample after recrystallization from benzene–cyclohexane as small red needles, 159–161°.

A solution of 0.484 g. of ethoxycycloöctatetraene in 30 ml. of absolute ethanol was added to 0.715 g. of prereduced platinum oxide in 25 ml. of absolute ethanol and hydrogenated at atmospheric pressure. Three molar equivalents of hydrogen was absorbed in 10 minutes, and 106% of four molar equivalents in 24 hours. The catalyst was separated and the solution was concentrated by fractionation through a semimicro column at atmospheric pressure. Distillation of the residue yielded 0.275 g. (54%) of cyclooöctyl ethyl ether, n^{25}D 1.4570, with an infrared spectrum indicating the presence of about 10% of a carbonyl compound as an impurity. A solution of the ether in 6 ml. of absolute ethanol was heated under reflux for 1 hour with 1.0 g. of Girard's reagent T and 1 ml. of glacial acetic acid. The solution was cooled, poured into 50 ml. of ice-water containing 0.9 g. of sodium carbonate, and extracted with four 15-ml. portions of ether. The extracts were dried over magnesium sulfate and distilled and yielded 0.042 g. of cyclooöctyl ethyl ether, n^{25}D 1.4553, with an infrared spectrum identical with the authentic sample described below except for weak absorption at 5.82 μ due to the presence of a trace of a carbonyl compound as an impurity.

Cyclooöctyl Ethyl Ether.—A solution of 2.62 g. of cyclooctanol in 25 ml. of dry benzene was heated under reflux with 1.0 g. of sodium hydride for 12 hours, after which 25 ml. of ethyl iodide was added and heating was continued for an additional period of 20 hours. The mixture was washed with water and concentrated slowly by distillation through a semimicro column under reduced pressure at room temperature. Fractionation of the residue yielded 1.56 g. (41%) of colorless cyclooöctyl ethyl ether, b.p. 85–86° (16 mm.), n^{25}D 1.4540, d^{25}_4 0.888.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.90. Found: C, 76.72; H, 12.78.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XXXI. Cycloheptatriene and Bicyclo[4.2.0]octa-2,4-diene Derivatives from Cycloöctatetraene and Mercuric Acetate

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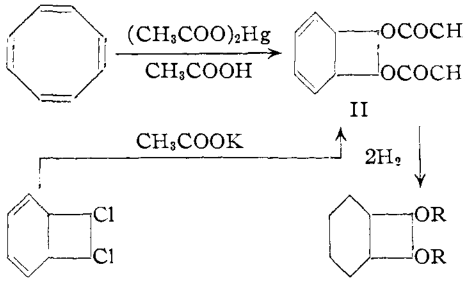
The reaction of cycloöctatetraene with mercuric sulfate (or mercuric acetate) in water forms phenylacetaldehyde as previously reported,[2] but cycloöctatetraene and mercuric acetate in glacial acetic acid form bicyclo[4.2.0]octa-2,4-diene-7,8-diol diacetate (II, 72%) rather than phenylethylidene diacetate, while the same reactants in methanol yield 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V, 88%), instead of phenylacetaldehyde dimethyl acetal. The principal product of the reaction of cycloöctatetraene dichloride (I) and sodium methoxide in methanol also is 2,4,6-cycloheptatriene-1-carboxaldehyde dimethyl acetal (V), rather than the bicyclic isomer XVI as previously formulated.[2]

Reppe, Schlichting, Klager and Toepel[2] have reported the conversion of cycloöctatetraene into phenylacetaldehyde or derivatives of that aldehyde through reaction with mercuric salts in hydroxylic solvents. The products stated to be formed from cycloöctatetraene were phenylacetaldehyde (70%) with mercuric sulfate and water, phenylethylidene diacetate (96%) with mercuric acetate and acetic acid and phenylacetaldehyde dimethyl acetal (78%) with mercuric acetate and methanol. Reinvestigation of these reactions has shown that the products formed in acetic acid and in methanol have structures different from those originally assigned.

The reaction of cycloöctatetraene with mercuric acetate in glacial acetic acid at 70–80° under the conditions previously described[2] yielded 72% of a crystalline compound, $C_{12}H_{14}O_4$, which after recrystallization melted at 61.4–62.5° and undoubtedly is the same product previously obtained from this reaction by Reppe, Schlichting, Klager and Toepel (reported m.p. 64–65°).[2] These authors state that this compound is phenylethylidene diacetate, but that substance as prepared from phenylacetaldehyde and acetic anhydride is a liquid.[3] Another compound with the formula $C_{12}H_{14}O_4$ that was first prepared by Reppe, Schlichting, Klager and Toepel from cycloöctatetraene dichloride (I) and potassium acetate is bicyclo[4.2.0]octa-2,4-dien-7,8-diol diacetate (II), reported as a solid with a melting point of 66°.[2] Proof that the product obtained from cycloöctatetraene and mercuric acetate in acetic acid also has structure II was obtained by quantitative reduction in the presence of a palladium catalyst with the absorption of 102% of two molar equivalents of hydrogen and formation of bicyclo[4.2.0]octane-7,8-diol diacetate (III) (92%), which on hydrolysis yielded *trans*-bicyclo[4.2.0]octane-7,8-diol (IV), m.p. 139.1–140.2°, identical with an authentic sample prepared by hydrogenation of bicyclo[4.2.0]octan-7-ol-8-one.[4]



II

I

III, R = COCH₃
IV, R = H

The reaction of cycloöctatetraene with mercuric acetate in methanol formed a liquid product, $C_{10}H_{14}O_2$ (V), in 88% yield. Although Reppe, Schlichting, Klager and Toepel stated that this reaction yielded phenylacetaldehyde dimethyl acetal, the infrared spectrum of the product (Fig. 1) indicated that it was not an aromatic compound, and the ultraviolet spectrum had a broad maximum at 258.5 mμ such as would be expected for a conjugated triene. Quantitative reduction of the

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[1] Atomic Energy Commission Fellow, 1951–1952.

[2] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[3] A. Wohl and R. Maag, *Ber.*, **43**, 3293 (1910); E. Späth, *Monatsh.*, **36**, 41 (1915).

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