Anal. Calcd. for $C_{10}H_{10}N_6O_2$: C, 48.78; H, 4.09; N, 34.13. Found: C, 48.92; H, 4.09; N, 34.13.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-diamine Dihydrochloride (XII).—Freshly prepared, moist diazide XI obtained from 1.0 g. of the dicarbohydrazide X, was suspended in 20 ml. of dioxane, 5 ml. of water and 3 ml. of concentrated hydrochloric acid. The reaction mixture was heated under reflux for 2 hours. The solvent was removed under reduced pressure. Recrystallization of the solid residue from acetone–methanol yielded 0.39 g. (42%) of the diamine dihydrochloride XII, a mixture of *cis* and *trans* isomers, m.p. >300°. Further recrystallization from acetone–methanol followed by drying provided an analytical sample, m.p. 395° (darkened at 350°).

Anal. Calcd. for $C_8H_{14}N_2{\cdot}2HCl$: C, 45.51; H, 7.64; N, 13.27; Cl, 33.59. Found: C, 45.43; H, 7.63; N, 13.40; Cl, 33.25.

Bicyclo[3.3.0]oct-1(5)-ene-3,7-bis-ethylcarbamate (XIII).—A suspension of 471 mg. of the diazide XI in 5 ml. of absolute ethanol was warmed until evolution of nitrogen ceased and then was heated to boiling. Crystallization occurred on cooling. The product was separated by filtration and dried. The yield of XIII, a mixture of *cis* and *trans* isomers, was 473 mg. (88%). An analytical sample was prepared by recrystallization from ethanol–water, m.p. 180–212° (dec., sintered and darkened at 170–180°).

Anal. Calcd. for $C_{14}H_{22}N_2O_4$: C, 59.55; H, 7.86; N, 9.92. Found: C, 59.86; H, 8.02; N, 9.85.

3,7-Bis-(dimethylamino)-bicyclo[3.3.0]oct-1(5)-ene (XIV).—Freshly prepared, moist diazide XI obtained from 2.0 g. of the dihydrazide X was suspended in a solution of 2 ml. of concentrated hydrochloric acid and 10 ml. of water. The reaction mixture was warmed on a water-bath maintained at 60° for 1 hour and then filtered. The filtrate was treated with 1.5 g. of potassium hydroxide and extracted with chloroform. Concentration of the combined chloroform extracts under reduced pressure yielded 0.84 g. (68%) of crude bicyclo[3.3.0]oct-1(5)-ene-3,7-diamine. The diamine was treated with 8 ml. of 85% formic acid and 4 ml. of 40% formaldehyde. The resultant solution was heated under reflux for 18 hours, treated with 4 ml. of 4 *N* hydrochloric acid, and concentrated under reduced pressure. The residue was dissolved in 5 ml. of water. The solution was made alkaline with 1 g. of potassium hydroxide and extracted with ether and chloroform. The solvent was removed from the combined organic extracts. Purification by sublimation at 90–110° (30 mm.) yielded 0.37 g. (31%) of the diamine XIV, a mixture of *cis* and *trans* isomers, m.p. 61.4–70.2°.

Anal. Calcd. for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.16; H, 11.29; N, 14.71.

3,7-Bis-(dimethylamino)-bicyclo[3.3.0]oct-1(5)-ene Dimethiodide (XV).—The diamine dihydrochloride XIV obtained from 2.0 g. of the dihydrazide X was immediately heated with 40 ml. of methanol, 4.56 g. of sodium bicarbonate and 15.34 g. of methyl iodide under reflux for 17 hours. The reaction mixture was filtered and the filtrate was concentrated to a small volume. The addition of acetone caused the precipitation of 2.24 g. (53%) of the dimethiodide XV, a mixture of *cis* and *trans* isomers. Recrystallization from methanol and from methanol–acetone furnished an analytical sample, m.p. 280–310° dec.

Anal. Calcd. for $C_{14}H_{28}I_2N_2$: C, 35.17; H, 5.88; I, 53.09; N, 5.86. Found: C, 35.53; H, 5.97; I, 53.12; N, 5.93.

The Hydrated Dihydrazine Salt of the Bis-diacylated Hydrazine Derived from 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]-oct-1(5)-ene (XVI).—Hydrazine hydrate (8.0 ml.) was added to a solution of 1.5 g. of 3,3,7,7-tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene[3] in 30 ml. of absolute ethanol at room temperature. After 4 days, 1.2 g. (89%) of the hydrated dihydrazine salt XVI had separated, m.p. 204.5° dec. When washed with absolute ethanol and dried, an analytical sample melted at 206.5° dec.

Anal. Calcd. for $C_{12}H_{12}N_4O_4{\cdot}2N_2H_4{\cdot}H_2O$: C, 40.22; H, 6.19; N, 31.27. Found: C, 39.98; H, 6.41; N, 31.51.

The Bis-diacylated Hydrazine Derived from 3,3,7,7-Tetracarbethoxybicyclo[3.3.0]oct-1(5)-ene (XVII).—A solution of 0.52 g. of XVI in 15 ml. of water was treated with excess hydrochloric acid. The precipitated diacylated hydrazine XVII, 0.36 g. (92%), was removed by filtration, washed with water and dried. A sample was washed with absolute ethanol, dried at 80° (0.5 mm.), and analyzed; m.p. >300°.

Anal. Calcd. for $C_{12}H_{12}N_4O_4$: C, 52.17; H, 4.38; N, 20.29. Found: C, 51.84; H, 4.62; N, 20.02.

Evaporation of the mother liquor from XVII to dryness at 100° yielded 0.23 g. (88%) of impure hydrazine dihydrochloride, m.p. 140–190° dec. Recrystallization from ethanol–water gave hydrazine monohydrochloride, m.p. 91–92°. A mixed melting point determination with an authentic sample of hydrazine monohydrochloride was undepressed.

Recrystallization of 0.71 g. of XVII from ethanol which contained hydrazine hydrate gave 0.85 g. (92%) of the hydrated dihydrazine salt XVI, m.p. 206° dec. A mixed melting point determination with XVI prepared from the tetracarboxylic ester and hydrazine as described above was 205.5° dec.

CAMBRIDGE, MASS.

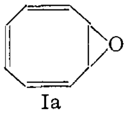
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

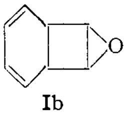
Cyclic Polyolefins. XLIV. The Structure of Cycloöctatetraene Oxide

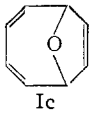
BY ARTHUR C. COPE, PHYLIS T. MOORE[1] AND WILLIAM R. MOORE

RECEIVED APRIL 1, 1958

Cycloöctatetraene oxide has been shown to be a 1,2- rather than a 1,4-oxide by chemical means, and to contain an unbridged eight-membered ring by its nuclear magnetic resonance spectrum.


Ia


Ib


Ic

Three structures (Ia, Ib and Ic) have been proposed for cycloöctatetraene oxide (I). The formation of cycloöctanol from the catalytic hydrogenation of I led Reppe, Schlichting, Klager and Toepel[2] to propose structure Ia. Friess and Boekelheide[3] have proposed structure Ib which they believed to be in agreement both with the ultraviolet absorption spectrum of I (λ_{max} 241mμ, log ϵ 3.60) and the absorption of only one mole of hydrogen by the maleic anhydride adduct of I. Cope and Tiffany favored structure Ia for I,[4] and pointed out that the absorption of only one mole of hydrogen by the maleic anhydride adduct of I does not exclude structure Ia since bridging as well as addition could occur in the formation of the

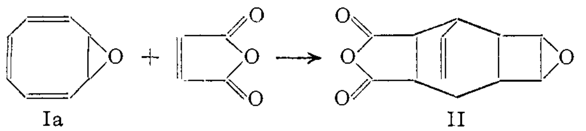
---

(1) National Science Foundation Fellow, 1955–1957.

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

(3) S. L. Friess and V. Boekelheide, THIS JOURNAL, **71**, 4145 (1949).

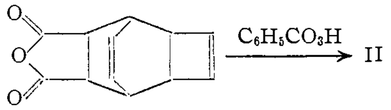
(4) A. C. Cope and B. D. Tiffany, *ibid.*, **73**, 4158 (1951).



Ia II

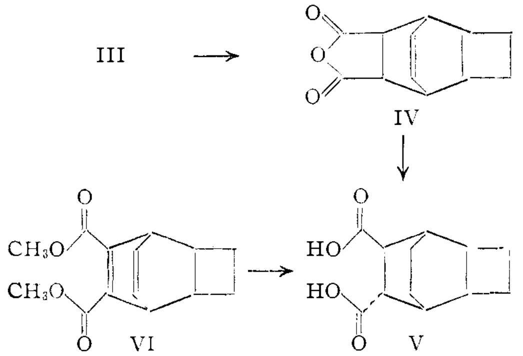
Diels–Alder adduct. Such bridging would be analogous to that which occurs in the formation of Diels–Alder adducts of cycloöctatetraene[2] and 1,3,5-cycloöctatriene.[5] Wheeler[6] has suggested that the ultraviolet absorption spectrum of I supports structure Ic and not Ib.

This paper presents experimental evidence excluding structures Ib and Ic and supporting Ia as the structure of I. The elimination of Ic as a possible structure of I was accomplished in the following manner. The maleic anhydride adduct of cycloöctatetraene was converted in good yield (91% crude, 66% pure) to its monoepoxide, II, by treatment with perbenzoic acid. The epoxide II was shown to be identical with the product of the



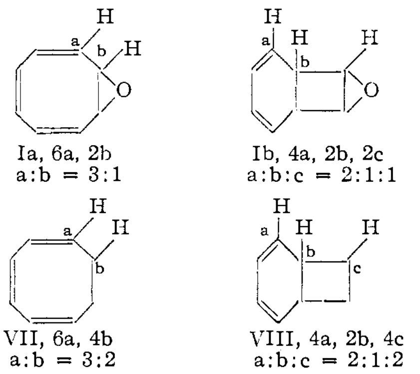
III

Diels–Alder reaction of cycloöctatetraene oxide (I) with maleic anhydride. This identity was established by comparison of infrared spectra and mixed melting points of samples of II prepared by the two routes. The adduct III has been converted to the maleic anhydride adduct of 1,3,5-cycloöctatriene, (IV) by hydrogenation.[5] The same *trans*-dicarboxylic acid V has been obtained from both IV and the dimethyl acetylenedicarboxylate adduct of 1,3,5-cycloöctatriene (VI).[5] Since conclusive evi-



dence for the presence of a cyclobutane ring in VI has been obtained (through pyrolysis of VI with formation of dimethyl phthalate and cyclobutene),[5] the *trans*-acid V and adducts II, III and IV all must possess a bicyclo[4.2.0]octane (or octene) ring. Since the maleic anhydride adduct of Ic could not have such a structure, it is eliminated.

Nuclear magnetic resonance spectra were employed to decide between structures Ia and Ib for I. Structure Ia has six vinyl and two allylic hydrogen atoms (attached to the carbon atoms bridged by the oxygen atom). The nuclear magnetic resonance spectrum of a compound possessing structure Ia should exhibit two main resonance peaks, the areas of which should be in the ratio of 3 to 1 (vinyl to allylic or a:b in Fig. 1). Structure Ib, which has four vinyl, two allylic (bridgehead) and two paraffinic hydrogen atoms (attached to the carbon atoms of the ethylene oxide ring), should have three main resonance peaks in its nuclear magnetic resonance spectrum; the areas under these three peaks would be expected to be in the ratio of 2:1:1 (a:b:c in Fig. 1). The experimentally determined nuclear magnetic resonance spectrum of cycloöctatetraene oxide (I) contains only two main resonance peaks, the areas of which are in the ratio of 3 to 1. Thus both the number of resonance peaks (two) and the area ratio (3 to 1) are evidence which supports Ia as the correct structure of I. The possibility that I has structure Ib and that two of the resonance peaks in its nuclear magnetic resonance spectrum coincide seems unlikely. An area ratio of 1 to 1 would be anticipated if the peaks corresponding to the allylic tertiary hydrogen atoms (type b in Fig. 1) and the tertiary hydrogen atoms attached to the epoxide ring (type c in Fig. 1) were not resolved. The overlap of the peak due to the allylic tertiary hydrogen atoms with the one ascribed to the vinyl hydrogen atoms (which would lead to the observed area ratio of 3 to 1) seems to be precluded by our study of proton chemical shifts in similar compounds (Table I).



Ia, 6a, 2b
a:b = 3:1

Ib, 4a, 2b, 2c
a:b:c = 2:1:1

VII, 6a, 4b
a:b = 3:2

VIII, 4a, 2b, 4c
a:b:c = 2:1:2

Fig. 1

The nuclear magnetic resonance spectra of 1,3,5-cycloöctatriene (VII) and bicyclo[4.2.0]octa-2,4-diene (VIII) were studied since these compounds possess structures quite similar to Ia and Ib. The spectra of both of these model compounds were in complete agreement with the spectra predicted for structures VII and VIII. The spectrum of 1,3,5-cycloöctatriene contains two main peaks, the area ratio (vinyl to allylic or a:b in Fig. 1) of which is 3 to 2. The nuclear magnetic resonance spectrum of bicyclo[4.2.0]octa-2,4-diene possesses three main resonance peaks with the area ratio (a:b:c in Fig. 1) of 2:1:2. The values of the proton chemical shifts and the theoretical and observed area ratios are summarized in Table I.

Experimental[7]

Nuclear Magnetic Resonance Spectra.—A Varian Associates V-4300-B high resolution spectrometer was used at a frequency of 40 Mc. Chemical shifts were measured with reference to a sealed Pyrex capillary filled with water and

---

(5) A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

(6) O. H. Wheeler, *ibid.*, **75**, 4858 (1953).

(7) All melting points were determined on a Kofler hot-stage. The infrared spectra were determined with a Baird double beam infrared recording spectrometer, model B, fitted with a sodium chloride prism.

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Proton chemical shifts, cycles/sec. Vinyl (a, Fig. 1)	Allylic (b, Fig. 1)	Paraffinic (c, Fig. 1)	Area ratios Calcd.	Obsd.
VII	39	−98		a:b = 3:2	a:b = 3:2
VIII	32	−96.5	−74	a:b:c = 2:1:2	a:b:c = 2:1:2
Ia	48	−56		a:b = 3:1	a:b = 3:1

placed inside the 5-mm. Pyrex tube containing the sample. The proton chemical shifts were measured by the method of superimposing audio-frequency sidebands from a calibrated Hewlett Packard 200-I oscillator, giving a precision of about ±2 c.p.s. The chemical shifts were determined for 1, 5 and 20% (by volume) solutions of the compounds in carbon tetrachloride and extrapolated to infinite dilution. The observed area ratios were determined with a precision of about 10%. We are indebted to Professor John S. Waugh for the determination of the nuclear magnetic resonance spectra.

Maleic Anhydride Adduct of Cycloöctatetraene Oxide (II). A. Epoxidation of Maleic Anhydride Adduct of Cycloöctatetraene (III).—To a solution of 0.50 g. of III[2] in 7 ml. of dry chloroform at 5° was added a solution of 0.44 g. of perbenzoic acid in 13.3 ml. of benzene. The reaction flask was swirled briefly and then placed in a refrigerator (5°) for the entire reaction period.

The progress of the reaction was followed by titration. Aliquots (0.50 ml.) were removed from the reaction flask periodically and treated with 2 ml. of an aqueous solution of potassium iodide to which an excess of glacial acetic acid had been added. The amount of iodine which was liberated by the peracid in each aliquot was determined by titration with a standard solution of sodium thiosulfate. The epoxidation proceeded very slowly and was stopped after 400 hours when 102% of one equivalent of perbenzoic acid had been consumed.

The white crystalline solid which had precipitated during the reaction period was collected and washed with a small amount of cold chloroform. The product thus obtained weighed 0.27 g. (m.p. 207–208°). The filtrate and washings from this solid were placed in a separatory funnel and washed with two 5-ml. portions of a saturated aqueous solution of sodium bisulfite followed by two 5-ml. portions of a saturated aqueous solution of sodium bicarbonate and finally with 5 ml. of water. The organic layer was dried over anhydrous sodium sulfate. Distillation of the organic solvent under reduced pressure afforded an additional 0.17 g. of product (m.p. 185–202°) as the crystalline residue. The total yield of crude product was 0.44 g. or 91% (yield corrected for aliquots removed for titration). Recrystallization of the crude product from a benzene–ligroin mixture (2:1) afforded 0.31 g. (66%) of II as white needles (m.p. 208.5–209.5°).

B. Addition of Maleic Anhydride to Cycloöctatetraene Oxide.—This preparation was carried out as described by Reppe, Schlichting, Klager and Toepel[2]; the product obtained melted at 209.5–210.0°. No depression in melting point was observed when a sample of II prepared by this method was mixed with II prepared by method A. The infrared spectrum of II (in potassium bromide) from this method was identical with that of II prepared by method A.

Nuclear Magnetic Resonance Samples.—Cycloöctatetraene oxide (I) was prepared by the method described in ref. 4 and had n^{25}_{D} 1.5380 (lit.[4] n^{25}_{D} 1.5383). 1,3,5-Cycloöctatriene (VII) was prepared by the procedure given in ref. 5, and had n^{25}_{D} 1.5243 (lit.[5] n^{25}_{D} 1.5249). Bicyclo[4.2.0]octa-2,4-diene (VIII) was prepared as described in ref. 5 and had n^{25}_{D} 1.5041 (lit.[5] n^{25}_{D} 1.5035). The purity of these hydrocarbons was ascertained by gas chromatography on a column (200 × 0.6 cm.) containing 25% (by weight) tetrahydroxyethylethylenediamine on 48–100 mesh firebrick. The column temperature was 60° and the preheater temperature was kept at 65° to avoid thermal isomerization. Helium at 10.1 p.s.i.g. and a flow rate of 100 ml. per min. was employed as the carrier gas; a thermal conductivity cell was used as a detector. By increasing the preheater temperature it was possible to obtain mixtures of bicyclo[4.2.0]octa-2,4-diene and 1,3,5-cycloöctatriene from pure 1,3,5-cycloöctatriene. The maximum amount of diene (20%) was obtained with a preheater temperature of 250° (column temperature 60°, flow rate 100 ml./min.). The presence of a small amount (less than 1%) of a thermally stable compound, probably 1,3,6-cycloöctatriene, in the samples of 1,3,5-cycloöctatriene (n^{25}_{D} 1.5243) was detected in these studies.

CAMBRIDGE, MASS.

[CONTRIBUTION NO. 2316 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small-ring Compounds. XX. 1,3-Dimethylenecyclobutane and Related Compounds[1]

BY FREDERICK F. CASERIO, JR., STUART H. PARKER,[2] RICHARD PICCOLINI AND JOHN D. ROBERTS

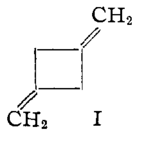
RECEIVED MAY 2, 1958

1,3-Dimethylenecyclobutane and 1-methyl-3-methylenecyclobutene have been synthesized by way of 3-methylenecyclobutanecarboxylic acid and (3-methylenecyclobutylcarbinyl)-dimethylamine. No clear experimental evidence was obtained for π-type electronic interaction across the ring of 1,3-dimethylenecyclobutane.

Introduction

The simple molecular-orbital (LCAO) method predicts a delocalization energy of about 0.066 β for cross-ring π-type electronic interaction in the 1,3-dimethylenecyclobutane (I) molecule if the 1,3-resonance integral is taken to be $\beta/3$. The objective of the present research was to synthesize I to see if evidence for such cross-ring interaction could be gained from studies of its chemical behavior and physical properties.

Synthesis of 1,3-Dimethylenecyclobutane and 1-Methyl-3-methylenecyclobutene.—A one-step synthesis of I through dimerization of allene is theoretically possible, but in practice only the 1,2-


I

dimethylenecyclobutane appears to be formed.[3] However, 3-substituted methylenecyclobutanes such as would be appropriate for conversion to I and related compounds, are readily available by the elegant cycloadditions of monosubstituted alkenes to allene developed by Cripps and co-

---

(1) Supported in part by the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is hereby made to the Donors of this Fund.

(2) Fellow of the Foreign Research Scientists Program, 1954–1956.

(3) S. Lebedev, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); *Chem. Zentr.*, **85**, 1402 (1914).