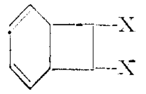
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XIX. Chloro- and Bromocyclooctatetraenes[1a]

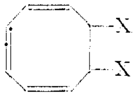
BY ARTHUR C. COPE AND MARION BURG[1b]

Cycloöctatetraene dichloride (I) and dibromide (II) have been isolated as low melting solids, m.p. 2.3° and 34.0–34.8°. Evidence supporting the bridged-ring structure I for the dichloride was obtained by oxidation to 3,4-dichloro-*cis*-1,2-cyclobutanedicarboxylic acid. Dehydrohalogenation of I and II by treatment with phenyllithium was accompanied by reopening of the bridged ring, and formed chlorocycloöctatetraene (V, 26%) and bromocycloöctatetraene (VI, 33%), respectively. The structures of V and VI were established by their quantitative hydrogenation with the absorption of five molar equivalents of hydrogen, forming cycloöctane. Bromocycloöctatetraene was isomerized to β-bromostyrene by heating for one-half hour at 90–103°. Chlorocycloöctatetraene proved to be more stable, but was isomerized to β-chlorostyrene by heating for two hours at 200–210°.

The chemical reactions reported for cycloöctatetraene dichloride (prepared from the hydrocarbon and sulfuryl chloride or chlorine) and for cycloöctatetraene dibromide[2] indicate that these compounds have the bridged-ring structures I and II.[3] In the present work both of the dihalides have been obtained as low-melting solids; the dichloride I melts at 2.3°, and the dibromide II at 34.0–34.8°. Accordingly, it is probable that the pure dihalides have unique structures, rather than being components of a tautomeric equilibrium (I and II $\rightleftarrows$ III).[4] The ultraviolet absorption spectra of I and II (Fig. 1) are very similar to the spectrum of 1,3,5-cycloöctatriene[5]; for I, $\lambda_{max.}$ 270 mμ; II, $\lambda_{max.}$ 270 mμ; 1,3,5-cycloöctatriene, $\lambda_{max.}$ 265 mμ. However, the absorption maximum of 1,3-cyclohexadiene occurs at 258 mμ, sufficiently close to the maxima observed for I and II to make difficult a choice between these bridged-ring structures and alternate unbridged structures, III.



I, X = Cl
II, X = Br



III

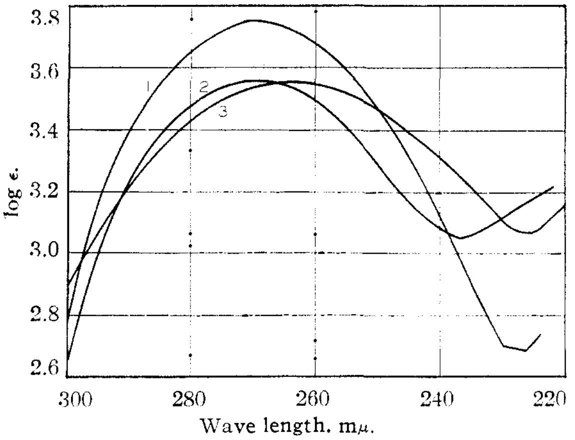
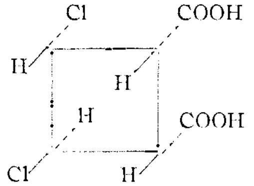
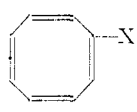


Fig. 1.—Ultraviolet absorption spectra: curve 1, cycloöctatetraene dichloride (I); curve 2, cycloöctatetraene dibromide (II); curve 3, 1,3,5-cycloöctatriene (ref. 5).

Additional chemical evidence supporting structure I for cycloöctatetraene dichloride has been obtained by its conversion into 3,4-dichloro-*cis*-1,2-cyclobutanedicarboxylic acid (IV), both by oxidation with potassium permanganate in acetone and by ozonization. The structure of IV was established by catalytic hydrogenation in the presence of Raney nickel in alkaline solution, which formed *cis*-1,2-cyclobutanedicarboxylic acid, m.p. 139°.[6]



IV



V, X = Cl
VI, X = Br

Oxidation of structure III would be expected to form *dl*-α,α′-dichlorosuccinic acid, which by coincidence has a melting point similar to IV.[7]

Investigation of the dehydrohalogenation of the cycloöctatetraene dihalides I and II showed that under certain conditions chlorocycloöctatetraene (V) and bromocycloöctatetraene (VI) were formed. The reaction of I and II with phenyllithium[8] at low temperatures formed V and VI in yields of 26 and 33%, respectively. Other bases which reacted with I to give V were lithium diethylamide (26% yield) and lithium 2,6-dimethylpiperidide (11%). The product obtained with these bases was not easily purified by distillation. Powdered potassium hydroxide and I yielded a mixture of V and β-chlorostyrene. Dehydrohalogenation of II with lithium diethylamide gave yields of VI comparable with those obtained with phenyllithium. Possible interpretations of the dehydrohalogenation of I and II yielding V and VI are the displacement of a proton by the base (such as occurs in the reaction of

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(1) (a) Presented at the Twelfth National Organic Chemistry Symposium, Denver, Colorado, June 14, 1951. Paper XVIII, THIS JOURNAL, **73**, 4158 (1951). (b) Sharp and Dohme Research Associate.

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

(3) A way in which bridging could occur during addition of the halogens has been suggested by S. L. Friess and V. Boekelheide, THIS JOURNAL, **71**, 4145 (1949).

(4) The possibility that cycloöctatetraene can form an isomeric bridged-ring structure is discussed in ref. 2, and by K. Ziegler and H. Wilms, *Ann.*, **567**, 26 (1950).

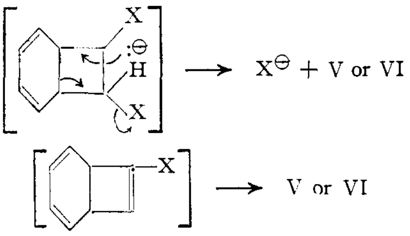
(5) A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

(6) Identified by direct comparison with an authentic sample kindly furnished by Dr. E. R. Buchman; E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, *ibid.*, **64**, 2696 (1942).

(7) The melting point of IV was 176.8–178° (dec.), while R. Kuhn and T. Wagner-Jauregg, *Ber.*, **61**, 501 (1928), report m.p. 170–172° (dec., cor.) for *dl*-α,α′-dichlorosuccinic acid and G. Aminott, *Arkiv Kemi, Mineral. Geol.*, **7**, No. 9, 5 (1918), reports m.p. 174–175° (dec.). The chlorine atoms in IV should be *trans*, from *trans* addition to a double bond, and for the same reason a dichlorosuccinic acid derived from III should be the *dl*-isomer.

(8) Used for the dehydrohalogenation of 1,2-dihalides by G. Wittig and G. Harborth, *Ber.*, **77B**, 306 (1944).

ethylene dichloride with phenyllithium[8]), followed by reversal of the bridging process.



VII

Alternately, a bridged triene structure (VII) could be formed from I and II, and V and VI could be produced by isomerization of VII. Another case in which the cycloöctatetraene nucleus is formed from the dichloride I is its reaction with sodium iodide, which yields the parent hydrocarbon, cycloöctatetraene.[9]

Chlorocycloöctatetraene and bromocycloöctatetraene were isolated as yellow and orange-yellow liquids, respectively. Their ultraviolet absorption spectra (Fig. 2) are similar to the spectrum of cycloöctatetraene. Infrared absorption spectra of V and VI, together with the spectra of the dihalides I and II, are shown in Fig. 3. Evidence establishing the structures of V and VI was obtained by catalytic hydrogenation in the presence of Adams platinum catalyst in acetic acid containing sodium acetate; V absorbed 98.6% and VI absorbed 98.5% of five molar equivalents of hydrogen, and the reduction product isolated in each case was cyclooctane.

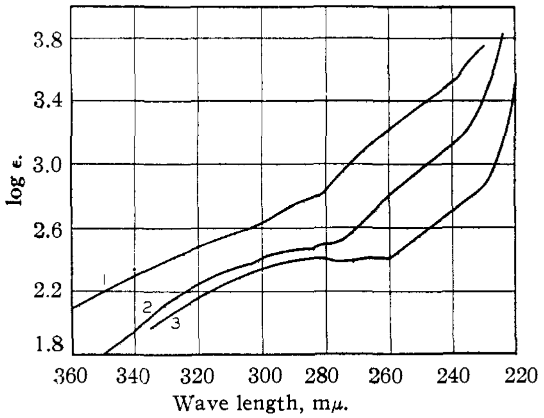


Fig. 2.—Ultraviolet absorption spectra: curve 1, bromocycloöctatetraene (VI); curve 2, chlorocycloöctatetraene (V); curve 3, cycloöctatetraene.

Several attempted preparations of bromocyclooctatetraene, following the initial successful preparation, yielded β-bromostyrene rather than VI, although apparently identical reaction conditions were used. The difficulty was traced to thermal instability of VI. On heating at 90–103° for one-half hour VI was isomerized into β-bromostyrene, which was identified by comparison of its ultraviolet (Fig. 4) and infrared spectra with the spectra of an authentic sample. Accordingly in the preparation of VI the temperature is kept as low as possible in removal of the solvent and distillation in order to avoid complete or partial isomerization to β-bromostyrene. Chlorocycloöctatetraene undergoes a similar thermal isomerization to β-chlorostyrene, but at a much higher temperature. The structure of β-chlorostyrene prepared by heating V at 200–210° for two hours was determined by its oxidation to benzoic acid with chromic acid, and reduction to ethylbenzene with the absorption of 99.2% of two molar equivalents of hydrogen. The ultraviolet absorption spectrum of β-chlorostyrene formed by

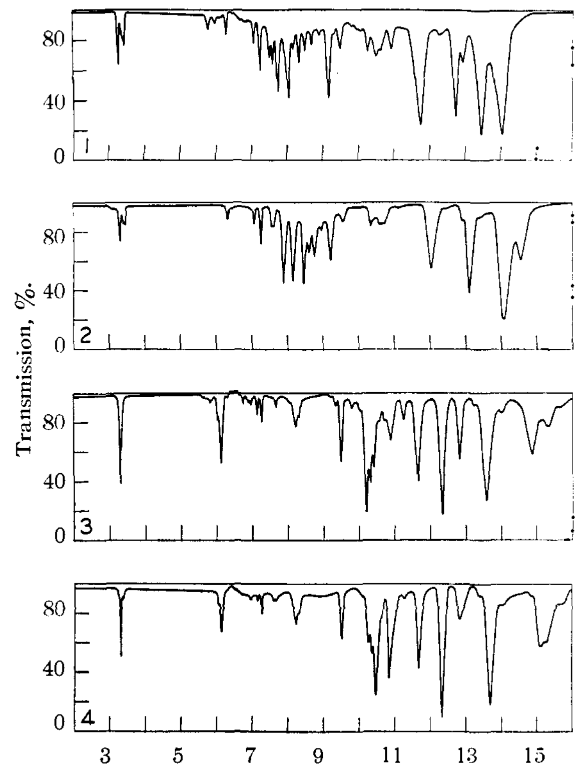


Fig. 3.—Infrared absorption spectra of solutions (100 mg./ml.) in carbon tetrachloride in the region 2–8μ and in carbon disulfide in the region 8–16μ: curve 1, cycloöctatetraene dichloride (I); curve 2, cycloöctatetraene dibromide (II); curve 3, chlorocycloöctatetraene (V): curve 4, bromocyclooctatetraene (VI).

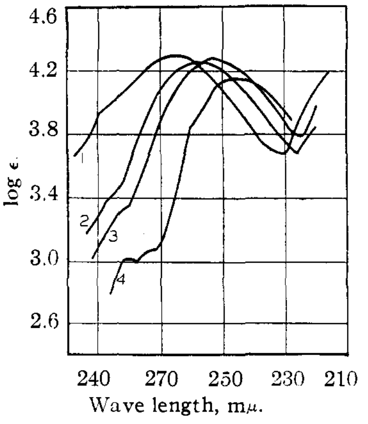


Fig. 4.—Ultraviolet absorption spectra: curve 1, β-iodostyrene (prepared by the method of Wright, ref. 11): curve 2, β-bromostyrene (authentic sample); curve 3, β-chlorostyrene (obtained by the procedure of Biltz, ref. 10); curve 4, styrene.

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(9) R. E. Benson and T. L. Cairns, THIS JOURNAL, **72**, 5355 (1950).

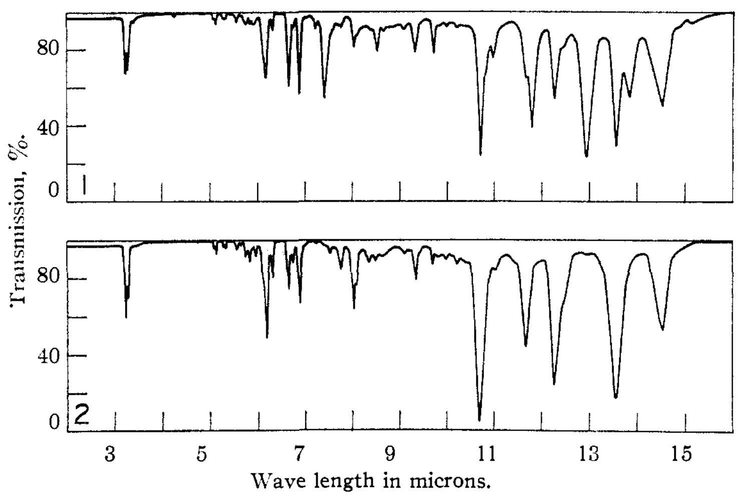

Fig. 5.—Infrared absorption spectra of solutions (100 mg./ml.) in carbon tetrachloride in the region 2–8μ and in carbon disulfide in the region 8–16μ: curve 1, β-chlorostyrene prepared by the procedure of Biltz (ref. 10); curve 2. *cis*-β-chlorostyrene obtained by rearrangement of V.

rearrangement of V was practically identical with the spectrum of an authentic sample prepared by the procedure of Biltz[10] (Fig. 4). However, the β-chlorostyrene formed from V had a higher refractive index (n^{25}D 1.5762), and there were significant differences in the infrared spectra of the two samples (Fig. 5). Comparison of the infrared spectrum of β-chlorostyrene formed from V with the spectrum of α-chlorostyrene established the fact that they were different. The only interpretation of these facts consistent with all of these data appears to be that β-chlorostyrene formed by rearrangement of V and by the procedure of Biltz differ stereochemically. Since a procedure analogous to the one used by Biltz for the preparation of β-chlorostyrene has been reported to yield *trans*-β-bromostyrene,[11] the isomer formed from V is tentatively designated as the *cis* form. The infrared spectrum of β-chlorostyrene prepared by the procedure of Biltz indicated that it was a mixture of that form and a larger amount of the other (presumably *trans*) geometric isomer. The isomer of β-chlorostyrene formed from V was heated with phosphorus pentachloride; the infrared spectrum of the product indicated that this treatment converted it into a mixture of the *cis* and *trans* forms.

It was of interest to compare the thermal stability of cycloöctatetraene with the stabilities of its chloro- and bromo-derivatives, V and VI. When samples of cycloöctatetraene were heated for one-half hour in sealed tubes under nitrogen in the presence of picric acid as a polymerization inhibitor at 185, 220 and 250°, the recovery of cycloöctatetraene was 80, 40 and 10%, respectively, the remainder being transformed into higher boiling material (presumably dimers and higher polymers). No cycloöctatetraene was recovered from a sample heated at 280° for one hour. Examination of the infrared spectra of the recovered cycloöctatetraene samples for the absorption band of styrene at 11.0 μ showed no detectable amount of styrene in the samples heated at 185 and 220°, and 3% in the sample heated at 250°. This small amount of styrene (corresponding to 0.3% of the original sample) might have been present in the original cycloöctatetraene sample and escaped detection, but a more likely interpretation is that cycloöctatetraene rearranges to some extent to styrene at 250°, but the styrene fails to appear in the product as such to an appreciable extent because it is largely converted into polymers or other high-boiling reaction products at the high temperature required for rearrangement.

Before the ease with which V and VI (particularly bromocycloöctatetraene) are isomerized to β-halostyrenes was known, an attempt was made to convert V into iodocycloöctatetraene by treatment with sodium iodide in boiling acetone. The product, which was isolated in 72% yield, was β-iodostyrene. The identity of the product was established by comparison of the ultraviolet (Fig. 4) and infrared spectrum with the spectrum of an authentic sample.[12] Since V is stable at the reaction temperature employed, the rearrangement forming β-iodostyrene is presumed to occur during the reaction with sodium iodide, or by isomerization of iodocycloöctatetraene.

Study of the properties and reactions of the halogen-substituted cycloöctatetraenes is being continued.

Experimental[13]

Cycloöctatetraene Dichloride (I).—A solution of 86 g. (0.82 mole) of cycloöctatetraene[14] in 200 ml. of carbon tetrachloride was placed in a 1-l. three-necked flask fitted with an efficient stirrer, a 300-ml. graduated separatory funnel to which was attached a condenser cooled with Dry Ice and trichloroethylene, and a two-armed tube through which a low temperature thermometer extended into the liquid. The other arm of the tube was connected to a calcium chloride tube. The solution was stirred and cooled to −30° with a bath containing Dry Ice and trichloroethylene, and a solution of 64.5 g. (0.91 mole) of dry chlorine in 200 ml. of carbon tetrachloride (prepared at −20°) was added through the dropping funnel during a period of 1.5 hours at a reaction temperature of −25 to −35°. The mixture was stirred at that temperature for 1 hour longer and then allowed to come to room temperature under an atmosphere of dry nitrogen. The solvent was removed under reduced pressure and the residue was flash distilled, separating 25 g. of a brown viscous residue from 127 g. of the crude dichloride, which was collected in a receiver cooled with Dry Ice as a colorless liquid, b.p. 66–72° (1.6 mm.). Redistillation through a 20 × 1.5-cm. Vigreux column separated a small fore-run from 111 g. (78%) of I, b.p. 73–74° (2.7 mm.), n^{25}D 1.5388, $d^{25}{}_4$ 1.2514, freezing point −1.4°.

Anal. Calcd. for $C_8H_8Cl_2$: C, 54.89; H, 4.60; Cl, 40.51. Found: C, 54.88; H, 4.76; Cl, 40.24.

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(10) H. Biltz. *Ann.*, **296**, 266 (1897); b.p. 60° (4.1 mm.), n^{25}D 1.5732, $d^{25}{}_4$ 1.1031.

(11) C. Dufraisse, *Compt. rend.*, **171**, 960 (1920); A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 608 (1928); G. F Wright, *J. Org. Chem.*, **1**, 457 (1936).

(12) Prepared by the method of Wright (ref. 11); b.p. 81.5° (1.25 mm.), n^{25}D 1.6598.

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

(14) A. C. Cope and L. L. Estes, Jr., THIS JOURNAL, **72**, 1129 (1950).

Three recrystallizations of I from ether raised the freezing point to a constant value of 2.3°; n^{25}D 1.5382. The ultraviolet absorption spectrum of the recrystallized sample (Fig. 1, curve 1) contained a maximum at 270 mμ (ϵ 5640) and a minimum at 226 mμ (ϵ 490). The infrared spectrum of I (m. p. 2.3°) is shown in Fig. 3, curve 1. The dichloride could be stored under nitrogen at −80°, but as previously noted[2] formed a solid dimer on standing at room temperature.

Oxidation of I to 3,4-Dichloro-*cis*-1,2-Cyclobutanedicarboxylic Acid (IV).—A solution of 83 g. (0.53 mole) of potassium permanganate in 400 ml. of water and 1 l. of acetone was cooled to 3° in an ice-bath. A solution of 10 g. (0.057 mole) of the dichloride I in 100 ml. of acetone was added with stirring over a period of 45 minutes at 3–5°. Stirring at that temperature was continued for 8 hours, after which the mixture was allowed to stand at room temperature for 33 hours. Excess permanganate was decomposed by addition of aqueous sodium bisulfite, and the manganese dioxide was separated by filtration and washed with aqueous acetone. The acetone was distilled fron the filtrate under reduced pressure and the aqueous residue was concentrated to half its original volume at 1 mm. without heating. The basic solution was washed with ether, acidified with hydrochloric acid to *p*H 3, and extracted with twelve 25-ml. portions of ether. The ethereal solution was dried over magnesium sulfate, concentrated, and the residual oil was crystallized by allowing it to stand at 1 mm. overnight. Two recrystallizations from a mixture of dry ether and 30–60° petroleum ether yielded 4.3 g. (35%) of IV, m. p. 176.8–178° (dec.).[15]

Anal. Calcd. for $C_6H_6O_4Cl_2$: C, 33.83; H, 2.84; Cl, 33.29; neut. equiv., 106.5. Found: C, 33.68; H, 3.08; Cl, 33.26; neut. equiv., 107.

A sample of IV identical with the one described above in melting point, mixed melting point, analysis and infrared absorption spectrum (nujol mull) was obtained from I in 35% yield by ozonization. A stream of oxygen and ozone delivering 25 mg. of ozone per minute was passed through a solution of 1 g. of I in 20 ml. of ethyl acetate at −60° for 35 minutes. The solution of the ozonide was hydrogenated in the presence of 10% palladium-on-Norit for 30 minutes while cooled with Dry Ice and for 30 minutes after removing the Dry Ice. The catalyst was separated, and the filtrate was added during a period of 10 minutes with stirring to a solution of 3.62 g. of potassium permanganate and 2.04 g. of magnesium sulfate in 200 ml. of water. The mixture was stirred for 4 hours and allowed to stand for 11 hours, after which the acid IV (0.38 g.) was isolated by the procedure described above.

Hydrogenation of a solution of 426 mg. of the acid IV in 4 ml. of water containing 0.80 g. of sodium hydroxide at room temperature and atmospheric pressure in the presence of 0.5 g. of W-7 Raney nickel[16] was complete in 24 hours and required 97% of two molar equivalents of hydrogen. The catalyst was separated, washed with water, and the filtrate was acidified to *p*H 3 with hydrochloric acid, with cooling in ice. Analytically pure *cis*-1,2-cyclobutanedicarboxylic acid, m.p. and mixed m.p. with an authentic sample[6] 139°, was isolated in low yield (25 mg. or 7.7%) by extraction with ether and re-extraction into sodium bicarbonate solution, which was acidified and again extracted with ether. Concentration of the ethereal solution left an oil which was dissolved in an equal volume of water. Crystals formed when the solution was concentrated at 50°, and recrystallization from a mixture of ether and 30–60° petroleum ether yielded the pure acid. Infrared absorption spectra of nujol mulls of *cis*-1,2-cyclobutanedicarboxylic acid derived from IV and the authentic sample[6] were identical.

Cycloöctatetraene Dibromide (II).—A solution of 81 g. (0.51 mole) of bromine in 100 ml. of methylene chloride was added with stirring over a period of 1.5 hours to 52 g. (0.5 mole) of cycloöctatetraene in 150 ml. of methylene chloride at a temperature of −15 to −8°. The crude dibromide was isolated in the same way as the dichloride I, and solidified on standing at −80°. Two recrystallizations from pentane followed by drying over paraffin for 6 hours at 20° or lower (some decomposition occurred at higher temperatures) yielded 111 g. (84%) of the dibromide II as a cream colored crystalline solid, m.p. 34.0–34.8°.

Anal. Calcd. for $C_8H_8Br_2$: C, 36.40; H, 3.05; Br, 60.55. Found: C, 36.41; H, 3.07; Br, 60.44.

The dibromide II decomposed fairly rapidly on standing at room temperature, and was stored under nitrogen at −80°. Its ultraviolet spectrum (Fig. 1, curve 2) showed a maximum ($\lambda_{\max}$ 270 mμ, ϵ 3640) and a mimimum ($\lambda_{\min}$ 236 mμ, ϵ 1134). The infrared spectrum of II is shown in Fig. 3, curve 2.

In ref. 2, p. 18, confirmation is reported of an earlier observation[17] of the formation of a dibromide with melting point of 71° from cycloöctatetraene and bromine in chloroform at −20°. No dibromide melting at 71° was encountered in this work, but it was found that styrene and bromine reacted in chloroform at −20° to give a dibromide with m.p. 72.4–73°. Since cycloöctatetraene may contain variable amounts of styrene,[18] the dibromide melting at 71° reported in refs. 2 and 17 may have been styrene dibromide. Reference 17 reports that the dibromide melting at 71° reacted with bromine with the evolution of hydrogen bromide, forming a tribromide ($C_8H_7Br_3$) melting at 53–55°, which may have been impure *p*-bromostyrene dibromide (reported m.p. 60°).[19]

Chlorocycloöctatetraene (V).—A solution of 0.111 mole of phenyllithium[20] in 270 ml. of ether was prepared under nitrogen in a 500-ml. two-necked flask containing an outlet closed by a stopcock at the bottom. A solution of 17.5 g. (0.1 mole) of cycloöctatetraene dichloride in 100 ml. of dry ether was placed under nitrogen in a 500-ml. three-necked flask fitted with a mercury-sealed stirrer, a thermometer extending into the liquid, an outlet attached to a drying tube, and a connection to the bottom outlet of the flask containing phenyllithium. The solution of phenyllithium was added with stirring and cooling during a period of 45 minutes at a reaction temperature of −5 to −2°. During the addition the mixture became turbid and a color change from yellow to red to blue occurred. The mixture was stirred for 3 hours with cooling after the addition was completed, and for 7 hours while the ice–salt-bath warmed to room temperature.[21] Cold water (100 ml.) was added, and the orange–yellow ether layer was washed with four 50-ml. portions of water. The water washings were extracted with 50 ml. of ether, the extract was washed twice with water, and the combined ethereal solutions were dried over magnesium sulfate. The ether was distilled through a packed column and the residue was fractionated through a semi-micro column.[22] The distillation separated a fore-run (0.72 g.), 2.11 g. of higher boiling fractions (b.p. 92–104° at 0.65 mm.), probably containing recovered I, and 5.7 g. of a dark viscous residue from 3.66 g. (26%) of yellow chlorocycloöctatetraene (V), b.p. 51–52° (5.5 mm.), n^{25}D 1.5542, d_4^{25} 1.1199; MD calcd. 39.94, found 39.70.

Anal. Calcd. for C_8H_7Cl: C, 69.33; H, 5.09; Cl, 25.58. Found: C, 69.33; H, 5.37; Cl, 25.26.

The ultraviolet absorption spectrum of V (Fig. 2, curve 2) is quite similar to that of cycloöctatetraene (Fig. 2, curve 3). The infrared absorption spectrum of V is shown in Fig. 3, curve 3.

Hydrogenation of a solution of 200 mg. of V in 3 ml. of glacial acetic acid containing 200 mg. of sodium acetate trihydrate in the presence of 50 mg. of prereduced platinum oxide was complete in 3 hours and required 98.6% of five molar equivalents of hydrogen. Cycloöctane was isolated as the reduction product by a procedure previously described (ref. 5, p. 2517) in a yield of 106 mg., n^{25}D 1.4552. After treatment with silica gel to remove traces of ether the cycloöctane had n^{25}D 1.4560 and m.p. 8–11° (indicating

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[15] The sample was sealed in a melting point tube, which was introduced into a bath 10° below the melting point, and the temperature was increased 2° per minute.

[16] H. Adkins and H. R. Billica, This Journal, **70**, 695 (1948).

[17] R. Willstätter and M. Heidelberger, *Ber.*, **46**, 517 (1913).

[18] A. C. Cope and C. G. Overberger, This Journal, **70**, 1433 (1948).

[19] J. Schramm, *Ber.*, **24**, 1335 (1891).

[20] H. Gilman, E. A. Zoellner and W. M. Selby, This Journal, **55**, 1252 (1933).

[21] There was no significant change in the yield of V when the mixture was decomposed a few minutes after the addition of phenyllithium was completed. When the phenyllithium was added at −30 to −20° and the mixture was hydrolyzed after stirring for 1.5 hours at that temperature the yield of V was reduced to 13%.

[22] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

98.5% purity[5]), and did not depress the melting point of an authentic sample.

Bromocycloöctatetraene (VI).—Phenyllithium (270 ml. of an ethereal solution containing 0.078 mole) was added to a solution of 21 g. (0.078 mole) of cycloöctatetraene dibromide in 100 ml. of dry ether under the conditions described for preparation of V. After the addition was complete the mixture was allowed to stand at −3° for 1 hour, and the product was isolated in the same manner as V. Ether and benzene were removed through a packed column under reduced pressure by warming in a bath at room temperature to 50°. The residue was distilled through a semi-micro column at a low pressure and temperature (to avoid thermal rearrangement); the condenser attached to the column was cooled with ice water, and the receiver also was cooled. The distillation separated a fore-run (5.7 g.), b.p. up to 42° (1.3 mm.), which contained benzene, bromobenzene and a very small amount of cycloöctatetraene from 6.6 g. of crude VI, b.p. 38–42° (1.3 mm.). A higher boiling fraction (3.4 g., b.p. 78–90° at 1.1 mm.) containing cycloöctatetraene dibromide also was collected, and the viscous residue amounted to 2.4 g. Two additional distillations of the crude VI yielded 4.64 g. (33%) of bromocycloöctatetraene, an orange-yellow liquid, b.p. 52.5–53° (1.8 mm.), n^{25}D 1.5870, d^{25}_4 1.4206; *M*D calcd. 42.84, found 43.26.

Anal. Calcd. for C_8H_7Br: C, 52.49; H, 3.85; Br, 43.66. Found: C, 52.59; H, 3.81; Br, 43.33.

In subsequent larger scale preparations of VI the solvent was removed without warming by gradually reducing the pressure to 4 mm. After removal of the fore-run at 0.35 mm. the crude bromocycloöctatetraene was separated from the higher boiling portion by a rapid evaporative distillation at room temperature and 0.05 mm., the distillate being collected in a receiver cooled with Dry Ice and trichloroethylene. The bromocycloöctatetraene was purified by two slow evaporative distillations at room temperature through a 23 × 1.3-cm. water-jacketed Vigreux column after removal of a fore-run at a column temperature of 0–20°.

The ultraviolet absorption spectrum of VI is shown in Fig. 2, curve 1, and its infrared spectrum in Fig. 3, curve 4.

Hydrogenation of a solution of 200 mg. of VI in 4 ml. of acetic acid containing 149 mg. of sodium acetate trihydrate in the presence of 50 mg. of prereduced platinum oxide was complete in 8.5 hours and required 98.5% of five molar equivalents of hydrogen. Cycloöctane was isolated as the reduction product in the manner previously described[5]; n^{25}D 1.4555, m.p. (and mixed m.p. with a known sample) 8.0–11.7° (indicating 99% purity).

Thermal Rearrangement of Chlorocycloöctatetraene (V) **to** *cis*-**β-Chlorostyrene**.—Chlorocycloöctatetraene (1.37 g., n^{25}D 1.5542) and a few milligrams of hydroquinone were heated under reflux in a nitrogen atmosphere for 2 hours in a bath at 200–210°. Distillation of the brown liquid through a semi-micro column yielded 1.25 g. of *cis*-β-chlorostyrene as a colorless liquid with a characteristic fragrant odor; b.p. 59° (3.5 mm.), n^{25}D 1.5762, d^{25}_4 1.1046.

Anal. Calcd. for C_8H_7Cl: C, 69.33; H, 5.09; Cl, 25.58. Found: C, 68.96; H, 5.06; Cl, 25.71.

The ultraviolet absorption spectrum of the *cis*-β-chlorostyrene obtained by the rearrangement described above had a maximum at 254 mμ (ε 16,575) and a minimum at 226 mμ (ε 4,620). A sample of β-chlorostyrene prepared by the procedure of Biltz,[10] n^{25}D 1.5732, also had a maximum at 254 mμ (ε 18,920) and a minimum at 226 mμ (ε 6,115) (Fig. 4, curve 3).

Examination of the infrared spectra of these two samples of β-chlorostyrene showed the presence of strong bands at 11.78 μ and 12.95 μ and weaker ones at 7.4, 11.65 and 13.83 μ for the authentic β-chlorostyrene (Fig. 5, curve 1) and the presence of a strong band at 11.65 μ and the absence of bands at 7.4, 11.78, 12.95 and 13.83 μ for the β-chlorostyrene obtained by the rearrangement of V (Fig. 5, curve 2).

Hydrogenation of a solution of 469 mg. of *cis*-β-chlorostyrene (obtained from V by rearrangement) in 5 ml. of 95% ethanol containing 540 mg. of sodium acetate trihydrate in the presence of 200 mg. of 1% palladium-on-calcium carbonate was complete in 1 hour and required 99.2% of two molar equivalents of hydrogen. The reduction product was isolated by ether extraction from alkaline solution and purified by distillation and passage through a micro column of activated alumina; the yield of ethylbenzene, n^{25}D 1.4923,[25] was 95 mg. Reduction of β-chlorostyrene prepared by the procedure of Biltz in the presence of 10% palladium-on-carbon required 99% of two molar equivalents of hydrogen and yielded ethylbenzene with n^{25}D 1.4927. Both samples of ethylbenzene prepared by reduction and an authentic sample (n^{25}D 1.4930) had identical infrared absorption spectra.

Oxidation of 139 mg. of *cis*-β-chlorostyrene by heating under reflux for 1.5 hours with 2 ml. of 13% sulfuric acid containing 3 millimoles of chromic acid followed by isolation of the product by extraction with ether and sublimation yielded 52 mg. (41%) of benzoic acid, m.p. and mixed m.p. with a known sample 121–123°.

Partial Conversion of *cis*-**β-Chlorostyrene to** *trans*-**β-Chlorostyrene**.—*cis*-β-Chlorostyrene (150 mg., prepared from V by rearrangement) and 3 mg. of phosphorus pentachloride were heated in an atmosphere of nitrogen in a sealed tube for 2 hours at 220–235°. An ethereal solution of the product was washed with water until the washings were neutral, concentrated, and the residue was distilled twice through a semi-micro column. The product was analytically pure β-chlorostyrene, n^{25}D 1.5740, which according to the absorption bands at 7.4, 11.65, 11.78, 12.95 and 13.83 μ was composed of *cis*- and *trans*-β-chlorostyrene.

Thermal Rearrangement of Bromocycloöctatetraene (VI) **to β-Bromostyrene**.—Bromocycloöctatetraene (0.75 g.) and a few milligrams of hydroquinone were heated in a nitrogen atmosphere at 90–103° for 0.5 hour. Distillation of the resulting brown liquid separated a small amount of high-boiling residue from 0.63 g. of analytically pure β-bromostyrene, a very pale yellow liquid with a fragrant odor, b. p. 55–56° (0.65 mm.), n^{25}D 1.6055, $\lambda_{max.}$ 258 mμ (ε 19,220). The properties of an authentic sample of β-bromostyrene (n^{25}D 1.6052) were identical within experimental error with the sample obtained by rearrangement of VI; $\lambda_{max.}$ 258 mμ (ε 18,050) (Fig. 4, curve 2). The infrared spectra of the two samples of β-bromostyrene were essentially identical. Both samples contain minor impurities which were present in smaller amount in the product formed by isomerization of VI.

Reaction of Chlorocycloöctatetraene with Sodium Iodide.—A solution of 1.38 g. of chlorocycloöctatetraene, 1.95 g. of sodium iodide and a few milligrams of hydroquinone in 11 ml. of acetone was heated under reflux in an atmosphere of dry nitrogen for 24 hours. The sodium chloride which separated amounted to 0.547 g. (94%). The acetone solution was added to 225 ml. of water and the orange oil which separated was extracted with ether. The extracts were dried over magnesium sulfate, concentrated, and the residue was distilled twice through a semi-micro column, yielding 1.65 g. (72%) of analytically pure β-iodostyrene, b.p. 74° (1 mm.), n^{25}D 1.6585. The ultraviolet absorption spectrum of the β-iodostyrene prepared by this route ($\lambda_{max.}$ 266 mμ, ε 20,400) was essentially identical with the spectrum of an authentic sample[12] ($\lambda_{max.}$ 264 mμ, ε 19,900) (Fig. 4, curve 1). The infrared spectra of the two samples also were identical within the limits of error except for the presence of a weak band at 6.5 μ for the β-iodostyrene obtained from V.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra plotted in Figs. 1, 2 and 4 were determined with solutions of the compounds in purified cyclohexane[23] using a Beckman model DU quartz ultraviolet spectrophotometer.

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[23] M. E. Maclean, P. J. Jencks and S. F. Acree, *J. Research Natl. Bur. Standards*, **34**, 271 (1945).