ethereal solutions were next extracted with 10% potassium hydroxide until all unreacted diketone had been removed, as indicated by colorless alkaline washings. It was then dried over anhydrous sodium sulfate, filtered and evaporated. The resulting solid material was recrystallized from methanol.

Diketone			I	II	III
Quinoxaline or Schiff base			Schiff	Quinoxaline	Quinoxaline
Color			Yellow	Yellow	Red
M. p., °C.			118	163	214
Molecular formula			$C_{42}H_{38}N_4O_6$	$C_{24}H_{21}N_3O_2$	$C_{24}H_{20}N_4O_4$
Analyses, %	C	Calcd.	72.7	75.0	67.4
		Found	73.0	74.9	67.4
	H	Calcd.	5.5	5.5	4.7
		Found	5.5	5.6	4.7
Mol. wt.		Calcd.	697	384	429
		Found	699	385.5	428.5

The quinoxalines as well as the Schiff base when added to concentrated sulfuric acid produced a dark red coloration.

Summary

1. Herein are reported the preparation and properties of two new chalcones, ethylene oxides and alpha diketones.

2. The introduction of one or two nitro groups into the mesityl nucleus of benzylmesitylglyoxal activates the highly hindered carbonyl or minimizes the ortho effect to the extent that quinoxaline formation occurs.

3. The introduction of a nitro group in the meta position of the phenyl group of benzylmesitylglyoxal does not make possible quinoxaline formation, but leads to the formation of a Schiff base.

WASHINGTON 1, D. C. RECEIVED JANUARY 3, 1950

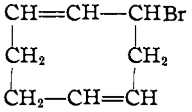
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

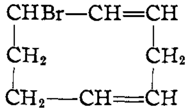
Cyclic Polyolefins. V. Preparation of Bromocycloöctadienes and 1,3,5-Cycloöctatriene from 1,5-Cycloöctadiene[1]

BY ARTHUR C. COPE, CALVIN L. STEVENS[2] AND F. A. HOCHSTEIN

This paper reports results obtained in continuing investigation of the preparation of cyclic polyolefins from the eight-membered cyclic dimer of chloroprene (2-chloro-1,3-butadiene).[3] 1,5-Cycloöctadiene was prepared in 69–74% yield by reduction of the dimer with sodium in liquid ammonia.[3] Careful fractionation of the product and determination of the refractive indices and infrared absorption spectra of the fractions indicated that 1,5-cycloöctadiene prepared in this way was a single pure isomer. Its melting point (−70 to −69°) corresponds to the melting point (−70°) reported by Ziegler and Wilms[4] for the 1,5-cycloöctadiene isomer (probably *cis-cis*) obtained by dimerization of 1,3-butadiene.

Reaction of 1,5-cycloöctadiene (I) with N-bromosuccinimide gave a mixture of monobromocycloöctadienes from which one isomer (II) could be obtained in pure form by low-temperature crystallization from ether (freezing point 0°, $n^{25}D$ 1.5554). Slow fractional distillation converted either the mixture of monobromocyclooctadienes or pure II into a lower boiling liquid isomer, III ($n^{25}D$ 1.5420). When III was heated it was partially reconverted to II; it is presumed that II and III are allylic rather than stereoisomers. Isomer II reacted with lithium aluminum hydride to give 1,5-cycloöctadiene and accordingly is 3-bromo-1,5-cycloöctadiene, unless an allylic rearrangement occurred during the reaction. Isomer III (6-bromo-1,4-cycloöctadiene) gave a mixture of cycloöctadienes on treatment with lithium aluminum hydride. Both isomers had the reactivity characteristic of allylic halides, and were characterized by catalytic hydrogenation to cycloöctane.


II


III

Infrared absorption spectra indicated that III purified by fractional distillation contained some of the isomer with m. p. 0°, II (the infrared absorption curve of II is shown in Fig. 1). It was possible to determine the approximate amounts of II and III present in a mixture of the two from the refractive index of the mixture. A plot of the refractive indices of samples of II (containing varying amounts of isomer III) against the freezing points of the samples was a straight line (Fig. 2), indicating that the solutions were ideal. A plot of the depression in freezing point of II produced by adding bromobenzene against the composition of the mixtures also was linear (Fig. 3). A plot of the composition of mixtures of II and III (determined from the observed freezing points and calculation of the composition from the freezing point depression interpolated from Fig. 3) against the refractive indices of the mixtures was linear (Fig. 4), and extrapolation of the line showed that the refractive index of pure III should be 1.5400. According to these data the sample of III with $n^{25}D$ 1.5420 contained 13% of II.

A mixture containing approximately 40% of II and 60% of III (prepared from I and N-bromosuccinimide) reacted with potassium *t*-butoxide

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[1] Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

[2] du Pont Postdoctorate Fellow, 1947–1948.

[3] Cope and Bailey, THIS JOURNAL, **70**, 2305 (1948).

[4] Ziegler and Wilms, *Naturwissenschaften*, **35**, 157 (1948).

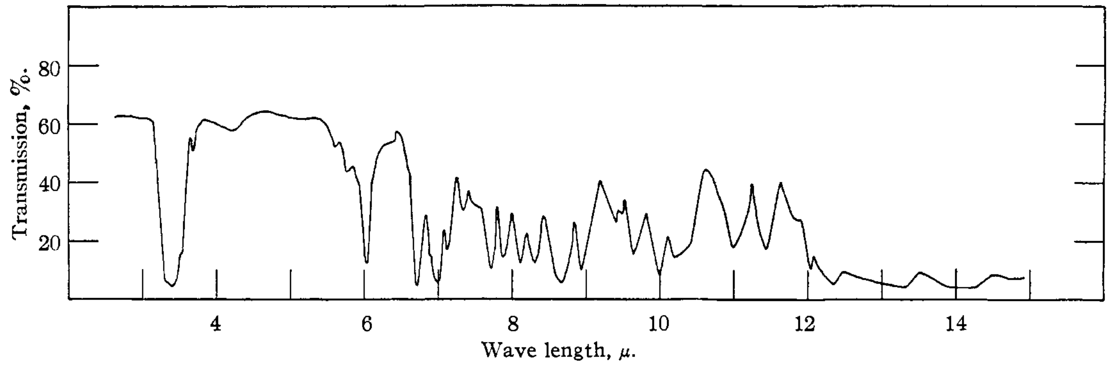


Fig. 1.—Infrared absorption spectrum of 3-bromo-1,5-cycloöctadiene (II).

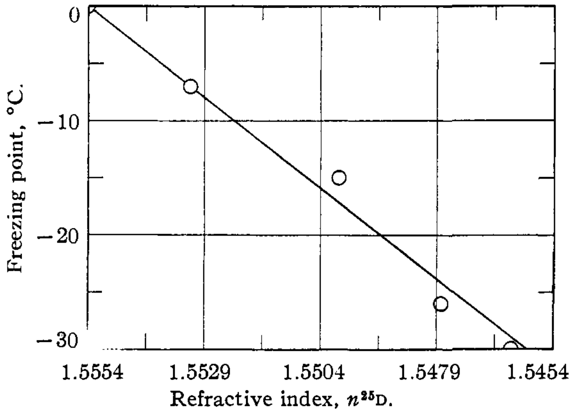


Fig. 2.—Plot of the refractive indices against the freezing points of mixtures of the isomeric monobromocyclooctadienes II and III.

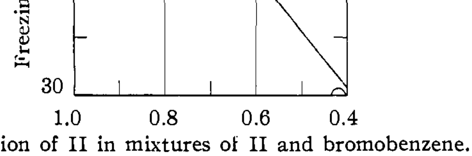


Fig. 3.—Plot showing the depression in freezing point produced by adding bromobenzene to 3-bromo-1,5-cyclooctadiene (II).

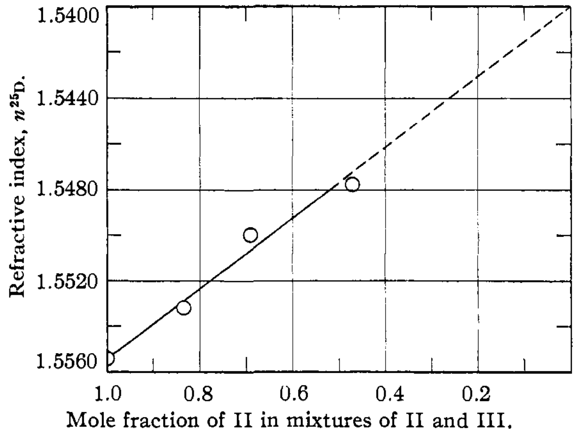
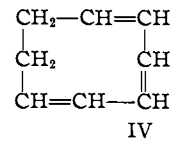


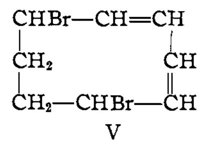
Fig. 4.—Plot showing the relationship of composition to refractive index of mixtures of the monobromocyclooctadienes II and III.

in *t*-butanol to give 1,3,5-cycloöctatriene (IV) in 71% yield. IV prepared in this manner was characterized as the 1,3,5-isomer by the fact that its ultraviolet absorption curve was practically identical with that of 1,3,5-cycloöctatriene prepared from pseudopelletierine.[5] Attempted dehydrogenation of 1,3,5-cycloöctatriene to cyclooctatetraene by reaction with chloroanil failed.

Reaction of 1,5-cycloöctadiene with two molar equivalents of N-bromosuccinimide gave an 86% yield of dibromocycloöctadiene, purified by rapid distillation under reduced pressure. The dibromide had been prepared by this method previously,[3] but was not distilled because of its instability. A solid isomer of the dibromide, m. p. 124–125°, crystallized from the distilled product in 0.5–1.0% yield on storage under nitrogen at −80°. The ultraviolet absorption spectra of the liquid dibromide and a dibromide prepared from 1,3,5-cycloöctatriene by addition of one molar equivalent of bromine were very similar (Fig. 5) and consistent with the conjugated unsaturated structure V, 5,8-dibromo-1,3-cycloöctadiene. This structure also is consistent with the allylic character of both bromine atoms in the distilled dibromide, which reacted with



IV



V

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(5) Cope and Overberger, This Journal, 70, 1433 (1948).

dimethylamine to give the diamine previously designated as 1,6-bis-(dimethylamino)-2,4-cyclooctadiene.[3,5]

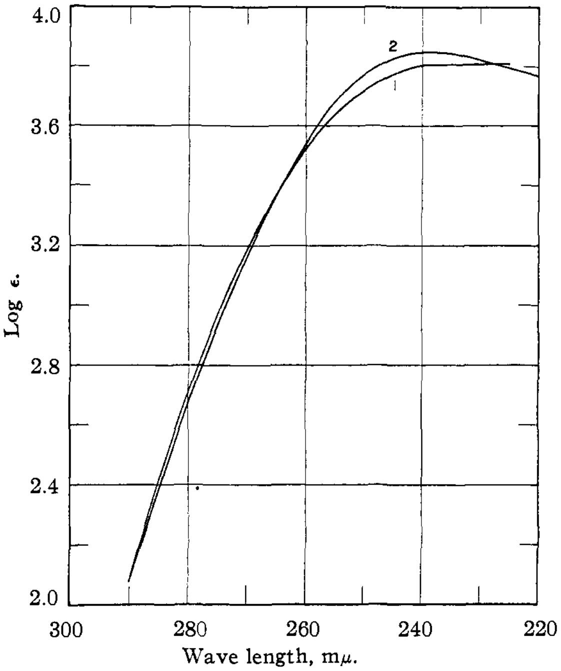

Fig. 5.—Ultraviolet absorption spectra of dibromocyclooctadiene: curve 1, sample prepared from 1,5-cyclooctadiene and N-bromosuccinimide; curve 2, sample prepared from 1,3,5-cycloöctatriene and bromine.

Reduction of V (prepared from I) with lithium aluminum hydride gave a mixture of cyclooctadienes, which was characterized by catalytic hydrogenation to cycloöctane, and catalytic hydrogenation of the dibromide V also yielded cycloöctane. Several attempts to obtain additional information concerning the structures of II, III and V by ozonization were unsuccessful (pure bromoacids were not isolated). The reaction of V with magnesium in ether gave a 53% yield of 1,3,5-cycloöctatriene, identified by its ultraviolet absorption spectrum and by hydrogenation to cycloöctane.

Rapid distillation of the dibromocycloöctadiene (V) at atmospheric pressure caused the elimination of hydrogen bromide and gave a 65% yield of a mixture of isomers with the composition C_8H_9Br. Examination of this mixture showed that it contained α-phenylethyl bromide, identified by conversion to N,N-dimethyl-α-phenylethylamine and α-phenylethyl isothiouronium picrate, and β-phenylethyl bromide, identified as β-phenylethyl isothiouronium picrate. Infrared analysis showed that the mixture contained approximately 50% of α-phenylethyl bromide and 25% of β-phenylethyl bromide. The manner in which V undergoes rearrangement and elimination of hydrogen bromide with the formation of α- and β-phenylethyl bromides is uncertain, but the rearrangement is similar to one which occurs in the reaction of cycloöctatetraene with hydrogen bromide, which according to Reppe, Schlichting, Klager and Toepel[6] yields α-phenylethyl bromide.

Experimental[7]

1,5-Cycloöctadiene (I).—The procedure previously described[3] for the preparation of I was modified as follows. A dry 5-l. three-necked flask was equipped with a stirrer, dropping funnel and a low temperature thermometer. Liquid ammonia (3 l.) was introduced into the flask, followed by 39.3 g. of sodium. The solution was protected from atmospheric moisture with a soda-lime tube, cooled to −75° with a Dry Ice-acetone-bath, and a solution of 75 g. of dichloro-1,5-cycloöctadiene[3,8] in 100 ml. of ether cooled to 0° (cooling to a lower temperature caused crystallization of the dichlorocycloöctadiene) was added with vigorous stirring in a period of one and one-half minutes, during which time the temperature rose from −75 to −35°. The mixture was stirred for one minute; then 80 g. of solid ammonium nitrate was added in a period of one-half to one minute, followed by 500 ml. of dry ether. The ammonia was allowed to evaporate overnight, the residual salts were dissolved in water and the ether layer was separated. The aqueous layer was extracted with ether, and the combined ether solutions were dried over magnesium sulfate and concentrated by distillation at atmospheric pressure. The products of two similar preparations were combined at this point and distilled under reduced pressure to separate polymeric material; b. p. 55–57° (30 mm.). The distillate was fractionated through a 15 × 1.5 cm. helix-packed column and yielded 69–74% (61.1 g., 69% in the preparation described) of 1,5-cyclooctadiene, b. p. 51–52° (25 mm.), m. p. −70 to −69°, $n^{25}D$ 1.4910, d^{25}_4 0.8760; *M*D calcd. 36.0, found 35.7.

Samples taken from the beginning and the end of the fractional distillation had the same refractive index and identical infrared absorption spectra, indicating that I prepared by this method is a single isomer.

Silver Nitrate Adduct of 1,5-Cycloöctadiene.—1,5-Cycloöctadiene (1.0 ml.) was shaken with a solution of 5.0 g. of silver nitrate in 10 ml. of water. The suspension was warmed until a homogeneous solution was obtained and then cooled. Elongated, colorless needles formed, which were separated by filtration and dried under reduced pressure over Drierite and 1,5-cycloöctadiene saturated with paraffin. The adduct had m. p. 128.5–131°.

Anal. Calcd. for $C_8H_{12}{\cdot}AgNO_3$: C, 34.55; H, 4.35; Ag, 38.80. Found: C, 33.55; H, 4.42; Ag, 39.63.

The silver nitrate adduct had the same m. p. after recrystallization from absolute ethanol. It lost I rapidly on exposure to air, or on evacuation.

Monobromocycloöctadienes.—The following modification of the procedure previously described[3] was used. A mixture of 47 g. (0.44 mole) of 1,5-cycloöctadiene, 53 g. (0.3 mole) of N-bromosuccinimide, 2 g. of benzoyl peroxide and 250 ml. of carbon tetrachloride was heated at the reflux temperature for three hours. The mixture was cooled, succinimide (26 g., 88%) was separated by filtration, and the filtrate was washed twice with dilute sodium carbonate solution and twice with warm water. Distillation under reduced pressure separated 15.2 g. (32%) of recovered 1,5-cycloöctadiene, 29.3 g. (53% based on N-bromosuccinimide) of analytically pure monobromocycloöctadiene, b. p. 56–60° (1 mm.), $n^{25}D$ 1.5462, and 6 g. of dibromocycloöctadiene. The monobromocycloöctadiene fraction solidified (freezing point −38°) when it was cooled with Dry Ice. It was crystallized from twice its volume of ether, and after each crystallization the freezing

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[6] Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948).

[7] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and his associates for analyses.

[8] We are indebted to William R. Schmitz and Mark R. Kinter for the preparation of this compound.

point was determined with a thermometer immersed in the liquid, which was stirred and seeded if necessary to avoid excessive supercooling. After six recrystallizations the higher melting isomer (II) was obtained with a constant freezing point of 0°; $n^{25}\text{D}$ 1.5554.

Anal. Calcd. for $C_8H_{11}Br$: C, 51.35; H, 5.93; Br, 42.72. Found: C, 51.21; H, 5.99; Br, 42.35.

Hydrogenation of 1.08 g. of II in the presence of 0.5 g. of prereduced Adams platinum oxide catalyst in 15 ml. of glacial acetic acid containing 1 g. of sodium acetate resulted in the uptake of 96% of three molar equivalents of hydrogen in thirty minutes. Distillation of the reduction product yielded 0.23 g. (37%) of cycloöctane, b. p. 147°, m. p. 10–11° (indicating 98.5% purity[9]), and 0.16 g. of a high boiling liquid which did not contain bromine (probably bicycloöctyl, $C_{16}H_{30}$). Titration of the aqueous washings of the reduction product with silver nitrate showed that 97% of the theoretical quantity of hydrogen bromide had been formed in the hydrogenation.

A 0.224-g. sample of II was heated under reflux for twenty-four hours with 5 ml. of an ether solution containing four millimoles of lithium aluminum hydride.[10] The excess lithium aluminum hydride was decomposed with dilute sulfuric acid and the ether layer was separated, dried over potassium carbonate and distilled. The distillate (approximately 50 mg.) was passed through a 10 × 1 mm. column of silica gel to remove traces of ether. The product was identified as 1,5-cycloöctadiene by its m. p., −72.5 to −70°, and mixed m. p. with a known sample, m. p. −70.5 to −69.5°, which was not depressed.

The ether mother liquors separated in the crystallization of I were combined and fractionated twice through a 15 × 1.5 cm. helix-packed column. The mid-fraction had b. p. 64–65° (1.5 mm.), $n^{25}\text{D}$ 1.5420, and was the "low boiling" isomer III containing 13% of II according to the refractive index–mole fraction curve (Fig. 4).

Anal. Calcd. for $C_8H_{11}Br$: C, 51.35; H, 5.93; Br, 42.72. Found: C, 51.18; H, 5.95; Br, 42.50.

In a quantitative hydrogenation of 0.80 g. of III in the presence of 0.40 g. of prereduced Adams platinum oxide catalyst in 10 ml. of glacial acetic acid containing 2 g. of sodium acetate, 93% of three molar equivalents of hydrogen was taken up. Cycloöctane of 95% purity[9] (m. p. 3–4.5°) was isolated in a yield of 0.10 g. (25%), plus a smaller amount of the high boiling liquid presumed to be bicycloöctyl. Dehalogenation of a sample of III by treatment with lithium aluminum hydride gave a mixture of cycloöctadienes which was not identified, but was characterized by catalytic hydrogenation, which yielded cyclooctane.

Isomerization of Monobromocycloöctadienes.—When the mixture of monobromocycloöctadienes obtained by the reaction of 1,5-cycloöctadiene with N-bromosuccinimide was purified by slow fractional distillation, the product was largely the "low boiling" isomer (III), $n^{25}\text{D}$ 1.5420, apparently formed in part in the bromination reaction and in part by rearrangement of II to III during the distillation. In an effort to determine whether the reverse rearrangement would occur, a sample of II purified by low temperature crystallization from ether was distilled slowly in the presence of 1% by weight of Darco and 0.1% of benzoyl peroxide (added as catalysts for the allylic rearrangement[11]). A 0.363-g. sample of the distillate, which contained 83% of the "low boiling" isomer (III) according to its refractive index ($n^{25}\text{D}$ 1.5428), was heated at 100° in a nitrogen atmosphere in the presence of 3 mg. of Darco and 0.3 mg. of benzoyl peroxide for six hours. The product was distilled to separate polymeric material and weighed 0.27 g., $n^{25}\text{D}$ 1.5452. Infrared analysis as well as the increase in refractive index indicated that the period of heating had resulted in an increase in the proportion of II present in the sample, for the following absorption bands characteristic of II were more intense in the sample after it had been heated: 6.05, 6.71, 6.87, 7.73, 7.88, 8.33, 8.94, 9.62, 11.43 and 12.05 μ.

Dibromocycloöctadiene.—A mixture of 32.6 g. of 1,5-cycloöctadiene, 120 g. of N-bromosuccinimide, 2 g. of benzoyl peroxide and 400 ml. of carbon tetrachloride was stirred and heated under reflux for three hours. The succinimide which was formed and excess N-bromosuccinimide were separated by filtration and washed with carbon tetrachloride. Part of the solvent was removed from the filtrate by concentration under reduced pressure, and the residue was washed with dilute sodium carbonate solution and with warm water, and distilled as rapidly as possible at 0.5 mm. Fairly rapid redistillation from a modified Claisen flask separated a small amount of forerun and yielded 69 g. (86%) of dibromocycloöctadiene (V); b. p. 95–105° (1 mm.), $n^{25}\text{D}$ 1.5954, d^{25}_4 1.7251.

Anal. Calcd. for $C_8H_{10}Br_2$: C, 36.12; H, 3.79; Br, 60.09. Found: C, 36.29; H, 3.86; Br, 60.05.

The dibromocycloöctadiene purified by distillation was colorless but darkened after storage at −80° under nitrogen for one week, and a small amount of solid precipitated. The solid, which amounted to 0.5 to 1% of the product, was purified by recrystallization from ether; m. p. 124–125°. Analysis and a molecular weight determination indicated that this solid was an isomer of the liquid dibromocycloöctadiene. No other evidence was obtained concerning its structure.

Anal. Calcd. for $C_8H_{10}Br_2$: C, 36.12; H, 3.79; Br, 60.09; mol. wt., 266. Found: C, 36.18; H, 3.92; Br, 59.95; mol. wt., 260 (freezing point method in glacial acetic acid).

Hydrogenation of 2.14 g. of V by the procedure described for hydrogenation of II in the presence of 1.0 g. of prereduced platinum oxide was complete in three hours and required 88% of four molar equivalents of hydrogen. Cycloöctane (0.17 g., 19%), m. p. 0–4° (95% purity[9]), and 0.36 g. of a higher boiling (dimeric) reduction product were isolated, and titration showed that 92% of the theoretical amount of hydrogen bromide had been formed.

Tests of the reactivity of the halogen in the distilled dibromocycloöctadiene showed that both bromine atoms were reactive (presumably allylic). A sample which was warmed with an excess of alcoholic sodium ethoxide at 50° for two hours liberated 100% of two molar equivalents of bromide ion, as determined by titration with silver nitrate. An 8-g. sample of the distilled dibromide was treated with an excess of dimethylamine by the procedure followed previously with the undistilled dibromide.[3] Bis-dimethylaminocycloöctadiene was obtained in a yield of 1.8 g. (31%); b. p. 83–85° (1 mm.), $n^{25}\text{D}$ 1.5015. Derivatives prepared from the diamine were the dipicrate, m. p. and mixed m. p. with a known sample[3] 192–194°, and the dimethiodide, m. p. 172–174° (ref. 5 reports m. p. 173–174°).

Treatment of 3.5 g. of V with an excess of lithium aluminum hydride by the procedure described for the similar reduction of II gave 0.8 g. of a mixture of cycloöctadienes which was not identified, but absorbed 100% of two molar equivalents of hydrogen in a quantitative reduction in the presence of Adams platinum catalyst and gave cycloöctane with m. p. 9–11° (98% purity[9]).

Preparation of Dibromocycloöctadiene from 1,3,5-Cycloöctatriene.—Bromine (3 g.) in 20 ml. of chloroform was added to a stirred solution of 2 g. of 1,3,5-cycloöctatriene in 20 ml. of chloroform at −15 to −25° in a nitrogen atmosphere in a period of one hour.[5] The product was distilled rapidly under reduced pressure; b. p. 95° (0.3 mm.), $n^{25}\text{D}$ 1.5954. The ultraviolet absorption spectrum of this product both before and after distillation was very similar to that of V prepared from 1,5-cycloöctadiene and N-bromosuccinimide (Fig. 5). Previous work had shown that dibromocycloöctadiene prepared by the two

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[9] See Cope and Hochstein, This Journal, 72, 2515 (1950).

[10] Use of this reagent for the reduction (hydrogenolysis) of alkyl halides has been described by Johnson, Blizzard and Carhart, This Journal, 70, 3664 (1948); Nystrom and Brown, *ibid.*, 70, 3738 (1948); Trevoy and Brown, *ibid.*, 71, 1675 (1949).

[11] Young and Lane, *ibid.*, 59, 2055 (1937); private communication from W. G. Young; M.A. thesis, Harry Wax, University of California at Los Angeles, January, 1941.

routes gave the same bis-dimethylaminocycloöctadiene by reaction with dimethylamine.[3] The infrared spectra of samples of V prepared by the two routes contained many of the same absorption bands, indicating that both contained the same isomer. The spectrum of V prepared from I and N-bromosuccinimide was more complex, probably indicating that it contained isomers which were not present in the other sample.

Preparation of 1,3,5-Cycloöctatriene. (a) **From Monobromocycloöctadiene.**—A solution of potassium *t*-butoxide prepared from 2 g. of potassium and 50 ml. of *t*-butanol was heated to the reflux temperature and a solution of 8 g. of monobromocycloöctadiene (n^{25}D 1.5460) in 10 ml. of *t*-butanol was added slowly. After one hour, titration of an aliquot with standard acid showed that the reaction was 95% complete. The mixture was cooled, centrifuged and the liquid was decanted. The salts were washed with ether, and the combined solutions were concentrated under reduced pressure. The distillate was condensed in a receiver cooled with Dry Ice. Distillation of the residue gave 1.2 g. of 1,3,5-cycloöctatriene, and fractionation of the ether–*t*-butanol solution distilled in concentrating the reaction mixture yielded an additional 2.0 g. (total yield 71%). After the product was washed with water to remove a trace of *t*-butanol and dried by treatment with silica gel[9] it had n^{25}D 1.5213 and an ultraviolet absorption spectrum practically identical with 1,3,5-cycloöctatriene prepared from pseudopelletierine[5] ($\lambda_{max.}$ 265 mμ, ϵ = 3350; $\lambda_{min.}$ 225, ϵ = 1240). In a quantitative hydrogenation, 0.995 g. of 1,3,5-cycloöctatriene prepared by this method absorbed 90% of three molar equivalents of hydrogen in the presence of Adams platinum catalyst[12] and gave a 65% yield of cycloöctane with an average purity of 95%.[9]

(b) **Preparation of IV from V.**—Magnesium turnings (1.3 g.) and 15 g. of dibromocycloöctadiene were allowed to react in 25 ml. of dry ether. The ether refluxed from the heat of reaction for one hour, and the mixture was stirred and heated under reflux for an additional one-half hour. The ether and the product were separated from the magnesium bromide by distillation at 0.1 mm. and condensed in a receiver cooled with Dry Ice. Redistillation gave 3.2 g. (53%) of 1,3,5-cycloöctatriene, which in a quantitative hydrogenation absorbed 97.5% of three molar equivalents of hydrogen and gave a 55% yield of cyclooctane of 90% purity.[9]

In an attempt to dehydrogenate 1,3,5-cycloöctatriene, a 1.0-g. sample and 2.5 g. of chloroanil in 10 ml. of diphenyl ether were heated in a bath at 160–170° for eight hours. Distillation yielded no low boiling product or recovered 1,3,5-cycloöctatriene. In a control experiment under the same conditions in which 1 g. of cycloöctatetraene was substituted for the cycloöctatriene, 0.5 g. of the cycloöctatetraene was recovered, indicating that it should have been possible to isolate cycloöctatetraene if an appreciable amount had been formed by dehydrogenation of the cycloöctatriene.

Thermal Decomposition of Dibromocycloöctadiene.—Dibromocycloöctadiene (25 g.) was distilled rapidly at atmospheric pressure from a 25-ml. modified Claisen flask. Hydrogen bromide was evolved during the distillation and 11.1 g. (65%) of a colorless product was obtained. Redistillation through a 30 × 0.7 cm. column gave 8.5 g. of a mixture of isomers with the composition C_8H_9Br; b. p. 62–64° (2 mm.), n^{25}D 1.5590.

Anal. Calcd. for C_8H_9Br: C, 51.91; H, 4.90; Br, 43.18. Found: C, 51.82; H, 4.82; Br, 43.08.

α-Phenylethyl bromide was identified as a component of this mixture by treating a portion of it with dimethylamine in benzene at room temperature for twenty-four hours. N,N-Dimethyl-α-phenylethylamine was obtained in 60% yield; b. p. 86–88° (28 mm.), n^{25}D 1.5002, m. p. of the picrate and mixed m. p. with a known sample[13] 138–139°. Another sample of the mixture of bromides (C_8H_9Br) was treated with thiourea. After addition of picric acid and recrystallization of the product α-phenylethylisothiouronium picrate was isolated, m. p. 166–167°.[14]

Infrared analysis of the mixture of bromides (C_8H_9Br) and comparison of the spectra of α- and β-phenylethyl bromides indicated that it was a mixture containing approximately 50% of α-phenylethyl bromide and 25% of β-phenylethyl bromide. A sample of the mixed bromides was treated with 80% aqueous acetone at 100° for two hours to hydrolyze the α-phenylethyl bromide.[15] Titration with standard sodium hydroxide showed that 76% of the bromide had hydrolyzed. The unhydrolyzed bromide was separated by dilution with water and extraction with petroleum ether. After concentration, reaction of the residue with thiourea followed by treatment with picric acid gave a small amount of β-phenylethyl isothiouronium picrate,[14] identified by m. p. and mixed m. p. with a known sample (m. p. 136–137°), which was not depressed. There was some evidence that the mixture of bromides contained a third component, for quantitative hydrogenation in the presence of 10% palladium-on-charcoal catalyst in glacial acetic acid required 1.35 to 1.43 molar equivalents of hydrogen. Under these conditions α- and β-bromoethylbenzene absorbed one molar equivalent of hydrogen. The infrared spectrum of the hydrogenation product indicated that it contained ethylbenzene, and little if any cycloöctane.

Absorption Spectra.—The ultraviolet absorption spectrum of V (Fig. 5) dissolved in purified cyclohexane was determined with a Beckman model DU quartz spectrophotometer. We are indebted to Dr. R. C. Lord, Mr. R. S. McDonald and Miss B. J. Fax for the measurement and interpretation of infrared spectra. The infrared and Raman spectra of 1,5-cycloöctadiene will be published by Ellis R. Lippincott and R. C. Lord.

Summary

Two isomeric monobromocycloöctadienes have been isolated from the product formed by reaction of 1,5-cycloöctadiene with N-bromosuccinimide. These compounds are interconvertible and appear to be allylic isomers. The reaction of a mixture of these isomers with potassium *t*-butoxide yielded 1,3,5-cycloöctatriene, which also was obtained by the reaction of 5,8-dibromo-1,3-cycloöctadiene with magnesium.

5,8-Dibromo-1,3-cycloöctadiene was prepared from 1,5-cycloöctadiene and two equivalents of N-bromosuccinimide and purified by rapid distillation at 1 mm. Distillation at atmospheric pressure caused the dibromide to lose hydrogen bromide and rearrange to a mixture of isomeric bromides containing α- and β-phenylethyl bromides.

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[12] 1,3,5-Cycloöctatriene with this refractive index prepared by other routes has been observed to absorb approximately 90% of three molar equivalents of hydrogen in quantitative reductions: see ref. 9.

[13] Prepared by Philip H. Towle: Cope, Foster and Towle, THIS JOURNAL, **71**, 3929 (1949).

[14] Levy and Campbell, *J. Chem. Soc.*, 1442 (1939).

[15] Walling, Kharasch and Mayo, THIS JOURNAL, **61**, 2693 (1939).