appear to be necessary in all solvents, and, if present, alters basically none of the arguments used before.

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HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reaction of Hydrogen Bromide with Cycloöctatetraene

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The reaction of cycloöctatetraene with two moles of hydrogen bromide in benzene solution and without solvent has been studied. Treatment of the unstable adduct with dimethylamine at room temperature gave largely a dimethylaminobromocycloöctadiene and a small amount of N,N′,α-trimethylbenzylamine. Hydrogenation of the dimethylaminobromocyclooctadiene gave dimethylaminocycloöctane identical in its properties and derivatives with the known compound. An attempt to demonstrate whether this was a radical or ionic reaction was inconclusive. The reaction of cycloöctatetraene with two moles of hydrogen bromide in glacial acetic acid gave largely α-bromoethylbenzene as previously reported when one mole of hydrogen bromide was used and also a small amount of dimethylaminobromocycloöctadiene after treatment with dimethylamine at room temperature.

In connection with current work designed to elucidate the structure of several cycloöctatetraene dimers, it became of interest to study the peroxide-catalyzed addition of hydrogen bromide to cyclooctatetraene in order to obtain information as to whether a radical such as a bromine atom would isomerize the ring. It soon became apparent that the reaction with hydrogen bromide could not be mechanistically categorized as easily as hoped. This paper will describe the addition of two moles of hydrogen bromide to cycloöctatetraene in benzene and without solvent, the course of the reaction when benzoyl peroxide is added, and the effect of radical inhibitors on the products of the reaction.

In addition, the work of Reppe and co-workers,[2] who added hydrogen bromide to cycloöctatetraene in glacial acetic acid, was repeated and an additional product was isolated and characterized when two moles of hydrogen bromide was employed.

Two moles of hydrogen bromide was added to cycloöctatetraene and, after treatment of the adduct with dimethylamine, the product, unstable in air, was either treated with picric acid to give a stable picrate, or, if the amine was to be used immediately, was distilled to give I in 68.4% yield based on cycloöctatetraene and a 5.5% yield of N,N′,α-trimethylbenzylamine (II). I was obtained from its picrate by chromatography on activated alumina in 85–94% yield. On the addition of one mole of hydrogen bromide, only I could be obtained in lower yield.[3]

The ultraviolet absorption spectrum, λ_{max} 222 mμ, log ε 3.78 (Fig. 1), indicates that a conjugated system of double bonds is present and demonstrates that this product is probably an eight-membered ring and not a bicycloöctene derivative. Cope and Overberger[4a] reported λ_{max} 220, log ε 3.9 for α-des-dimethylgranatanine. Quantitative reduction over platinum at atmospheric pressure (97%, calculated for 3 moles of hydrogen) gave dimethylaminocyclooctane identical in its physical properties with that reported in references 7 and 13. The infrared spectrum[5] of the methiodide of dimethylaminocycloöctane prepared in this way was identical with the spectra of the methiodides prepared as described by 4a and 4b. The melting point of the picrate derivative is also identical with that reported in references 4b and 13.

The N,N′,α-trimethylbenzylamine (II) was identical with a known sample prepared from α-bromoethylbenzene. A mixed melting point with a known sample of its picrate was not depressed.

When the reaction was carried out in the presence of benzoyl peroxide, a similar result was obtained: the average yield of I was 42.3%, and of N,N′,α-trimethylbenzylamine, 8.1%. When the reaction was carried out in the presence of different concentrations of radical inhibitors, such as *p*-thiocresol, *sym*-trinitrobenzene and *p*-*t*-butylcatechol, the reaction gave about the same proportion of products.

When hydrogen bromide was added to cyclooctatetraene in glacial acetic acid according to the procedure of Reppe, *et al.*, α-bromoethylbenzene was obtained as reported. The physical constants of the product were shown to be identical with a known sample. The infrared spectrum was identical with the spectrum of a known sample. When the reaction was carried out with two moles of hy-

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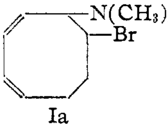
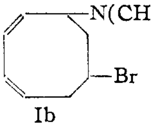
[1] This paper comprises a portion of a thesis presented by Morton A. Klotz in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

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

[3] The most probable structures for the dimethylaminobromocyclooctadiene are Ia and Ib. Evidence for the position of the bromine and



Ia



Ib

dimethylamino groups is not reviewed in this paper. Evidence accumulated thus far has revealed that the bromine is not in an allylic or vinyl position and that a vinyl amine is not present. It is always possible that the intermediate dibromo compound is a bicyclic derivative but it is unlikely.

[4] (a) A. C. Cope and C. G. Overberger, THIS JOURNAL, **70**, 1433 (1948); (b) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950).

[5] We are indebted to Professors A. C. Cope and R. C. Lord of the Massachusetts Institute of Technology for the samples of methiodides and the infrared spectra, respectively.

drogen bromide under similar conditions and the reaction mixture treated with dimethylamine at room temperature, a small amount of I was also obtained along with the N,N',α-trimethylbenzylamine. The X-ray diffraction pattern of the picrate of I obtained in this way was identical with that obtained from the picrate obtained in previous experiments.

Experimental[6]

Cycloöctatetraene.—The cycloöctatetraene used in the later portions of this work was obtained from the General Aniline and Film Corporation; that used in earlier experiments was prepared from acetylene in these laboratories by a modification of the procedure of Reppe, Schlichting, Klager and Toepel,[2] except that a rocker-type stainless steel high pressure autoclave was employed.

(A) **Cycloöctatetraene and Hydrogen Bromide, without Solvent.**—A typical vacuum manifold system was used. Anhydrous hydrogen bromide (obtained from the Matheson Company) was condensed to a liquid and distilled into the reaction tubes. Cycloöctatetraene was freshly distilled and gave a negative test for peroxides by the method of Kharasch and Mayo.[7]

In each reaction tube, 3.0 g. (0.029 mole) of cyclooctatetraene was treated with 2.00 ml. (5.54 g., 0.0684 mole) of hydrogen bromide for three hours at room temperature with intermittent agitation. The contents of the tubes were combined in pairs and treated with a solution of 12 g. (0.27 mole) of dimethylamine in 48 g. of benzene with cooling, and the mixture allowed to stand at room temperature for 18–24 hours. After the first five minutes a crystalline precipitate had begun to separate. The mixture was then treated with 150 ml. of 1:1 hydrochloric acid with cooling. The aqueous layer was separated, made alkaline with excess 20% sodium hydroxide solution with cooling, and extracted with ten 50-ml. portions of ether. After drying the combined extracts over magnesium sulfate, a few crystals of hydroquinone were added and the solution was concentrated by distillation of the ether. The dark brown oily residue was then distilled through a semimicro modified Claisen apparatus, collecting a low-boiling forerun in a Dry Ice trap, yielding, in representative experiments, 9.13 g. (68.8%) and 9.03 g. (68.0%) of I, a pale yellow oil, b.p. 63–66° (0.25 mm.), $n^{25}\mathrm{D}$ 1.5114, $d^{25}{}_{4}$ 1.237.

Anal. Calcd. for $C_{10}H_{16}NBr$: C, 52.18; H, 7.01; N, 6.09; Br, 34.72. Found: C, 52.44; H, 7.16; N, 6.25; Br, 34.75.

The low-boiling foreruns consisted of N,N',α-trimethylbenzylamine (II), 0.45 g. (5.2%) and 0.51 g. (5.9%), respectively; identified by conversion to the picrate, m.p. 137–138° and 137–138.5°,[8] mixed m.p. with an authentic sample, 136.5–138°.

In experiments identical to the above except that in each of the reaction tubes was placed 0.70 g. (0.1 mole % based on cycloöctatetraene) of recrystallized benzoyl peroxide, the yield of I averaged 5.63 g. (42.3%), and the yields of II averaged 0.70 g. (8.1%).

In experiments identical to the above with no benzoyl peroxide except that in each of the reaction tubes was placed 0.36 g. (0.1 mole % based on cycloöctatetraene) of redistilled *p*-thiocresol, the yields of I averaged 8.15 g. (61.6%), and the yields of II averaged 0.20 g. (2.9%).

In other similar experiments no appreciable variations in the yields were produced by variations in reaction temperature from 0 to 65°, by variations in catalyst or inhibitor quantities from 0 to 50%, or by combinations thereof. The radical inhibitors *p*-*t*-butylcatechol and *sym*-trinitrobenzene produced similar results.

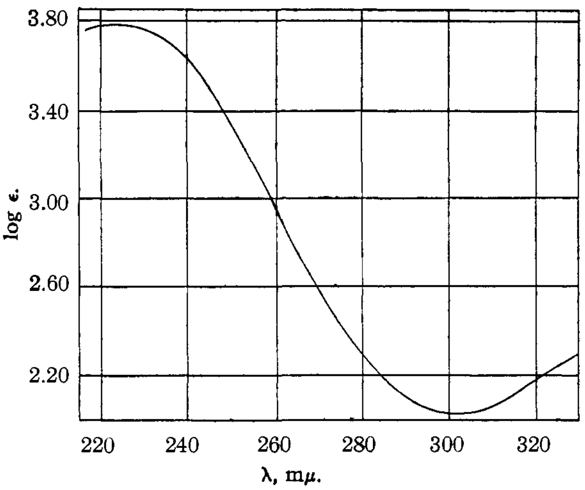


Fig. 1.—Ultraviolet absorption spectrum of the dimethylaminobromocycloöctadiene (I).

I was unstable in air, darkening rapidly. It could be stored safely under nitrogen at −70°. If the amine was not to be used immediately, it was not distilled but was precipitated as the picrate. To the crude mixture was added 10 ml. of ethanol and a saturated solution of picric acid in ethanol was added dropwise until no further precipitate formed. As the picric acid solution was added a brown tar separated along with the yellow crystalline picrate. By swirling the flask the tar was made to adhere to the walls along with a small amount of picrate while the major portion of the picrate remained in suspension and was decanted and filtered. An analytical sample recrystallized from methanol melted at 156–157.5° (dec.).

Anal. Calcd. for $C_{16}H_{19}N_4O_7Br$: C, 41.84; H, 4.17; N, 12.20; Br, 17.40. Found: C, 41.76; H, 4.06; N, 12.30; Br, 17.24.

I was obtained from its picrate by chromatographing an acetone solution on a column of activated alumina and eluting with acetone, testing the eluate periodically for halogen by the Beilstein test. When the test was no longer positive one more liter of eluate was collected. Concentration of the eluate and vacuum distillation yielded approximately 50 g. of diacetone alcohol (identified by boiling point, refractive index and melting point of the 2,4-dinitrophenylhydrazone) per gallon of acetone, and I in 85–94% yield.

The ultraviolet absorption spectrum of I (Fig. 1) was obtained with a Beckman spectrophotometer using purified cyclohexane as the solvent.[9]

(B) **Cycloöctatetraene and Hydrogen Bromide in Glacial Acetic Acid.**—The procedure described by Reppe, *et al.*,[2] was repeated. An analytical sample was distilled through a semimicro center-tube column, b.p. 60° (2.4 mm.), $n^{25}\mathrm{D}$ 1.5592, ($n^{20}\mathrm{D}$ 1.5612).[2]

Anal. Calcd. for C_8H_9Br: C, 51.92; H, 4.90. Found: C, 52.18; H, 5.20.

An authentic sample of α-bromoethylbenzene, obtained by fractional distillation of technical grade material (The Matheson Company) had a b.p. 60° (2.4 mm.), $n^{25}\mathrm{D}$ 1.5598.

The infrared spectra of α-bromoethylbenzene obtained from cycloöctatetraene and of the authentic sample were obtained using 10% solutions in carbon disulfide, in a Baird Associates infrared spectrophotometer with a sodium chloride prism.

To one-half of the crude product of this reaction (initially containing 15.0 g. (0.144 mole) of cycloöctatetraene, and 10.0 g. (0.124 mole) of hydrogen bromide, was added a solution of 50.0 g. (1.1 moles) of dimethylamine in 150 g. of benzene. Crystals began to separate after 15 minutes. After 3.5 days the mixture was treated with an excess of 1:1 hydrochloric acid and the non-aqueous layer was discarded. The aqueous solution was made basic with 20% sodium hydroxide solution and extracted with ten 50-ml. portions of ether. After drying and evaporation of the solvent the

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[6] Melting points are corrected and boiling points are uncorrected. Compounds that melted with decomposition were placed in the bath 10 degrees below the melting point and heated at a rate of 2 degrees per minute. Analyses by Mr. H. S. Clark, Urbana, Illinois; Mr. Harry Biletch and Dr. David Bandel of this Institute; Drs. Weiler and Strauss, Oxford, England; and Dr. F. Schwarzkopf, New York, N. Y.

[7] M. S. Kharasch and F. R. Mayo, THIS JOURNAL, **55**, 2468 (1933).

[8] Values are recorded in the literature (uncor.) from 134 to 141°: A. Skita and F. Keil, *Ber.*, **63**, 34 (1930); T. S. Stevens, *J. Chem. Soc.*, 2107 (1930); T. S. Stevens, J. M. Cowan and J. MacKinnon, *ibid.*, 2568 (1931); T. Thomson and T. S. Stevens, *ibid.*, 2607 (1932).

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

residue was distilled through a semi-micro center-tube fractionating column at 0.4 mm. A large fraction boiling below room temperature was collected in a Dry Ice trap, followed by a small intermediate fraction boiling from room temperature to 70°, and then a single fraction of 2.27 g., b.p. 70–75° (0.4 mm.). This fraction was treated with picric acid but the picrate of I could not be isolated from the precipitate.

The low boiling fraction was a yellow oil which on redistillation gave 3.50 g. (18.9% based on hydrogen bromide) of impure N,N′,α-trimethylbenzylamine (II), b.p. 69–70° (10 mm.). After redistillation, the product was dissolved in 10 ml. of ethanol and was treated with excess saturated ethanolic picric acid, yielding 6.86 g. (78.8%) of the picrate of II, m.p. 137–138.5°. After three recrystallizations from absolute ethanol and one from 95% ethanol this sample had a m.p. 138–139°.[8] A mixed melting point with an authentic sample was not depressed, m.p. 138–139°.

An authentic sample of II was prepared by treatment of 6.81 g. (0.0368 mole) of an authentic sample of α-bromoethylbenzene with a five-fold excess of dimethylamine in benzene as described for the cycloöctatetraene product above. Distillation through a semi-micro center-tube fractionating column yielded a total of 4.13 g. (75.4%) of colorless oil, b.p. 64–66° (9 mm.). A center cut taken for an analytical sample had b.p. 64–64.5° (9 mm.), n^{25}_{D} 1.5009.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.5. Found: C, 80.40; H, 10.29; N, 9.4.

The picrate of this authentic sample was prepared in the usual manner in 65% yield, m.p. 138–139° after two recrystallizations from 95% ethanol.

(C) Cycloöctatetraene and Hydrogen Bromide in Glacial Acetic Acid Using Two Molar Equivalents of Hydrogen Bromide.—The procedure was similar to that described by Reppe, *et al.*,[2] except that the reaction mixture was allowed to stand for 4 days instead of 2 days and 2 moles of hydrogen bromide was used. Thirty grams (0.288 mole) of cyclooctatetraene in glacial acetic acid was treated with 46.6 g. (0.576 mole) of hydrogen bromide. Acetic acid was removed by vacuum distillation and to the residue was added a cold solution of 54 g. (1.2 moles) of dimethylamine in 260 g. of benzene. After standing at room temperature for 3 days the mixture was worked up in the manner described above. The resulting mixture of amines was then fractionated through a semi-micro center-tube column at 0.1 mm., collecting a low boiling forerun in a Dry Ice trap. After a small intermediate cut two fractions were collected, 1.97 g., b.p. 59–71° (0.1 mm.) and 6.78 g., b.p. 71–79° (0.1 mm.), both pale yellow oils. In 25 ml. of absolute ethanol, 1.0 g. of the second fraction was dissolved. On addition of excess saturated ethanolic picric acid a red oil separated. The mixture was heated to boiling, decanted from a small amount of undissolved oil, allowed to cool until cloudy, and was seeded with a small crystal of the picrate of I. On standing overnight 0.52 g. of a yellow crystalline solid mixed with a small amount of brown tarry material separated. After two recrystallizations from ethanol this had an m.p. of 155–156° (dec.) and the mixed melting point with a sample obtained by procedure A showed no depression, m.p. 155–156° (dec.). Proof of the identity of these materials was provided by the X-ray diffraction patterns[10] which were obtained with a North American Philips Co. Geiger Counter Recording X-Ray Spectrophotometer using CuK α radiation.

Redistillation of the contents of the Dry Ice trap yielded 9.17 g. (21.2%) of II, n^{25}_{D} 1.5014.

Dimethylaminocycloöctane.—Hydrogenation of 0.725 g. of I at atmospheric pressure in the presence of 0.2 g. of prereduced Adams platinum catalyst in 20 ml. of absolute ethanol in a semi-micro apparatus required 95.7% of three molar equivalents of hydrogen.

In a preparative run 6.6 g. of I obtained from its picrate was hydrogenated over Adams platinum catalyst in ethanol solution at 38 p.s.i. After separation of the catalyst the solution was concentrated by distillation of the solvent until a white precipitate separated (presumably the amine hydrobromide). The precipitate was dissolved in water, treated with a large excess of 20% sodium hydroxide solution and extracted with ten 30-ml. portions of ether. After drying the combined extracts over magnesium sulfate and concentration of the solution, distillation yielded 4.25 g. (80%) of product, b.p. 38–40° (0.2 mm.). The distillate was dissolved in a small excess of 5% sulfuric acid and extracted with eight 50-ml. portions of ether. The aqueous layer was made basic with a large excess of 20% sodium hydroxide solution and extracted with eight 50-ml. portions of ether. The combined extracts, after drying over magnesium sulfate, were concentrated and distilled through a Craig[11] micro fractionation column, and yielded 2.97 g. (56%) of dimethylaminocycloöctane. The properties of a center cut taken for an analytical sample were b.p. (micro) 216° (765 mm.), 216–217° (760 mm.),[12] n^{25}_{D} 1.4707, (n^{25}_{D} 1.4707).[4b]

Anal. Calcd. for $C_{10}H_{21}N$: C, 77.34; H, 13.63; N, 9.02. Found: C, 77.25; H, 13.78; N, 9.08.

The methiodide of dimethylaminocycloöctane was prepared by the method of ref. 4a, m.p. 273–275° (dec.), m.p. 274–275° (dec.).[4a]

Anal. Calcd. for $C_{11}H_{24}NI$: C, 44.45; H, 8.14; N, 4.71. Found: C, 44.61; H, 7.99; N, 4.33.

The picrate of dimethylaminocycloöctane was prepared in ethanolic solution and recrystallized four times from ethanol, m.p. 195.8–197.4° (m.p. 197.4–198.2°),[4b] (m.p. 197.2–197.8°).[13]

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[10] We are indebted to Messrs. A. D. Turissini and L. Adlum, of the Laurel Hill Research Laboratory of the General Chemical Division Allied Chemical and Dye Corporation, who obtained and interpreted the X-ray diagrams.

[11] L. C. Craig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 441 (1937).

[12] R. Willstätter and E. Waser, *Ber.*, **44**, 3423 (1911).

[13] A. C. Cope, H. R. Nace and L. L. Estes, Jr., THIS JOURNAL, **72**, 1123 (1950).