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

Cyclic Polyolefins. VI. Preparation of Cycloöctatrienes from Cycloöctatetraene[1]

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Samples of 1,3,5-cycloöctatriene prepared from pseudopelletierine,[2] R-homotropinone[3] and bromocycloöctadienes[4] have had practically identical ultraviolet absorption spectra, but have varied in refractive index from n^{25}D 1.5217 to 1.5248. We have investigated the preparation of cyclooctatrienes from cycloöctatetraene, in an effort to develop an improved synthesis and to determine the reason for the observed discrepancies in refractive index.

Reppe, Schlichting, Klager and Toepel[5] reported that lithium adds to cycloöctatetraene in ether to give a dilithium derivative, which on reaction with methanol yields 1,3,6-cycloöctatriene. Sodium also was reported to add to cyclooctatetraene under similar conditions. In our work, cycloöctatetraene was added to an excess of powdered lithium in ether, and the hydrocarbon formed on decomposition of the lithium compounds with methanol was examined. It proved to be a mixture composed of approximately 20–30% of 1,3,6-cycloöctatriene, 20–30% of 1,3,5-cycloöctatriene, 17% of cycloöctadienylcyclooctadienes (reducible to bicycloöctyl,[6] $C_{16}H_{30}$), 10–20% of C_8 hydrocarbons less unsaturated than cycloöctatrienes and 7% of polymers. The cycloöctatriene fraction gave a maleic anhydride adduct with m. p. 144–145° as reported,[7] but the adduct proved to be identical (m. p. and mixed m. p.) with the maleic anhydride adduct of 1,3,5-cycloöctatriene prepared from pseudopelletierine, and accordingly is presumed to be derived from the conjugated triene. It proved to be possible to isomerize the 1,3,6-cycloöctatriene present in the product to 1,3,5-cycloöctatriene by heating the mixture with potassium *t*-butoxide in *t*-butyl alcohol.

A less complex product was obtained by the addition of two equivalents of sodium to cyclooctatetraene in liquid ammonia. Reaction occurred immediately to give a deep orange colored sodium derivative, which was decomposed by addition of solid ammonium chloride (or addition of the sodium derivative to a solution of ammonium chloride in liquid ammonia, which gave an identical product). The product obtained in this manner contained about 10% of cyclooctatetraene, which was easily removed by washing the mixture with aqueous silver nitrate. With the exception of a small amount of polymer, the remainder of the product was composed of a mixture of approximately equal amounts of 1,3,6-cycloöctatriene (I) and 1,3,5-cycloöctatriene (II). Slow fractional distillation separated 1,3,6-cyclooctatriene (contaminated with 4–6% of 1,3,5-cycloöctatriene) from the mixture as a lower boiling fraction. Both the ultraviolet (Fig. 1) and infrared absorption spectra (Figs. 2 and 3) of the two isomers differed, and could be used for estimation of the amounts of each in mixtures of the two. In addition to evidence furnished by the spectra, the structure of 1,3,6-cyclooctatriene was confirmed by ozonization and decomposition of the ozonide with hydrogen peroxide, which yielded malonic acid.

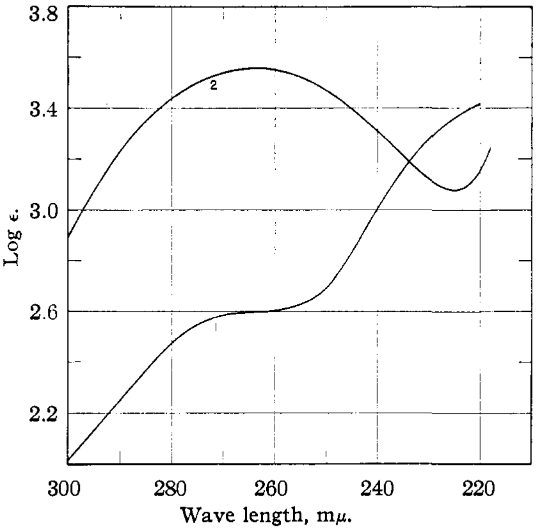
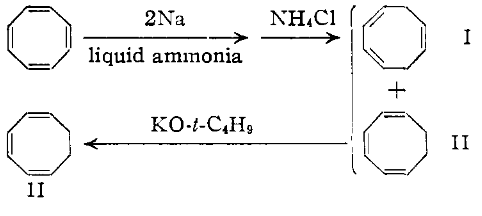


Fig. 1.—Ultraviolet absorption spectra: curve 1, 1,3,6-cycloöctatriene (I); curve 2, 1,3,5-cycloöctatriene (II) purified through the silver nitrate adduct, n^{25}D 1.5254 (both determined in purified cyclohexane as a solvent with a Beckmann quartz spectrophotometer).



The 1,3,6-cycloöctatriene present in mixtures of 1,3,6- and 1,3,5-cycloöctatrienes was isomerized to the 1,3,5-isomer by heating with potassium *t*-butoxide in *t*-butyl alcohol. The product obtained was not homogeneous, and was separated by fractional distillation into fractions with n^{25}D from 1.5151 to 1.5239. All of these fractions had

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

[2] Cope and Overberger, THIS JOURNAL, **70**, 1433 (1948).

[3] Cope, Nace and Estes, *ibid.*, **72**, 1123 (1950).

[4] Cope, Stevens and Hochstein, *ibid.*, **72**, 2510 (1950).

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

[6] Ruzicka and Boekenoogen, *Helv. Chim. Acta*, **14**, 1327 (1931).

[7] Ref. 5, p. 44.

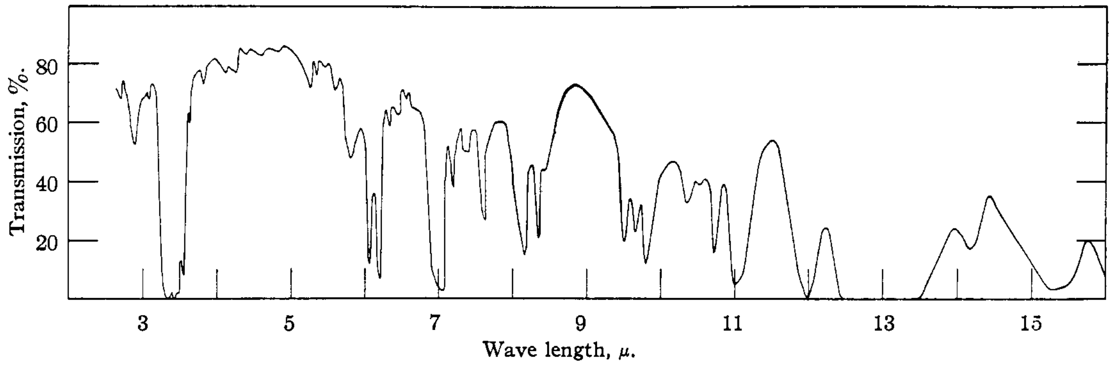


Fig. 2.—Infrared absorption spectrum of 1,3,6-cycloöctatriene (I).

ultraviolet absorption spectra which were nearly coincident, within experimental error, and accordingly contained little if any 1,3,6-cyclooctatriene. Their infrared spectra were similar but not identical (Fig. 3). Partial isomerization appeared to occur during the fractionation, with an increase in the proportion of a lower boiling component with a lower refractive index. Fractions with a low refractive index on re-heating with potassium *t*-butoxide were raised in refractive index to what may be an equilibrium value of n^{25}D 1.5215–1.5226.

A fraction with n^{25}D 1.5215 was proved to be identical with 1,3,5-cycloöctatriene prepared from pseudopelletierine (n^{25}D 1.5212) by m. p. and mixed m. p. (−92.5 to −91°), identity of ultraviolet and infrared spectra (samples with n^{25}D 1.5215), and preparation of identical maleic anhydride and silver nitrate adducts. It was possible to purify 1,3,5-cycloöctatriene (n^{25}D 1.5214, prepared from cyclooctatetraene) by preparation of an adduct with silver nitrate ($C_8H_{10}{\cdot}AgNO_3$), m. p. 125–126°, which could be recrystallized from absolute ethanol. The 1,3,5-cyclooctatriene liberated from this adduct on heating under reduced pressure appeared to be a single pure compound, with n^{25}D 1.5254 and m. p. −83.5 to −83°; it absorbed 100% of three molar equivalents of hydrogen on quantitative reduction and yielded pure cycloöctane, m. p. 13.4–14°. When this sample was heated at 100° under nitrogen for seven hours its properties changed to n^{25}D 1.5215, m. p. −90.5 to −89.5°, indicating the occurrence of isomerization such as took place on slow fractionation of 1,3,5-cycloöctatriene.

The fractions of 1,3,5-cycloöctatriene of low refractive index absorbed less than three molar equivalents of hydrogen and gave less pure cyclooctane than did 1,3,5-cycloöctatriene with n^{25}D 1.5254 purified through the silver nitrate adduct. Hydrogenation of a fraction with n^{25}D 1.5195 resulted in absorption of 92% of three molar equivalents of hydrogen, and gave a product which contained 5–10% of bicyclo[4.2.0]octane

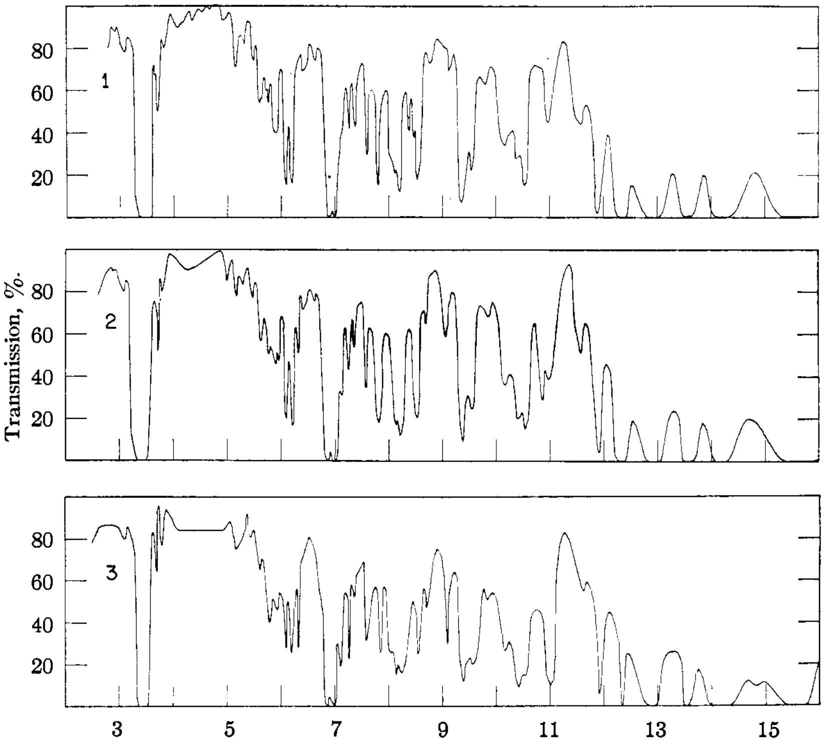
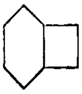
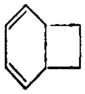


Fig. 3.—Infrared absorption spectra: curve 1, 1,3,5-cycloöctatriene (II) purified through the silver nitrate adduct, n^{25}D 1.5254: curve 2, 1,3,5-cycloöctatreine with n^{25}D 1.5215 obtained by heating the sample with n^{25}D 1.5254 at 100°; curve 3, 1,3,5-cycloöctatriene with n^{25}D 1.5151 (lowest boiling fraction from the isomerization with potassium *t*-butoxide).

(III),[8] according to its infrared spectrum, and 2% of dimeric products.

These data support the conclusion that 1,3,5-cycloöctatriene rearranges reversibly into an isomer with a lower boiling point and refractive index, which is not 1,3,6-cycloöctatriene. This isomer has not been obtained pure. It is possible that the two forms are stereoisomers; Ziegler and Wilms[9] recently have presented evidence that both cycloöctene and 1,5-cycloöctadiene exist in two stereoisomeric forms. It is also possible that the form with a low refractive index is a conjugated bicyclo[4.2.0]octadiene such as IV, which would account for the formation of bicyclo[4.2.0]octane on hydrogenation. Alternately, partial bridging with formation of this hydrocarbon must occur on hydrogenation of the isomer with low refractive index, if it is a stereoisomeric 1,3,5-cycloöctatriene.


III


IV

A further complication in work with 1,3,5-cycloöctatriene was its reaction with one molar equivalent of oxygen, in an air or oxygen atmosphere, to form a polymeric adduct with the approximate composition $(C_8H_{10}O_2)_n$. This was overcome by maintaining an inert atmosphere in its preparation and purification.

Cycloöctatetraene reacted with an excess of sodium in liquid ammonia to give a product which contained ethylbenzene, in addition to hydrocarbons reducible to cycloöctane, dimers and polymers.

Reppe, Schlichting, Klager and Toepel[10] reported that cycloöctatetraene formed a crystalline adduct with silver nitrate; no experimental details were given. Incidental to this work, it was found that at least three distinct addition compounds are formed, with compositions corresponding to $2C_8H_8 \cdot AgNO_3$, $C_8H_8 \cdot AgNO_3$ and $2C_8H_8 \cdot 3AgNO_3$. On heating, the first two lose cycloöctatetraene, and all three melt at the same temperature with decomposition. The complexes can be used for the purification of cycloöctatetraene. Recrystallization from 20% aqueous silver nitrate or from ethanol gave the complex $2C_8H_8 \cdot 3AgNO_3$, which could be decomposed conveniently with aqueous sodium chloride and steam distilled to give cycloöctatetraene of high purity.

Acknowledgment.—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.

Experimental[11]

Preparation of a Mixture of Isomeric Cycloöctatrienes (A) from Cycloöctatetraene.—A solution of 18.5 g. (0.80 g. atom) of sodium in 300 ml. of liquid ammonia was added with stirring during five minutes to a solution of 41.5 g. (0.40 mole) of cycloöctatetraene[12] (m. p. −5 to −4°, containing less than 0.5% of styrene), in 2 l. of liquid ammonia at −45 to −35°. The reaction was slightly exothermic and cooling was required to control the temperature. Solid ammonium chloride (47 g., 0.90 mole) was added to the resulting deep orange solution in small portions as rapidly as possible, during ten minutes. Alternately the solution of the sodium compound was added to a stirred solution of the ammonium chloride in liquid ammonia. Dry ether (500 ml.) was added, and the ammonia was allowed to evaporate overnight. The solid was dissolved in water and the ether solution was separated, washed with three 500-ml. portions of water, and dried over calcium chloride. Distillation of the solution through a 15 × 1.0 cm. helix-packed column after addition of 50 mg. of picric acid as a polymerization inhibitor gave 33.8 g. of a yellow product, b. p. 58–61° (44 mm.), $n^{25}\mathrm{D}$ 1.5130, and 1 g. of a tarry residue. The product contained 10% of cycloöctatetraene, estimated colorimetrically. The cycloöctatetraene was removed (with some loss of cycloöctatrienes) by washing with four 10-ml. portions of a solution of 40 g. of silver nitrate in 100 ml. of water (adding water if necessary to dissolve any crystalline adduct which separated), followed by one washing with water, which gave 26 g. (61%) of a colorless mixture of cyclooctatrienes, $n^{25}\mathrm{D}$ 1.5110. Careful fractionation through a 15 × 1.0 cm. helix-packed column gave a series of fractions, b. p. 66–70° (55 mm.), with $n^{25}\mathrm{D}$ increasing from 1.5072 to 1.5200. Measurement of the extinction coefficient at 265 mμ in the ultraviolet absorption spectra of the fractions indicated that their content of 1,3,5-cyclooctatriene increased from 30 to 75% as the b. p. and refractive index increased (based on a value of ϵ_{265} for pure 1,3,5-cycloöctatriene of 3600 and the assumption that ϵ_{265} for pure 1,3,6-cycloöctatriene is 200).

1,3,6-Cycloöctatriene (I).—Fractionation of the low boiling component from 6 g. of the mixture of isomeric cycloöctatrienes (A) described above through a center-tube column with a rated efficiency of 75 theoretical plates[13] resulted in separation of six fractions totalling 2 g. (fractions 2–7) with $n^{25}\mathrm{D}$ 1.5036–1.5049. Spectral analysis indicated that a fraction with $n^{25}\mathrm{D}$ 1.5046 contained 4–6% of 1,3,5-cycloöctatriene, based on ϵ_{265} in the ultraviolet spectrum. This sample of 1,3,6-cycloöctatriene had b. p. 68° (60 mm.); d^{25}_4 0.8940; m. p. −62 to −56°. Curve 1, Fig. 1 shows its ultraviolet absorption spectrum and Fig. 2 its infrared spectrum.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.14; H, 9.87.

On microhydrogenation of a 114-mg. sample of I over 100 mg. of pre-reduced Adams platinum catalyst in 5 ml. of glacial acetic acid, 96% of three molar equivalents of hydrogen was absorbed in fifteen minutes, and 56 mg. (50%) of cycloöctane with $n^{25}\mathrm{D}$ 1.4558 and m. p. 9–10.5° (98% purity, based on an approximate freezing point constant of 2° per mole % impurity and m. p. 14° for pure cycloöctane) was isolated by the following procedure, which also was used for isolating cycloöctane from microhydrogenations cited subsequently. The catalyst was separated and the acetic acid solution was neutralized with aqueous sodium hydroxide in a 50 ml. volumetric flask, with cooling to prevent volatilization of the product.

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[8] We are indebted to Dr. Marion Burg for the preparation of a sample of this hydrocarbon by the method described in ref. 5, p. 52.

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

[10] Ref. 5, p. 11.

[11] Melting points are corrected and boiling points are uncorrected. Low temperature melting points were determined by freezing samples in capillary tubes and allowing them to melt in a stirred acetone-bath cooled with an inserted test-tube containing Dry Ice or liquid nitrogen. We are indebted to Mr. S. M. Nagy and Mrs. Louise W. Spencer for analyses.

[12] Cope and Estes, THIS JOURNAL, **72**, 1128 (1950).

[13] Naragon and Lewis, *Ind. Eng. Chem., Anal. Ed.*, **18**, 448 (1946).

Water was added to bring the liquid level to the neck of the flask, 1–2 ml. of alcohol-free ether was added, and the mixture was shaken thoroughly. The phases were separated after the mixture stood overnight, or was centrifuged slowly for fifteen minutes. The ether solution was withdrawn with a pipet and distilled through a 20 × 0.6 cm. semi-micro column containing a wire spiral.[14] After removal of the ether the cycloöctane was distilled without fractionation at 60–40 mm. pressure. The cyclooctane was transferred with a micro pipet to a 1 mm. capillary tube constricted at the lower end and containing a 10 mm. column of 26–200 mesh silica gel. The constricted end of the capillary was placed in a tared m. p. capillary tube, and the product was filtered into this receiver by slow centrifuging, weighed, and used for m. p. and refractive index measurements.

A 0.145-g. sample of (I) in 15 ml. of ethyl acetate was ozonized at −33° for fifteen minutes, after which the solvent was removed under reduced pressure. The ozonide was dissolved in 1 ml. of glacial acetic acid and heated on a steam-bath with 1 ml. of 37% hydrogen peroxide for ninety minutes. Distillation to dryness at a bath temperature of 50° and 0.1 mm. pressure gave 150 mg. of a crude crystalline product, which after three crystallizations from a mixture of benzene and dioxane yielded a small amount of malonic acid, m. p. 132.5–133°, identified by mixed m. p. with an authentic sample, which was not depressed. A control experiment with pure malonic acid showed that it was partially decomposed and recovered in poor yield after treatment with hydrogen peroxide under these conditions, so that the yield obtained from the ozonization is not significant.

1,3,5-Cycloöctatriene.—A mixture of cycloöctatrienes (A) (7.9 g., n^{25}D 1.5094, containing 65% of 1,3,5-cyclooctatriene according to its ϵ_{265} value of 2170) was heated on a steam-bath with 2.6 millimoles of potassium *t*-butoxide in 9 ml. of dry *t*-butanol under nitrogen for eighteen hours. Samples (1 ml.) were withdrawn periodically and the hydrocarbon was recovered from them by a procedure similar to the one noted below for the main portion. Refractive index measurements indicated that the isomerization was complete after one hour. The mixture was poured into 200 ml. of water and the hydrocarbon layer was separated and washed with 100 ml. of water. It was passed through a column containing 2 ml. of silica gel to remove *t*-butanol and water; yield 5.9 g. (75%), n^{25}D 1.5226. A yield of 90% was obtained in a similar preparation from which no samples were withdrawn during the isomerization. Rapid distillation (b. p. 71–73° at 60 mm.) did not change the refractive index. Slow fractionation through a 20 × 0.6 cm. semimicro column containing a wire spiral gave a 95% recovery of fractions with n^{25}D from 1.5151 to 1.5239 and a mean value of n^{25}D of 1.5197, indicating some isomerization during distillation which resulted in lowering the refractive index. Evidence that these fractions contained very little if any 1,3,6-cycloöctatriene was derived from their ultraviolet absorption spectra, which coincided closely with the spectrum of 1,3,5-cycloöctatriene purified through the silver nitrate adduct (described below) (Curve 2, Fig. 1). The spectrum of the pure sample had a maximum (ϵ_{265} = 3600) and a minimum (ϵ_{225} = 1190). Fractions from the above distillation showed the following extinctions at these wave lengths: (1), n^{25}D 1.5151, ϵ_{265} = 3420; ϵ_{225} = 1075; (2), n^{25}D 1.5170, ϵ_{265} = 3460; ϵ_{225} = 1065; (6), n^{25}D 1.5239, ϵ_{265} = 3560, ϵ_{225} = 1180.

The m. p. of a fraction of 1,3,5-cycloöctatriene with n^{25}D 1.5215 was −92.5 to −91°, and a mixed m. p. with a sample of 1,3,5-cycloöctatriene prepared from pseudopelletierine, n^{25}D 1.5212, m. p. −92.5 to −91°, was not depressed. The ultraviolet and infrared spectra of these samples (n^{25}D 1.5215) also were identical. Samples of 1,3,5-cycloöctatriene from this preparation and derived from pseudopelletierine also gave identical silver nitrate adducts, prepared by the method described below (m. p. and mixed m. p. 124–125.5°), and identical maleic anhydride adducts, m. p. and mixed m. p. 143.3–144.3°.

A sample of 1,3,5-cycloöctatriene prepared from pseudopelletierine[15] initially had n^{25}D 1.5229. Slow fractional distillation through a semimicro column[14] resulted in lowering the mean refractive index to 1.5198, and the separation of fractions with n^{25}D from 1.5185 to 1.5235. This change parallels closely the changes which occurred in the fractionation of 1,3,5-cycloöctatriene prepared from cycloöctatetraene. A fraction with n^{25}D 1.5190 absorbed 90% of three moles of hydrogen on microhydrogenation and gave cycloöctane with m. p. 3–6° (96% purity).

Treatment of a sample of II prepared from pseudopelletierine (n^{25}D 1.5185) with potassium *t*-butoxide in the manner described previously raised its refractive index to n^{25}D 1.5215.

Purification of a 1,3,5-Cycloöctatriene Isomer through its Silver Nitrate Adduct.—1,3,5-Cycloöctatriene, n^{25}D 1.5214 (7.15 g., 0.0675 mole) was added to a suspension of 11.8 g. (0.0695 mole) of powdered silver nitrate in 35 ml. of boiling absolute ethanol. The silver nitrate dissolved immediately on adding the hydrocarbon. The solution was cooled and the solid product was recrystallized ten times from hot absolute ethanol, yielding 9.0 g. of the silver nitrate adduct, which was air dried for five minutes and then melted at 125–126°, when placed in a bath at 115° rising at 2° per minute. Longer drying resulted in loss of II and depression of the melting point. An analytical sample was dried to constant weight at 20 mm. over calcium chloride and 1,3,5-cycloöctatriene saturated with paraffin.

Anal. Calcd. for $C_8H_{10}\cdot AgNO_3$: C, 34.56; H, 3.63; Ag, 38.82. Found: C, 34.50; H, 4.18; Ag, 39.18.

An 8.0-g. sample of the air-dried silver nitrate adduct was heated slowly from 65 to 120° at 0.2 mm. and the cycloöctatriene which volatilized was collected in a receiver cooled to −80°. The distillate was filtered through silica gel to remove any ethanol which might be present, and yielded 2.64 g. (87%) of the high boiling, high refractive index isomer of 1,3,5-cycloöctatriene; n^{25}D 1.5254; d^{25}_4 0.8970; m. p. −83.5 to −83°.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.47; H, 9.78.

This sample of 1,3,5-cycloöctatriene on microhydrogenation absorbed 100% of three molar equivalents of hydrogen and yielded pure cycloöctane, n^{25}D 1.4558; m. p. 13.4–14.0°.

A 0.91-g. sample of 1,3,5-cycloöctatriene purified in this manner, n^{25}D 1.5254, was heated in a sealed tube under nitrogen at 100° for seven hours. No polymer or gas was formed by this treatment. The colorless product had n^{25}D 1.5215, which was not changed by rapid distillation at 72.5° (60 mm.); d^{25}_4 0.9013; m. p. −90.5 to −89.5°.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.21; H, 9.73.

This sample of 1,3,5-cycloöctatriene on microhydrogenation absorbed 95% of three molar equivalents of hydrogen and gave cycloöctane of 97.5% purity, n^{25}D 1.4565; m. p. 8.0–9.1°.

Properties of Low Boiling Fractions of 1,3,5-Cycloöctatriene with Low Refractive Index.—A sample of 1,3,5-cycloöctatriene after treatment with potassium *t*-butoxide and fractionation as described above, n^{25}D 1.5200 (4.5 g.), was hydrogenated in the presence of 0.225 g. of pre-reduced Adams platinum catalyst in 17 ml. of glacial acetic acid. Hydrogen absorption amounted to 92% of three molar equivalents. (The per cent. hydrogen absorption was not increased by use of palladium on charcoal catalyst or use of ethanol as the solvent with platinum or palladium catalyst. Hydrogenation in the presence of platinum in glacial acetic acid at 0° and at 30° gave the same per cent. hydrogen absorption.) Distillation of the product separated three fractions: (1) a forerun (0.35 g.), b. p. 73–76.5° (97 mm.), m. p. −9 to −4° (91% cycloöctane);

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[14] Gould, Holzman and Niemann, *Anal. Chem.*, **20**, 361 (1948).

[15] We are indebted to Mr. Alfred A. D'Addieco for the preparation of this material by the procedure of ref. 2.

(2) 2.75 g., b. p. 76.5–79° (97 mm.), m. p. 4.5–6.0° (96% cycloöctane); (3) 0.10 g. of a dimeric product, b. p. 120° (0.2 mm.), $n^{25}\mathrm{D}$ 1.5038.

The infrared absorption spectrum of the low boiling fraction indicated that it contained, in addition to cyclooctane, 10–20% of bicyclo[4.2.0]octane,[8] according to the presence of characteristic absorption bands at 7.25, 7.55, 7.63, 8.03, 8.12, 8.56, 9.89, 10.64, 10.81, 10.93, 11.17, 13.42 and 15.95 μ.

The 1,3,5-cycloöctatriene with $n^{25}\mathrm{D}$ 1.5215 had an ultraviolet absorption spectrum identical with the sample purified through its silver nitrate adduct, and infrared spectra of the two samples were very similar (Fig. 3). A sample with $n^{25}\mathrm{D}$ 1.5151, m. p. $< -100°$, which was obtained by slow fractionation of a sample with $n^{25}\mathrm{D}$ 1.5226, gave an infrared spectrum which contained no bands that were not present in the sample with $n^{25}\mathrm{D}$ 1.5215 (Fig. 3).

Reaction of 1,3,5-Cycloöctatriene with Oxygen.—A sample of II prepared from pseudopelletierine (0.55 g.), $n^{25}\mathrm{D}$ 1.5203, was stirred with air in a microhydrogenation apparatus at 35° for three hours, and then with oxygen for fifteen hours, at which time the yellow product was so viscous that it could no longer be stirred. Oxygen absorption amounted to 67% of one molar equivalent according to the change in volume, and 63% according to the increase in weight. Distillation separated 27% of recovered 1,3,5-cycloöctatriene, $n^{25}\mathrm{D}$ 1.5228, and left a polymeric residue which was not volatile at 150° (0.3 mm.). A sample which was freed from 1,3,5-cycloöctatriene by evacuation at 0.1 mm. and room temperature was analyzed.

Anal. Calcd. for $(C_8H_{10}O_2)_n$: C, 69.52; H, 7.29. Found: C, 67.18; H, 7.26.

Reaction of Cycloöctatetraene with Excess Sodium in Liquid Ammonia.—A solution of 30.2 g. (1.31 g. atoms) of sodium in liquid ammonia was added with stirring to a solution of 21.4 g. (0.2 mole) of cycloöctatetraene in 1.5 l. of liquid ammonia at −45 to −35°. A change in color from deep orange to greenish brown occurred after 0.8 ± 0.1 g. atom of sodium had been added. After stirring for twenty minutes following completion of the addition, 1.5 moles of solid ammonium chloride was added in small portions, and the product was isolated in the manner described for preparation of cycloöctatrienes. Fractionation gave 12.2 g. of a major fraction, b. p. 65.5–67° (55 mm.), $d^{25}{}_4$ 0.8265, $n^{25}\mathrm{D}$ 1.4850, m. p. below −120°, 3.5 g. of "dimers," b. p. 130–140° (0.25 mm.), and 1.0 g. of polymeric material. Indication that the major fraction contained aromatic hydrocarbons was obtained by catalytic hydrogenation, for 102% of two molar equivalents of hydrogen was absorbed in the presence of Adams platinum catalyst in acetic acid (conditions which reduce aromatic hydrocarbons), and approximately one molar equivalent of hydrogen was absorbed in the presence of palladium on charcoal in acetic acid. Infrared absorption spectra indicated that the material contained 40–50% of ethylbenzene, identified by its characteristic absorption bands at 5.15, 5.43, 5.62, 6.22, 6.67, 9.17, 9.69 and 11.06 μ.

A sample which had been hydrogenated in the presence of palladium on charcoal in acetic acid to saturate cyclic olefins was condensed with tetrachlorophthalic anhydride in the presence of aluminum chloride and yielded a small amount of *o*-(4-ethylbenzoyl)-tetrachlorobenzoic acid[16] (identified by m. p. and mixed m. p.), providing chemical evidence for the presence of ethylbenzene in the sample. Infrared analysis of a sample which was hydrogenated in the presence of Adams platinum catalyst in glacial acetic acid indicated that it contained about 50% of cycloöctane (absorption bands at 7.77, 9.58, 10.46, 11.72, 13.04 μ) and 50% ethylcyclohexane (bands at 7.30, 8.39, 10.14, 11.27, 11.90, 13.24 μ).

Reaction of Cycloöctatetraene with Lithium.—Cyclooctatetraene (41.3 g., 0.39 mole) was added with stirring during one-half hour to a suspension of 10 g. (1.4 g. atoms) of powdered lithium in 700 ml. of dry ether. The mixture was heated under reflux and stirred in a nitrogen atmosphere for twenty-four hours, at which time an additional 1 g. of powdered lithium was added to the tan colored suspension, and heating and stirring were continued for an additional twenty-four hours. Methanol (85 ml., 2 moles) was added slowly, followed by 300 ml. of water. The ether layer was separated, washed with two 100-ml. portions of water, and dried over calcium chloride. Picric acid (50 mg.) was added, and the solution was distilled through a 15 × 1.0 cm. helix-packed column. The fractions separated were: (1) 7.0 g., b. p. 61–64° (52 mm.), $n^{25}\mathrm{D}$ 1.5043; (2) 21 g., b. p. 64–65° (52 mm.), $n^{25}\mathrm{D}$ 1.5062. Distillation of the residue from a Claisen flask yielded: (3) 7.0 g., b. p. 107–112° (0.25 mm.), $n^{25}\mathrm{D}$ 1.5422, and 2.9 g. of a polymeric residue.

Fraction (2) was passed through one-half its volume of silica gel to remove any traces of methanol which might be present, and then had $n^{25}\mathrm{D}$ 1.5058. The following data indicated that it contained hydrocarbons with less unsaturation than cycloöctatriene.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 89.98; H, 9.87.

Microhydrogenation in the presence of Adams platinum catalyst in acetic acid resulted in the absorption of 2.67 molar equivalents of hydrogen, and yielded cycloöctane with m. p. 2–7° (96% purity). The ultraviolet absorption spectrum of fraction (2) had $\epsilon_{265} = 1650$, indicating the presence of 45% of 1,3,5-cycloöctatriene. Reaction with maleic anhydride[3] gave a low yield of the adduct of 1,3,5-cycloöctatriene, m. p. and mixed m. p. with a known sample prepared from 1,3,5-cycloöctatriene prepared from pseudopelletierine, 144–145°. Isomerization of 2.7 g. of fraction (2) in the presence of potassium *t*-butoxide in the manner previously described gave 2.1 g. of a product with $n^{25}\mathrm{D}$ 1.5140 and $\epsilon_{265} = 2600$, which corresponds to a 1,3,5-cycloöctatriene content of 70%; the infrared absorption spectrum of this fraction indicated the presence of 80 ± 10% of 1,3,5-cycloöctatriene.

Fraction (3) was washed with 5% potassium carbonate to remove picric acid and then purified by two evaporative distillations at a bath temperature of 110° and 0.1 mm. The following data indicate that this product was a mixture of cycloöctadienylcycloöctadienes: $n^{25}\mathrm{D}$ 1.5435; $d^{25}{}_4$ 0.9718; m. p. −65 to −55°.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.65; H, 10.29.

The hydrocarbon readily absorbed oxygen from the air and yielded a very viscous colorless product.

Hydrogenation over Adams platinum catalyst in acetic acid resulted in absorption of 99% of four molar equivalents of hydrogen and yielded bicycloöctyl,[6] $n^{25}\mathrm{D}$ 1.4998; $n^{20}\mathrm{D}$ 1.5015; $d^{25}{}_4$ 0.9215; $d^{20}{}_4$ 0.9245; m. p. 10–11°.

Silver Nitrate Adducts of Cycloöctatetraene (a).—Twenty milliliters of 10% aqueous silver nitrate and 3.0 ml. of cycloöctatetraene were shaken together for fifteen minutes. The solid granular precipitate was separated from the mother liquor and the excess cycloöctatetraene, and sucked and pressed on the funnel for two minutes. The solid product was dried to constant weight (twenty hours) over Drierite and cycloöctatetraene saturated with paraffin wax, and yielded 1.28 g. (29%) of pale yellow crystals.

Anal. Calcd. for $2C_8H_8 \cdot AgNO_3$: C, 50.80; H, 4.27; Ag, 28.54. Found: C, 51.12; H, 4.51; Ag, 28.1.

When the adduct was placed in a bath at 170° rising at 2° per minute cycloöctatetraene was lost, and the sample melted with decomposition at 173–174°.

(b) Two grams of silver nitrate in 5.0 ml. of water was shaken with 2.0 ml. of cycloöctatetraene in 5 ml. of 50–60° ligroin. The mixture was warmed to 50° to dissolve the fine crystalline precipitate, and on slow cooling precipitated a mass of large homogeneous lathe-shaped crystals. The precipitate was collected on a funnel, sucked dry in air for one minute, and dried over Drierite and cycloöctatetraene saturated with paraffin at 20 mm. for twenty-four hours.

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[16] Underwood and Walsh, This Journal, **57**, 940 (1935).

Anal. Calcd. for $C_8H_8 \cdot AgNO_3$: C, 34.81; H, 2.92; Ag, 39.1. Found: C, 34.54; H, 3.00; Ag, 39.7.

When this adduct was placed in a bath at 170° rising at 2° per minute, cycloöctatetraene was lost, and the residual solid melted with decomposition at 173 ± 0.5°.

(c) When the complexes of formula $C_8H_8 \cdot AgNO_3$ or $2C_8H_8 \cdot AgNO_3$ were recrystallized from 20% aqueous silver nitrate, or from ethanol, a third compound was formed. The pale green crystalline product obtained after three recrystallizations from 15 parts of hot absolute ethanol, after drying at 30 mm. for twelve hours over calcium chloride and cycloöctatetraene saturated with paraffin, melted at 173–174° when placed in a bath at 170° rising at 2° per minute. There was no detectable prior loss of cycloöctatetraene.

Anal. Calcd. for $2C_8H_8 \cdot 3AgNO_3$: C, 26.70; H, 2.25; Ag, 45.10. Found: C, 26.73; H, 2.59; Ag, 45.51.

When the complex $C_8H_8 \cdot AgNO_3$ was evacuated to 0.1 mm. at room temperature, it lost cycloöctatetraene rapidly until a composition approximating $2C_8H_8 \cdot 3AgNO_3$ was reached. Continued evacuation at 70–85° resulted in virtually complete removal of unchanged cycloöctatetraene.

Both the complexes $C_8H_8 \cdot AgNO_3$ and $2C_8H_8 \cdot AgNO_3$ suffered partial decomposition when dissolved in water. A portion of the cycloöctatetraene could be recovered by steam distillation or by ether extraction of the solutions. A better recovery of cycloöctatetraene was effected by pouring the aqueous solution of complexes into cold concentrated ammonium hydroxide.

When 30.5 g. of the $2C_8H_8 \cdot 3AgNO_3$ complex was dissolved in 100 ml. of water, 25 g. of sodium chloride in 100 ml. of water was added, and the mixture steam distilled, 7.85 g. (90%) of cycloöctatetraene, n^{25}_D 1.5348, m. p. −4.5 to −3.5°, was recovered. Infrared absorption spectra, utilizing the characteristic absorption band of styrene at 11.01 μ, indicated the product to be virtually free from styrene. The starting material had contained 0.5% of styrene.

Summary

The reaction of cycloöctatetraene with two equivalents of sodium in liquid ammonia, followed by addition of ammonium chloride, has been found to yield a mixture of 1,3,6- and 1,3,5-cycloöctatrienes, from which the 1,3,6-isomer has been separated in 94–96% purity by fractional distillation. Treatment of the mixture of isomers with potassium *t*-butoxide resulted in rearrangement of the unconjugated to the conjugated isomer, and this procedure provides a convenient synthesis for 1,3,5-cycloöctatriene.

1,3,5-Cycloöctatriene has been found to rearrange on heating to an isomer with lower refractive index and a nearly identical ultraviolet absorption spectrum, which is not 1,3,6-cyclooctatriene, and may be either a stereoisomer or a bridged structural isomer.

Three crystalline addition compounds of cyclooctatetraene with silver nitrate have been prepared, and a crystalline adduct of silver nitrate with 1,3,5-cycloöctatriene. These addition compounds have proved to be useful as derivatives and for purification of the hydrocarbons, which can be regenerated from them.

Cambridge, Massachusetts

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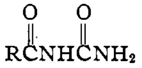
Anticonvulsant Drugs. III. Some Allophanates

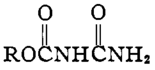
By M. A. Spielman, J. D. Barnes and W. J. Close

An earlier communication[1] described the synthesis of some acylureas (I) which were tested for their anticonvulsant activity. Each known anticonvulsant drug contains in its molecule a lipophilic and a hydrophilic component, and in the acylureas the hydrophilic part is the carbonylurea fragment $-CONHCONH_2$. With the idea of modifying the latter, an oxygen atom may be intercalated at the point of junction, and the resulting products are allophanates (II) which offer an interesting field for exploration in the search for drugs against epilepsy.



$RC(=O)NHC(=O)NH_2$

I



$ROC(=O)NHC(=O)NH_2$

II

The esters of allophanic acid have been known for more than a century[2] but their pharmacological characteristics have been little examined except that a few have been tested as hypnotics.[3] Of these, *t*-amyl allophanate was found to be of some interest, although it has never become established in clinical use.

Several procedures for the preparation of allophanates have been published[2,4] but we found that when small amounts were desired, the method of choice was that of passing cyanic acid vapor into an alcohol without solvent. Alcohols in limited amount were diluted with dry ether. Like others[5] we observed that significant amounts of carbamates were formed in the reaction and often led to reduced yields. Preparation of allophanates by acidifying a solution or suspension of potassium cyanate in an alcohol[4] gave erratic results; from 3-methyl-2-butanol, for example, we isolated only the carbamate.

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[1] Spielman, Geiszler and Close, This Journal, **70**, 4189 (1948).

[2] A history of allophanates and a bibliography of preparative methods are given by Bougault and Leboucq, *Bull. soc. chim.*, [4] **47**, 594 (1930).

[3] Fraenkel, "Arzneimittelsynthese," Julius Springer, Berlin, 1927, p. 525; German Patent 226,228; Remfry, *J. Chem. Soc.*, **99**, 625 (1911).

[4] Werner and Gray, *Proc. Roy. Soc. Dublin*, **24**, 209 (1947); German Patent 248,164; Davis and Blanchard, This Journal, **51**, 1809 (1929).

[5] Béhal, *Compt. rend.*, **168**, 945 (1919); German Patent 120,864.