

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 72

JANUARY 2, 1951

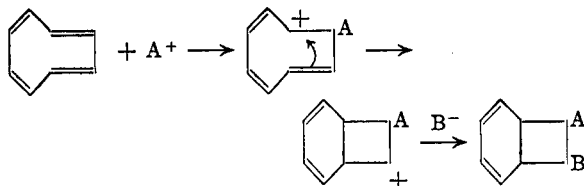
NUMBER 12

[CONTRIBUTION NO. 282 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

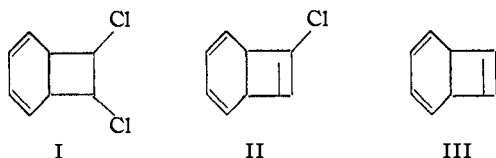
Some New Reactions of Cycloöctatetraene

BY RICHARD E. BENSON AND THEODORE L. CAIRNS

One of the most unusual chemical reactions of cycloöctatetraene is its facile conversion into derivatives of bicyclo[4.2.0]octane¹ through reactions which probably proceed by a carbonium ion mechanism. The proposals of Friess and Boekelheide concerning the possible steps in the mechanism of formation of halogenated derivatives² appear reasonable and probably should be extended to the general case of the reaction of AB (*e. g.*, chlorine or bromine) with cycloöctatetraene as represented by the equation



This work was undertaken to determine if a typical bicycloöctane derivative, cycloöctatetraene dichloride (I), could be converted to the corresponding monosubstituted derivative, 7-chlorobicyclo[4.2.0]2,4,7-octatriene (II) or to the parent hydrocarbon (III). It was found that



removal of the chlorine atoms from I under very mild conditions with sodium iodide in acetone

(1) Reppe, Schlichting, Klager and Toepel, *Ann.*, **560**, 1 (1948); see also Copenhagen and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 191.

(2) Friess and Boekelheide, *THIS JOURNAL*, **71**, 4145 (1949).

led only to cycloöctatetraene itself and not to the new bicyclo[4.2.0]2,4,7-octatriene (III). Under a wide variety of conditions it was not possible to dehydrochlorinate I to a monochloro derivative of either the bicycloöctatriene or of cycloöctatetraene. The only non-resinous material formed in these dehydrochlorination experiments was β -chlorostyrene obtained by the pyrolytic displacement of hydrogen chloride. It thus appears that the bicycloöctatriene ring system is unstable with respect to both the cycloöctatetraene and styrene systems.

During the course of this work the previously unreported Diels-Alder adducts of cycloöctatetraene and of I with acrylonitrile were prepared. It was also found that the action of hydrogen peroxide on cycloöctatetraene led to formation of phenylacetaldehyde and phenylacetic acid.

Experimental

Cycloöctatetraene Dichloride (7,8-Dichlorobicyclo[4.2.0]2,4-octadiene).—The synthesis of cycloöctatetraene was conducted essentially as reported by Reppe.¹ The refractive index of the product obtained, n_D^{25} 1.5350, is in closer agreement with the value reported by Willstätter and Waser,³ n_D^{20} 1.5389, than with that of Reppe,¹ n_D^{20} 1.5290.

The theoretical amount of chlorine was passed over a vigorously stirred solution of cycloöctatetraene (2 moles) in chloroform at -10 to -5° . At the completion of the reaction, the solution was flushed with nitrogen and allowed to warm to room temperature. Distillation gave 77–82% yields of I, *b. p.* $67-69.5^\circ$ (1.4–1.5 mm.), n_D^{25} 1.5369; *lit.*¹ *b. p.* $67-68^\circ$ (1.2 mm.), n_D^{20} 1.5417. A small amount of cycloöctatetraene was recovered and some of its more highly chlorinated derivatives were formed.

A sample stored under nitrogen at 5° for two weeks deposited crystalline material. Redistillation indicated a conversion of about 10% to a product of *m. p.* $147-156^\circ$ after two recrystallizations from glacial acetic acid. A "dimeric dichloride," *m. p.* 191° , has been previously reported.¹

(3) Willstätter and Waser, *Ber.*, **43**, 1180 (1910).

Microhydrogenation analysis⁴ (PtO₂ catalyst, ethanol solvent) gave the following results: 0.0248, 0.0250 g. H₂/g. sample; titration of hydrogen chloride liberated gave 0.0736, 0.0731 g. HCl/g. sample. Correction of the hydrogenation values to account for the hydrochloric acid formed gives 0.0208 g. H₂/g. sample: theory, 0.0231 g. H₂/g. sample (two double bonds); 0.0347 g. H₂/g. sample (three double bonds).

The above data are in accord with the structure of the dichloride proposed by Reppe on the basis of chemical evidence.

Reaction of Cyclooctatetraene Dichloride with Sodium Iodide.—To a mixture of 60 g. of sodium iodide and 25 g. of sodium bisulfite in 300 ml. of acetone was added a solution of 35 g. of cyclooctatetraene dichloride in 60 ml. of acetone over a period of two hours. The red color of free iodine developed immediately and the reaction mixture was allowed to stand at room temperature for 45 hours. At the end of this time it was warmed to 50° for 30 minutes and water added until the iodine color had disappeared. The resulting solution was steam distilled and the product separated to give 7.0 g. (35%) of yellow oil, *n*_D²⁵ 1.5297. Distillation of the liquid through a 5-mm. 18-inch platinum gauze-packed column indicated the product to be cyclooctatetraene, b. p. 69.6° (66 mm.), *n*_D²⁵ 1.5331. *Microhydrogenation analysis.*—Calcd. for cyclooctatetraene, 0.077 g. H₂/g. sample (four double bonds). Found: cyclooctatetraene (authentic) 0.080, 0.077 g. H₂/g. sample; product obtained above, 0.075, 0.078 g. H₂/g. sample. *Melting point determinations.*—Cyclooctatetraene (authentic) -5.72°, -5.78°; m. p. of above product, -5.58°; mixed m. p. -5.62°.

Pyrolysis of Cyclooctatetraene Dichloride.—A small distilling flask was equipped with a dropping funnel and a condenser to which were attached two flasks in series. The first flask contained glass wool and was suspended in an ice-bath, and the second flask was cooled with a Dry Ice-acetone mixture. Several small clay chips were placed in the distilling flask and the flask heated gently by means of a flame. Cyclooctatetraene dichloride (125 g.) was added dropwise by means of the funnel onto the clay chips. Copious amounts of hydrogen chloride fumes were evolved and the addition required about three hours. The distillates in the two receivers were combined, ether added and the solution washed with water, sodium bicarbonate and dried over magnesium sulfate. Distillation gave 46.5 g. of slightly yellow liquid, b. p. 88-96° (28 mm.), *n*_D²⁵ 1.5693. Upon refractionation the main fraction distilled at 75-77° (10 mm.) and had the following physical properties: *n*_D²⁵ 1.5741, *d*₄²⁵ 1.1033; the reported physical constants for β-chlorostyrene⁵: b. p. 79.5° (11 mm.), *n*_D²⁵ 1.5736, *d*₄²⁵ 1.1040. Analytical data, including microhydrogenation proved the product to be β-chlorostyrene.

Miscellaneous dehydrochlorination experiments con-

(4) The analyses were performed under the direction of Dr. J. W. Stillman.

(5) E. H. Huntress, "Preparation, Properties, Chemical Behavior and Identification of Organic Chlorine Compounds," John Wiley & Sons, New York, N. Y., 1948.

ducted with I either gave good recovery of the dichloride or led to extensive tar formation. In the presence of pyridine and such solvents as diethyl ether, tetrahydrofuran or cyclohexane at reflux temperatures, I was recovered in 60-70% yields. A similar result was obtained with triethylamine in acetone. With other solvents at higher temperatures, some "dimeric dichloride"¹ was formed in addition to viscous polymeric products.

Cyclooctatetraene-Acrylonitrile Adduct (Tricyclo[4.2.2.0]^{2,3,9}-decadiene-7-carbonitrile).—A mixture of 104 g. of cyclooctatetraene, 160 g. of acrylonitrile, 200 ml. of chlorobenzene and 1 g. *p*-*t*-butylcatechol was heated in a stainless steel bomb at 180° for six hours. The resulting product was fractionated through a 14-inch platinum gauze-packed column to give 22 g. (33% conversion, based on acrylonitrile) of a viscous, colorless oil, b. p. 103-110° (2.0-2.5 mm.) which upon refractionation gave a colorless liquid of b. p. 67-68° (0.2 mm.), *n*_D²⁵ 1.5236, *d*₄²⁵ 1.0742. *Anal.* Calcd. for C₁₁H₁₁N: C, 84.03; H, 7.04; N, 8.91. Found: C, 84.13, 83.69, 83.64; H, 7.08, 7.36, 7.14; N, 9.43, 9.44.

Cyclooctatetraene Dichloride-Acrylonitrile Adduct (3,4-Dichlorotricyclo[4.2.2.0]^{2,6,9}-decene-7-carbonitrile).—A solution of 52.5 g. of cyclooctatetraene dichloride, 56 g. of acrylonitrile and 300 ml. of chlorobenzene was heated in a stainless steel bomb at 150° for six hours. Fractionation gave 38 g. (56% yield) of viscous liquid, b. p. 177-184° (3.4-3.9 mm.), *n*_D²⁵ 1.5472. *Anal.* Calcd. for C₁₁H₁₁Cl₂N: C, 57.91; H, 4.86; Cl, 31.09. Found: C, 58.28, 58.62; H, 5.14, 4.94; Cl, 30.20, 30.46.

Reaction of Cyclooctatetraene with Hydrogen Peroxide in Formic Acid.—To a mixture of 52 g. of cyclooctatetraene and 400 g. of 98-100% formic acid was added slowly with stirring and occasional cooling 179 g. of 30% H₂O₂ (Merck Superoxol). The temperature was maintained at 35-40° and after the initial reaction had subsided the mixture was stirred at room temperature for 18 hours, then at 40-42° for an additional 24 hours. The formic acid was removed by distillation and the product fractionated through a 4-inch Vigreux column. There was obtained 12.1 g. of phenylacetaldehyde (20%), identified by boiling point, refractive index and the 2,4-dinitrophenylhydrazone derivative, and 33.6 g. of phenylacetic acid (49%), m. p. 74-76°, mixed m. p. with authentic phenylacetic acid, 73.5-75°. The m. p. of the *p*-bromophenacyl ester derivative was not depressed by an authentic sample.

A second experiment conducted similarly indicated that a small amount of benzaldehyde was also formed in this reaction.

Summary

Dechlorination of cyclooctatetraene dichloride with sodium iodide leads to cyclooctatetraene and not to bicyclo[4.2.0]2,4,7-cyclooctatriene, while dehydrochlorination by pyrolysis forms β-chlorostyrene.

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RECEIVED JUNE 8, 1950