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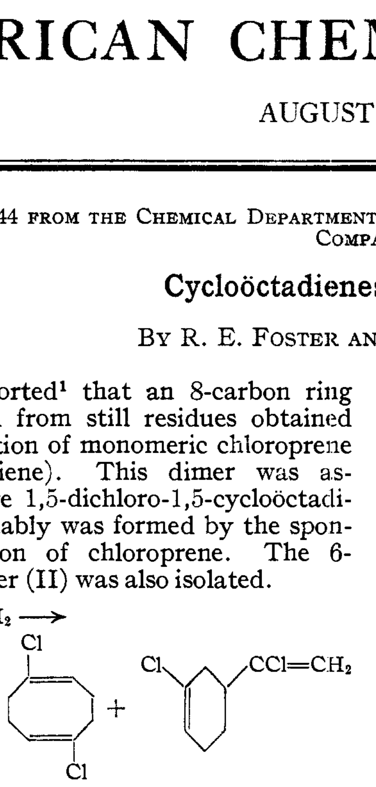
Cycloöctadienes from Dienes

BY R. E. FOSTER AND R. S. SCHREIBER

It has been reported[1] that an 8-carbon ring dimer was isolated from still residues obtained during the purification of monomeric chloroprene (2-chloro-1,3-butadiene). This dimer was assigned the structure 1,5-dichloro-1,5-cycloöctadiene (I) and presumably was formed by the spontaneous dimerization of chloroprene. The 6-membered ring dimer (II) was also isolated.

$4CH_2{=}CCl{-}CH{=}CH_2 \longrightarrow$



(I) (II)

Further, at the Reconstruction Finance Corporation Neoprene Plant, Louisville, Ky., operated by the E. I. du Pont de Nemours and Company, Mallonee and and Wooding isolated a third, lower-boiling product which tentatively has been assigned the structure 3-chloro-1-vinyl-1,3-cyclohexadiene. This material probably was formed by the dehydrochlorination of 1,3-dichloro-1-vinyl-3-cyclohexene, an isomer of (II).

Carothers[2] demonstrated earlier that a mixture of dimers was obtained by heating monomeric chloroprene. The components of this mixture were not identified, but it seems probable on the basis of comparable boiling points that two, or perhaps all three, of these compounds were present in the "β-polychloroprene" described by Carothers.

The purpose of this paper is to report the confirmation of the dimerization of chloroprene to a mixture of 6- and 8-membered ring compounds and to record two additional examples of the dimerization of conjugated dienes, 1,3-butadiene itself and 2,3-dichloro-1,3-butadiene,[3] to the corresponding cycloöctadienes.[4]

By heating chloroprene at 80° for one hundred and twenty hours in the presence of phenothiazine to inhibit polymerization and activated charcoal,[5] greater than 20% conversion to dichloro-1,5-cycloöctadiene was obtained.[5a] In addition, the two 6-membered ring compounds mentioned above were isolated. The structures of the carbon skeletons of these three materials were established by the reduction of the chloro compounds over platinum oxide in the presence of sodium acetate to the known saturated hydrocarbons. The fraction boiling at 147–149° was presumed to be impure cycloöctane on the basis of its boiling point and freezing point (9°); the 8-carbon ring was confirmed by oxidation with nitric acid to suberic acid.

The dimerization of 1,3-butadiene at 100–120° proceeded to give a preponderance of vinylcyclohexene, although the presence of 1–5% of an 8-membered ring dimer was demonstrated. The total dimerization product was hydrogenated and fractionated. The infrared spectra of the final fractions were compared with those of known mixtures of cycloöctane and ethylcyclohexane (see Fig. 1), and the proportion of cycloöctane in the

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(1) Brown, Rose and Simonsen, *J. Chem. Soc.*, 101 (1944).

(2) Carothers, Williams, Collins and Kirby, THIS JOURNAL, 53, 4211 (1931).

(3) Carothers and Berchet, U. S. Patent 1,965,369.

(4) During the preparation of this paper, it was brought to our attention that Dr. Karl Ziegler has reported the conversion of 1,3-butadiene at temperatures above 200° to a mixture of vinylcyclohexene, cycloöctadiene, and octahydrobiphenyl. Details of this work have not been published. Ziegler, "A New Approach to the Cycloöctane Series," meeting of the German Chemical Society, Heidelberg, April 15–18, 1947.

(5) Although the evidence is not unequivocal, there are indications that the yield of dimers is improved by the inclusion of activated charcoal, possibly as a result of the increased surface area.

(5a) Cope and Bailey, THIS JOURNAL, 70, 2205 (1948), have developed a modified procedure for conducting this dimerization at atmospheric pressure.

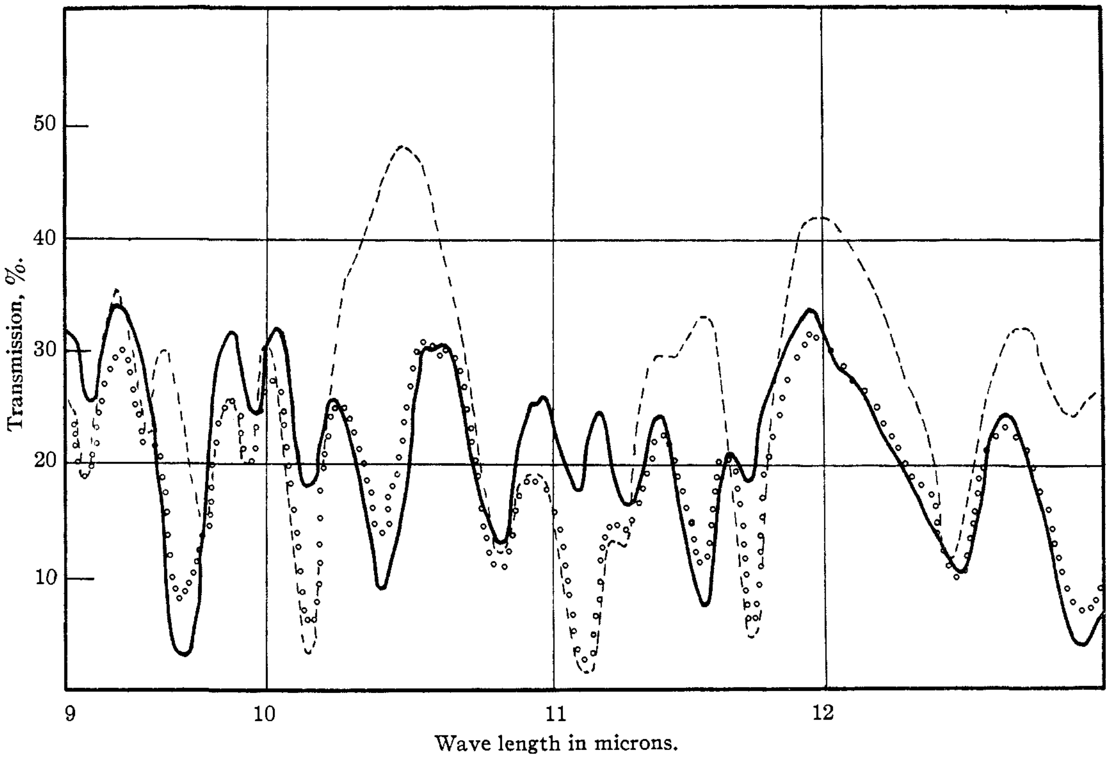

Fig. 1.—Infrared absorption spectra of cycloöctane, —; ethylcyclohexane, ---; and 1:1 cycloöctane–ethylcyclohexane, O-O-O.

total reduced dimer mixture was readily calculated. The identity of the final fractions was established by isolating cycloöctane in the pure state and subsequently oxidizing it to suberic acid.

The dimerization of 2,3-dichloro-1,3-butadiene was carried out at 80° for one hundred and twenty hours. Only one dimeric product, formed in 12.5% yield, was isolated; the remainder was converted to polymer. The dimer was shown to possess an 8-carbon ring by reduction to cycloöctane.

Experimental

Dimerization of Chloroprene.—One hundred and fifty grams of chloroprene, 3 g. of phenothiazine, and 10 g. of Darco (Grade S-51) were sealed in a pressure bottle under nitrogen and agitated at 80° for one hundred and twenty hours. The dark, mobile product was filtered to remove a small amount of polymer and charcoal (15 g.) and the filtrate (119 g.) was distilled. Unchanged monomer (25 g.) was removed at atmospheric pressure and the remainder was distilled under reduced pressure. The following fractions were obtained: (A) 3-chloro-1-vinyl-1,3-cyclohexadiene (15 g., 16%) 67–70° (17 mm.); (B) 3-chloro-1-α-chlorovinyl-3-cyclohexene (19 g., 20%) 96–100° (17 mm.); (C) dichloro-1,5-cycloöctadiene (28.2 g.) 109–118° (17–18 mm.). Infrared data indicated this last fraction to contain 75% 8-membered ring compound which corresponds to 22% yield of dichloro-1,5-cycloöctadiene. The total yield of dimeric products was 66% based on 96 g. of chloroprene, the amount consumed during the reaction.

These samples were refractionated for analysis. Fraction A: B. p. 61–62° (8.5 mm.), $n^{25}\text{D}$ 1.5138, d^{25}_4 1.051, *Anal.* Calcd. for C_8H_9Cl: C, 68.33; H, 6.45; Cl, 25.22; mol. wt., 141. Found: C, 67.45, 67.31; H, 6.49, 6.51; Cl, 27.02, 26.75; mol. wt., 154, 155 (ebullioscopic method in benzene).

Fraction B: B. p. 89–89.5° (8 mm.), $n^{25}\text{D}$ 1.5138, d^{25}_4 1.169. *Anal.* Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.91, 54.96; H, 5.83, 5.94; Cl, 39.62, 39.73.

Fraction C: B. p. 105–106° (8 mm.), $n^{25}\text{D}$ 1.5312; d^{25}_4 1.203. *Anal.* Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.47, 54.77; H, 5.97, 5.99; Cl, 39.42, 39.45.

Reduction of Fraction C.—A mixture of 9 g. of the dimer boiling at 109–118° (17–18 mm.), 50 ml. of glacial acetic acid, 13 g. of hydrated sodium acetate, and 1 g. of platinum oxide was agitated under 45 lb. hydrogen pressure until the reduction in pressure was 18 lb. (theory, 17.5 lb.). This mixture was filtered into water and subsequently extracted with an ether–benzene solution (1:1, by volume). The organic layer was dried over magnesium sulfate and distilled through a small column. The cycloöctane, boiling at 147–149°, 2.2 g. (34.4%), was employed in the following oxidation.

One gram of the hydrocarbon was added to 10 ml. of concentrated nitric acid (sp. gr. 1.42) and heated at 78–80° for twenty-four hours. The mixture was cooled in an ice-bath and the crystalline solid, 0.35 g., was isolated by filtration. The crude material crystallized from water as white plates, m. p. 140–141°. A mixture with an authentic sample of suberic acid melted at 140–141°.

Reduction of Fractions A and B.—In a manner similar to that described above, Fractions A and B were hydrogenated to give in each case ethylcyclohexane, b. p. 130–131°, $n^{25}\text{D}$ 1.4342.

Dimerization of Butadiene.—A mixture of 4800 g. of butadiene, 480 g. of Darco (Grade S-51), and 100 g. of *p*-*t*-butylcatechol was heated in a 3-gal. autoclave at 120° for sixty hours. At the end of this time, 490 g. of butadiene was recovered by venting the autoclave through a Dry Ice trap. The product was filtered (3861 g.) and hydrogenated at room temperature under 1500 lb. pressure in the presence of 15 g. of ruthenium dioxide. From the reduced hydrocarbon mixture, ethylcyclohexane (2355 g.) was removed at 130–131°, or 68–69° (100 mm.), $n^{25}D$ 1.4312. The residue was rapidly distilled through a short-path still to remove the hydrocarbon from *p*-butylcatechol. This distillate was separated by distillation through a 10-inch helices-packed column into the following fractions: (D) b. p. 135–142°, $n^{25}D$ 1.4480, 18.5 g.; (E) b. p. 143–150°, $n^{25}D$ 1.4531, 30.8 g.; (F) b. p. 151–153°, $n^{25}D$ 1.4551, m. p. 6–7°, 1.1 g. On the basis of refractive indices and infrared data, these fractions contain: (D) 66% cycloöctane; (E) 86% cycloöctane; (F) 94% cycloöctane. The total yield of cycloöctane amounted to approximately 1%. Fractionation and infrared analyses of smaller preparations indicated cycloöctane yields of 3–5%. Fraction F was conclusively identified by nitric acid oxidation to a solid acid, m. p. 140–141°, which showed no depression in melting point when mixed with an authentic sample of suberic acid.

Dimerization of 2,3-Dichloro-1,3-butadiene.—A mixture of 91.3 g. of 2,3-dichloro-1,3-butadiene,[3] 3 g. of phenothiazine, and 5 g. of Darco (Grade S-51) was agitated in a pressure bottle at 80° for one hundred and twenty hours. The resulting solid mass was extracted with several 200-ml. portions of ethanol. The alcohol was removed through a Vigreux column and the tarry solid was distilled at reduced pressure to give 11.3 g. (12.5%) of a solid, b. p. 140–146° (3.6 mm.). This was the only distillable product, and on crystallization from an acetone–alcohol–water mixture (5:5:1, by volume) gave white plates, m. p. 98–99°. The material appeared to be a very stable compound.

Anal. Calcd. for $C_8H_8Cl_4$: Cl, 57.66; mol. wt., 246. Found: Cl, 57.0, 56.8; mol. wt., 241, 241 (ebullioscopic method in benzene).

This material was hydrogenated in acetic acid solution in the same manner as that described for the dimer from 2-chloro-1,3-butadiene. The reduction mixture was added to water, and the hydrocarbon was isolated by extraction with benzene. The organic solution was dried and distilled, and the fraction boiling at 140–150° was shown to be approximately 80% cycloöctane by comparison of its infrared absorption curve with that of an authentic sample of cycloöctane.

The Removal of Chlorine from Dichloro-1,5-cycloöctadiene.—The action of sodium in liquid ammonia was found to effect the removal of the halogens from dichloro-1,5-cycloöctadiene without simultaneous reduction of the carbon–carbon double bonds.

Thirty-six grams of dichloro-1,5-cycloöctadiene was mixed with 200 ml. of liquid ammonia and approximately 100 ml. of absolute ether was added to effect homogeneity. Ten grams of sodium was added in small pieces and the mixture was stirred and allowed to reflux under a Dry Ice condenser until the sodium had dissolved. This required about two hours. The ammonia was then allowed to evaporate and the residue was filtered. There was obtained 43.4 g. of black solid (theory for NaCl is 23.2 g.), suggesting that considerable polymerization of the product had occurred. The filtrate was dried and distilled; the product boiling at 149–160° weighed 3.9 g., which corresponded to a 19% yield of cycloöctadiene. This was redistilled, and the pure material boiling at 150–152° was presumed to be 1,5-cycloöctadiene.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.78, 88.99; H, 10.94, 11.11.

Cope and Bailey[5] have found conditions for this reaction which give a 56% yield of the product.

Acknowledgment.—The authors are indebted to Dr. J. W. Stillman, under whose supervision the microanalyses were carried out, and to Miss Doris Huck for the infrared curves.

Summary

The dimerization of chloroprene to a mixture of 6- and 8-membered ring compounds has been confirmed. This unusual dimerization to 8-membered ring compounds has been extended to 1,3-butadiene and 2,3-dichloro-1,3-butadiene.

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

Cyclic Polyolefins. II. Synthesis of Cycloöctatetraene from Chloroprene[1]

BY ARTHUR C. COPE AND WILLIAM J. BAILEY[2]

Cycloöctatetraene has been prepared by the thirteen-step Willstätter synthesis from pseudopelletierine,[3,4] and by a catalytic process from acetylene.[5] We have continued an investigation of synthetic routes to cycloöctatetraene in a search for a reasonably short synthesis which could be adapted to the preparation of functional derivatives of cycloöctatetraene, which are not accessible through any reactions reported for the hydrocarbon.[5] This paper describes a seven-step synthesis of cycloöctatetraene from chloroprene (2-chloro-1,3-butadiene).

A method for the preparation of a cyclic dimer of chloroprene containing an eight-membered ring (previously isolated from chloroprene distillation residues[6]) has been developed by Foster and Schreiber.[7] By a modification of their procedure, chloroprene was heated in the presence of phenothiazine as a polymerization inhibitor and converted into a mixture of dimers. The eight-membered ring dimer (I) was separated from six-membered ring dimers by fractional distillation, treatment with alcoholic alkali to remove a dimer containing reactive chlorine which otherwise was difficult to separate, and refractionation. The eight-membered ring structure of I is established by its hydrogenation to cycloöctane,[6,7] which we have

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[1] Presented at the Tenth National Organic Chemistry Symposium, Boston, Massachusetts, June 13, 1947.

[2] Arthur D. Little Postdoctorate Fellow, 1946–1947.

[3] Willstätter and Waser, *Ber.*, **44**, 3423 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

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

[5] Described in Department of Commerce reports of German technological developments, including a translation of a paper by W. J. Reppe reprinted in "German Synthetic Fiber Developments," p. 631, Textile Research Institute, New York, N. Y., 1946 (P. B. 7416).

[6] Brown, Rose and Simonsen, *J. Chem. Soc.*, 101 (1944).

[7] Foster and Schreiber, THIS JOURNAL, **70**, 2303 (1948).