[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Studies in the Bicyclo[2.2.1]heptane Series. V. Reactions of Bicyclo[2.2.1]heptadiene[1]

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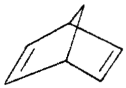
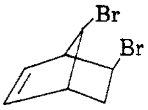
Received March 6, 1957

The course of the reaction of bicyclo[2.2.1]heptadiene (norbornadiene) with water, methanol, performic acid, hydrobromic acid, and nitrosyl chloride is described and the preparation of a sample of 3,5-dibromonortricyclene free of olefinic isomers is reported.

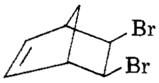
In connection with previous investigations in this Laboratory of the preparation and properties of compounds containing the bicyclo [2.2.1] heptyl ring system, it seemed of interest to study the addition of certain common reagents to bicyclo [2.2.1] heptadiene (norbornadiene) (I), the preparation of which has been reported by Hyman,[3] by Parham and his co-workers,[4] and by Hine and his co-workers.[5] The addition of ionic reagents to the diene has been shown in some instances to proceed with rearrangement to the nortricyclenic system and in others to give unrearranged addition products. Bromination of I at low temperature has been reported by Schmerling and his co-workers[6] to give a complex mixture of isomeric dibromides; namely, 5,7-dibromo-2-norbornene (II), 5,6-dibromo-2-norbornene (III), and 3,5-dibromonortricyclene (IV). The bromination of I has also been reported by Winstein and Shatavsky.[7] Addition of formic acid resulted in the formation of 3-formylnortricyclene (V), and hydrogen chloride and hydrogen bromide gave a mixture of unsaturated and nortricyclenic halides.[6] On reaction with *p*-methylthiophenol,[8] the diene again afforded two products, a nortricyclenic (VI) and an isomeric olefinic addition product (VII). A series of nortricyclenic halides,[9] esters,[10] and ethers[11] has also been reported recently in the patent literature. The present paper describes the addition to norbornadiene of water, methanol, performic acid, nitrosyl chloride, and hydrobromic acid and the preparation of a sample of 3,5-dibromonortricyclene (IV) free of olefinic impurity.[6]



I



II



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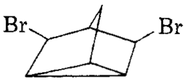
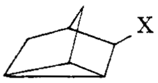
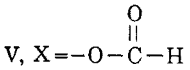


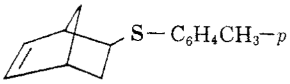
IV





$V, X = -O-\overset{\overset{\Large O}{\|}}{C}-H$

VI, $X = -S-C_6H_4CH_3-p$



VII

The low temperature bromination of bicycloheptadiene was repeated and the results of Schmerling and his co-workers were duplicated.[6] The complex mixture of dibromides was treated with a slight excess of performic acid to remove olefinic dibromides II and III in order to furnish a sample of pure 3,5-dibromonortricyclene (IV). This latter dibromide was found to be stable toward performic acid, bromine in carbon tetrachloride solution, and hydrogen over Adams' oxide. In the presence of sodium amide in liquid ammonia IV gave an intractable material from which no pure compound could be isolated.

When bicycloheptadiene was heated under reflux with hydrobromic acid a dibromo compound was obtained along with a small amount of 3-bromonortricyclene (IX) and some carbinol impurity.[12] This new dibromo-heptane gave no

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[1] (a) For previous paper in this series, see A. Winston, G. Youngblood, and P. Wilder, Jr., *J. Org. Chem.*, **22**, 876 (1957). (b) Taken in part from a thesis submitted by G. T. Youngblood to the Graduate School of Duke University in partial fulfillment of the requirements for the Ph.D. degree, October, 1956.

[2] American Cyanamid Pre-doctoral Fellow, 1955–1956.

[3] J. Hyman, Belgian Patent **498,178** (1951).

[4] W. E. Parham, W. T. Hunter, R. Hanson, and T. Lahr, *J. Am. Chem. Soc.*, **74**, 5646 (1952).

[5] J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Am. Chem. Soc.*, **77**, 594 (1955).

[6] L. Schmerling, J. R. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

[7] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *Chem. & Ind.* (*London*), 56 (1956).

[8] S. J. Cristol and G. D. Brindell, Abstracts of Papers presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955, page 35N.

[9] H. Bluestone, S. B. Soloway, J. Hyman, and R. E. Lidov, U. S. Patent **2,730,548** (1956).

[10] S. B. Soloway, R. E. Lidov, H. Bluestone, and J. Hyman, U. S. Patent **2,738,356** (1956).

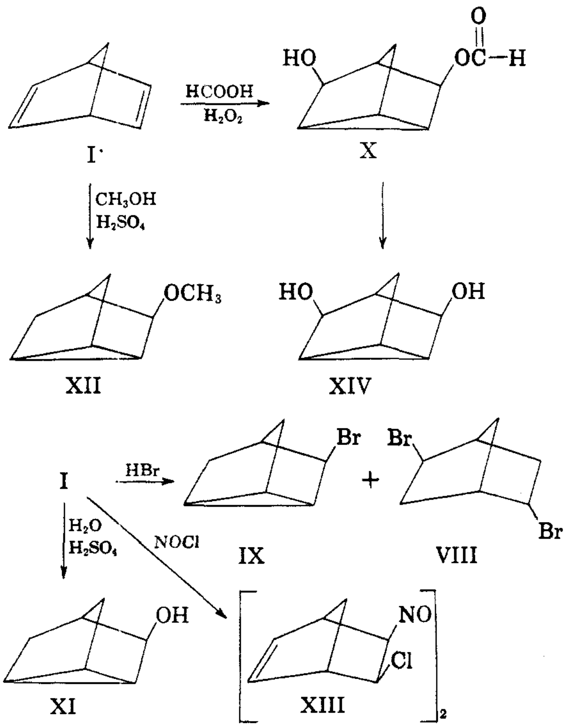
[11] H. Bluestone, S. B. Soloway, J. Hyman, and R. E. Lidov, U. S. Patent **2,782,238** (1957).

[12] The formation of 3-bromonortricyclene under conditions approximating those used in this investigation has been reported (*cf.* ref. 9), but no mention was made of a dibromo derivative.

spectroscopic evidence of a three-membered ring and was smoothly reconverted into I by sodium amide in liquid ammonia, chemical evidence that the two bromine atoms were attached to different ethylene bridges in the molecule. While the stereochemistry of the dibromide has not been definitively established the structure VIII is assigned in the assumption that the initial bromine atom will exert an anchimeric effect and influence the avenue of approach of the second bromine.[13]

Hydroxylation with performic acid yielded a mixture of products consisting of the hydroxyformate (X) and a product or products formed possibly by addition of two moles of peracid per mole of diene. These latter products were not investigated. The structure X was assigned to the hydroxyformate on the basis of a band at 12.3 μ in the infrared[6,14,15] and by analogy with the dibromide IV. Compound X was related by hydrolysis to the 3,5-dihydroxynortricyclene of Roberts,[9,16] which was in turn prepared by the hydrolysis of *trans*-2,3-dichlorobicyclo [2.2.1] heptene-5.

Hydration of norbornadiene in the presence of sulfuric acid gave the carbinol, 3-hydroxynortricyclene (XI), which had been previously prepared and characterized by Roberts.[15] In a similar reaction in methanol solution the product was the methyl ether XV, which was contaminated with some olefinic and hydroxylic material and by the addition of a second molecule of methanol to one of the initial reaction products.[11] Only after this material was passed through an alumina column at room temperature were all traces of carbonyl and olefin removed by adsorption.



Similar to other compounds containing the norbornylene ring, norbornadiene gave with nitrosyl chloride an addition product to which is assigned the dimeric structure XIII by analogy with dicyclopentadiene.[17] The elemental analysis of the adduct is consistent with a 1 : 1 addition product. Infrared spectroscopy indicated that the product contained an olefinic linkage[18] (6.36 μ), but no evidence for the presence of the nortricyclenic ring system was obtained. Further evidence that rearrangement did not occur in this instance was the conversion of the dimeric nitroso chloride XIII by the method of Wieland and Bergel[19] into the monomeric oxime which in an exchange reaction with 2,4-dinitrophenylhydrazine gave the known dinitrophenylhydrazone of 2-ketobicyclo[2.2.1]-5-heptene[4] and not that of 3-keto-nortricyclene.[15] The adduct of I and phenyl azide was prepared without difficulty, but limited solubility in organic solvents made purification virtually impossible.[4]

On the basis of the limited data available, it would be difficult to make any generalizations concerning the several competitive avenues of reaction for bicycloheptadiene, although the temperature of the reaction and the nature of the reactant seem to affect the course of the reaction. Work along these lines is continuing in this Laboratory.

EXPERIMENTAL[20]

Bromination of bicyclo[2.2.1]heptadiene[21] (I). A solution of 46 g. (0.50 mole) of the diene dissolved in 300 ml. of carbon tetrachloride was treated dropwise with a solution of 84 g. (0.55 mole) of bromine in 300 ml. of the same solvent at −70°, according to the directions of Schmerling.[6] A yield of 106 g. (84%) of a mixture of dibromides II, III, and IV was obtained, b.p. 100–102° (2 mm.); n_D^{25} 1.5771 [reported[6] 99–102° (5 mm.); n_D^{25} 1.5795].

A mechanically stirred solution of 73 g. of the combined dibromides in 200 ml. of 88% formic acid was treated dropwise with 30 g. of 30% hydrogen peroxide. Stirring was continued for 15 hr. at room temperature. The reaction mixture was poured into a liter of water and was extracted twice with ether. The ether extract was washed first with a saturated

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(13) It should be pointed out here that VIII may indeed be the 2,6-dibromide.

(14) A. Winston and P. Wilder, *J. Am. Chem. Soc.*, **76**, 3045 (1954).

(15) J. D. Roberts, E. P. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(16) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

(17) Unpublished work of P. Wilder and G. T. Youngblood; G. T. Youngblood, Ph.D. thesis, Duke University, October, 1956.

(18) P. R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **78**, 5702 (1956).

(19) H. Wieland and F. Bergel, *Ann.*, **446**, 13 (1926).

(20) All melting points and boiling points are uncorrected. Infrared spectra were obtained by the use of a Perkin-Elmer, Model 21, double beam recording spectrophotometer with sodium chloride prism, using a solution of the substance in a suitable solvent in a 1-mm. sodium chloride cell or pressed KBr pellets. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(21) A sample of this material was kindly furnished by the Shell Chemical Corp., Houston, Tex.

aqueous solution of sodium bicarbonate and then with water and was dried over anhydrous magnesium sulfate. The ether was removed by evaporation, and the residue was distilled to yield 50.4 g. of IV, b.p. 105–107° (4 mm.). On redistillation an analytical sample was obtained, b.p. 95–96° (2 mm.); d_4^{20} 1.8686; n_D^{25} 1.5779.

Anal. Calcd. for $C_7H_8Br_2$: C, 33.37; H, 3.20. Found: C, 33.50; H, 3.32.

The infrared spectrum gave no evidence of an olefinic linkage. The dibromide failed to discolor a solution of bromine in carbon tetrachloride. Catalytic hydrogenation in ethyl acetate over Adams' catalyst at room temperature did not alter the compound.

To a solution of sodium amide prepared by dissolving 6.5 g. (0.29 mole) of sodium in 400 ml. of liquid ammonia was added in one portion 35 g. (0.14 mole) of the dibromide. After the addition of 300 ml. of anhydrous ether the mixture was stirred for 3 hr. and was then treated with wet ether to decompose excess amide ion. The ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. After removal of the ether, there was isolated a dark brown rubbery mass which could not be redissolved in any of the usual organic solvents.

The experiment was repeated using 61.0 g. (0.24 mole) of the dibromide and 5.8 g. (0.25 mole) of sodium. Only 18.8 g. (31%) of unchanged dibromide and the same rubbery intractable mass were isolated.

Addition of hydrobromic acid. A mixture of 46 g. (0.5 mole) of the diene and 100 g. of 48% hydrobromic acid was heated at 70–80° for 5 hr. The mixture was then diluted with water and extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. After evaporation of the ether on a steam bath, distillation of the residue yielded 5 g. (6%) of the rearranged bromide IX, b.p. 74–75° (20 mm.); d_4^{20} 1.4651; n_D^{25} 1.5241 [reported[15] 86–88° (32 mm.); d_4^{25} 1.4609; n_D^{25} 1.5269].

There was also obtained 36.1 g. (29%) of the dibromo compound (VIII). After being dissolved in 250 ml. of anhydrous ether, the dibromo compound was passed through an alumina column to remove carbinol impurities. The ether was removed and the residue was distilled under reduced pressure, b.p. 75° (0.5 mm.).

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.05; H, 3.98. Found: C, 33.21; H, 3.95.

To a solution of 5.75 g. (0.25 mole) of sodium in 400 ml. of liquid ammonia was added 25.7 g. (0.11 mole) of dibromide. After the addition of 100 ml. of anhydrous ether the mixture was stirred for 3 hr. Wet ether was added to decompose excess amide ion, and then 100 ml. of water was added. The ether layer was separated, washed with ether, and dried over anhydrous magnesium sulfate. The ether was removed and distillation of the residue yielded 4.1 g. (40%) of norbornadiene, b.p. 89–91° (758 mm.). The diene gave a negative Beilstein test for halogen.

Addition of performic acid. A mixture of 46 g. (0.50 mole) of norbornadiene, 150 g. of 88% formic acid, and 115 g. of 30% hydrogen peroxide was stirred rapidly in an ice bath. After the ice melted, the system was allowed to come to room temperature. After being stirred for 10 hr., the solution was poured into 1 liter of water and extracted with ether. The ether extract was washed first with sodium bicarbonate solution, then with ferrous sulfate solution, and finally with water and was dried over anhydrous magnesium sulfate. The ether was removed, and the residue on distillation yielded 7.0 g. (9%) of hydroxyformate X, b.p. 127° (9 mm.); n_D^{25} 1.4858.

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.33; H, 6.49. Found: C, 62.55; H, 6.38.

An infrared spectrum of X gave evidence of an O—H band at 2.80 μ, an ester carbonyl group at 5.77 μ, and a nortricyclenic ring system at 12.3 μ.

Hydrolysis of hydroxyformate. To 1.0 g. of hydroxyformate was added one gram of potassium hydroxide and 4 ml. of absolute ethanol. The mixture was shaken at intervals for 5.5 hr. The reaction mixture was diluted with 50 ml. ether and the precipitate, which formed during reaction, was removed by filtration. To the ether solution was added 25 ml. of hexane. The ether was removed by evaporation and the hexane-ethanol solution was boiled until all ethanol was removed. At this point the diol was precipitated. The solid was separated by filtration and washed with hexane. A quantitative yield was obtained, m.p. (after sublimation) 160–161° (reported[16] 161–163°).

Addition of methanol. To a solution of 10 g. of concentrated sulfuric acid in 100 g. of absolute methanol was added 23 g. (0.25 mole) of diene. The mixture was heated under slow reflux for 1 hr. Methanol was removed by evaporation on a steam bath under reduced pressure, and the residue was taken up in water and ether. The ether layer was separated and dried over anhydrous magnesium sulfate. Removal of the ether and distillation of the residue yielded 3.2 g. (9.5%) of material, b.p. 125–126° (40 mm.) and 185–186° (758 mm.); n_D^{25} 1.4586. Hydroxyl and unsaturated impurities were removed by passage of the crude yield in anhydrous ether over an alumina column.

Anal. Calcd. for $C_8H_{12}O$: C, 77.42; H, 9.67. Found: C, 77.23; H, 9.79.

An infrared spectrum of XII gave evidence for the nortricyclenic structure at 12.35 μ and the methoxy group by the intense band at 8.90–9.25 μ.

Addition of water to norbornadiene. To a flask fitted with reflux condenser, stirrer, and dropping funnel was added 100 ml. of 50% (by volume) sulfuric acid. The solution was cooled to 0° in an ice bath, and 46 g. (0.50 mole) of norbornadiene was added dropwise (caution!) over a period of 2 hr. After addition was complete, the mixture was stirred for an additional hour. To the reaction mixture, cooled in an ice bath, was added rapidly 200 ml. of water. The reaction mixture was saturated with sodium chloride and was extracted with ether. The ether layer was washed with water and was then saturated with sodium bicarbonate solution. The ether solution was dried over magnesium sulfate. The yield of 3-hydroxynortricyclene (XI) was 8.7 g. (16%), m.p. 95–100° after three sublimations (reported[15] m.p. 107–108.8°). The phenylurethane derivative was prepared, m.p. 146° (reported[15] 146–147.5°).

The addition of nitrosyl chloride. To a rapidly stirred solution of 10 g. (0.12 mole) of norbornadiene, 20 ml. of glacial acetic acid, 20 ml. of 95% ethanol, and 20 g. (0.17 mole) of isoamyl nitrite, cooled in an ice bath, was added during 20 min. a solution of 25 ml. (0.25 mole) of 36% hydrochloric acid in 50 ml. of 95% ethanol. The color of the mixture turned green immediately, and after about 5 min. precipitation of a white solid occurred. The solid, which was removed by filtration, was washed with ethanol (95%) and collected. The yield was 12 g. (71%). An analytical sample was purified by two recrystallizations from toluene, m.p. 164° (darkened at 162°).

Anal. Calcd. for C_7H_8NOCl: C, 53.33; H, 5.08. Found: C, 53.74; H, 5.09.

A band at 6.36 μ in the infrared clearly indicated the presence of a norbornene[18] ring; there was no evidence at 12.3 μ for a nortricyclene ring. A sample of the dimeric nitroso chloride was converted by the method of Wieland and Bergel[19] into the monomeric oxime which in an exchange reaction with 2,4-dinitrophenylhydrazine gave a product, m.p. 134–136° (reported[4] for the 2,4-dinitrophenylhydrazone of 2-ketobicyclo[2.2.1]-5-heptene, m.p. 133–137°; reported[15] for the 2,4-dinitrophenylhydrazone of 3-ketonortricyclene, m.p. 188.2–189.6°).

Acknowledgment. This investigation was supported in part by a grant from the Research Corp.

DURHAM, N. C.