[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

# Debromination of 9,10-Dibromotetrahydro-*exo*-dicyclopentadiene with Sodium Amide[1]

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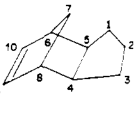
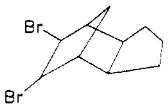
The vicinal dibromide *trans*-9,10-dibromotetrahydro-*exo*-dicyclopentadiene (II) on treatment with either iodide ion or zinc was found to give the olefin I. On treatment with sodium amide in liquid ammonia dibromide II afforded two products: olefin I and a vinyl bromide III. Possible mechanisms for the sodium amide reaction are discussed.

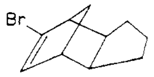
During the course of an investigation of the reactivity of a series of 9-halo-*exo*-dicyclopentadienes[3] toward nucleophilic reagents, the compound *trans*-9,10-dibromotetrahydro-*exo*-dicyclopentadiene[4] (II) was prepared by low temperature bromination of olefin I. It was shown that dibromide II could be converted into olefin I by iodide ion in acetone solution and by zinc in alcohol, corroborating evidence that the compound is a vicinal dibromide. In the presence of sodium amide in liquid ammonia, dibromide II was smoothly converted into two products in approximately equimolar amounts. One of these compounds was shown unequivocally to be the original olefin I. The other compound contained bromine, decolorized a solution of bromine in carbon tetrachloride and could be recovered unchanged from an alcoholic silver nitrate solution or from a solution of alcoholic caustic. Even after extensive treatment with an excess of amide ion in liquid ammonia, the unsaturated bromide could be recovered unchanged. Neutral permanganate oxidation of the bromo-compound afforded a dibasic acid which contained no bromine and was identical with the dibasic acid obtained by oxidation of olefin I under the same experimental conditions. These data suggest that the unsaturated bromide is a vinyl bromide of structure III.



I



II

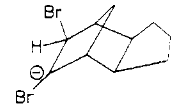


III

## Discussion

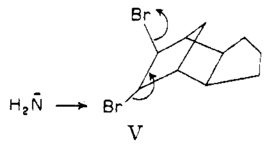
Debromination of a vicinal dibromide is not an obscure reaction. Various vicinal dibromides have been debrominated with varying success by sodium sulfide and sodium thiosulfate in alcoholic and aqueous media, respectively.[5] In the presence of iodide ion vicinal dibromides have been converted smoothly into olefin and bromide ion. The mechanism of this conversion has been studied in the case of 2,3-dibromobutane by Winstein, Pressman and Young, who suggested that one bromine atom is displaced by nucleophilic attack of iodide ion on bromine with the simultaneous formation of the double bond and the expulsion of the second bromine atom as an anion.[6] In the case of 1,2-dibromides with more pronounced $S_N2$ reactivity, Hine and Brader have proposed an initial nucleophilic displacement on carbon.[7]

In the present investigation, dibromide II was readily reconverted into olefin I in the presence of sodium iodide, but the conversion of the dibromide into olefin by sodium amide in liquid ammonia is remarkable. Strong bases, in contrast to sulfide or iodide ion, generally give rise to elimination reactions which yield vinyl bromides or acetylenic derivatives. In the case at hand the *trans*-dibromide afforded the carbanion IV which lost a bromide ion by *cis* elimination[8] or underwent an $\alpha$-elimination to produce an unstable moiety[9] which then rearranged. The result in either case would be the vinyl bromide III. It is interesting in this connection that no vinyl bromide was obtained when the dibromide was treated with sodium iodide. The recovery of 97% of the vinyl bromide unchanged from sodium amide in liquid ammonia precludes the possibility of a vinyl bromide intermediate in the formation of olefin I.



IV

A second mechanism, totally different from that described above, must also be operative in the sodium amide–dibromide reaction. The strong base amide ion appears to act like a nucleophilic iodide ion in a displacement mechanism (V) closely akin to



V

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[1] (a) For previous paper in the bicyclo[2.2.1]heptane series, see P. Wilder, Jr., and A. Winston, THIS JOURNAL, **78**, 868 (1956). (b) Taken in part from a thesis submitted by George T. Youngblood to the Graduate School of Duke University in partial fulfillment of the requirements for the M.A. degree, October, 1955.

[2] American Cyanamid Predoctoral Fellow, 1955–1956.

[3] The system of numbering used in this paper is that of Alder and Stein (*Ann.*, **496**, 204 (1932)).

[4] Recently two examples of *cis*-bromination in this series have been reported, one by Kwart and Kaplan (THIS JOURNAL, **76**, 4078 (1954)) and another by Berson (*ibid.*, **76**, 4069 (1954)), but the present structure has no neighboring electronegative groups to stabilize the incipient bromonium ion and effect *cis*-addition.

[5] B. G. Gavrilon and V. E. Tischenko, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 967 (1947); **18**, 1687 (1948).

[6] S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939).

[7] J. Hine and W. H. Brader, *ibid.*, **75**, 3964 (1953); **77**, 361 (1955).

[8] S. J. Cristol, *ibid.*, **69**, 338 (1947).

[9] C. R. Hauser, *ibid.*, **62**, 933 (1940).

that proposed by Winstein and his co-workers.[6] Nucleophilic attack by strong bases on the halogen atom of alkyl halides (except iodides[7]) is not a commonplace reaction. Reported examples of such nucleophilic attack on halogen include the studies of Meyer and Findeisen[10] and of Hauser and Hudson[11] upon the reaction of sodium enolates with sulfonyl chlorides, the halogen–metal interconversion[12] in the formation of the lithium reagent and the debromination of stilbene dibromide[13] and cinnamic acid dibromide,[14] both in excellent yield, by sodium amide. It is somewhat surprising in the cases of stilbene and cinnamic acid that neither unsaturated bromides nor acetylenic compounds resulted from the reaction.

## Experimental[15]

**1,2-Dihydro-*exo*-dicyclopentadiene (I).**—This olefin was prepared from the saturated alcohol 9-hydroxytetrahydro-*exo*-dicyclopentadiene,[16] which was obtained by catalytic hydrogenation of dicyclopentenyl alcohol[17] (hydroxydihydro-*exo*-dicyclopentadiene). The saturated alcohol was dehydrated by the method[18] of Bruson and Riener, with certain exceptions. The amount of phosphoric acid was increased threefold and the heating period was extended to 5 hr. Under these conditions 258 g. (1.70 moles) of alcohol was dehydrated to 113 g. (50%) of olefin, b.p. 88–90° (40 mm.) (reported, yield 39%, b.p. 89–91° (39 mm.)).

***trans*-9,10-Dibromotetrahydro-*exo*-dicyclopentadiene (II).**—A solution of 16 g. (0.10 mole) of bromine in 50 ml. of carbon tetrachloride was added dropwise with stirring to a solution of 13.4 g. (0.10 mole) of 1,2-dihydro-*exo*-dicyclopentadiene in 50 ml. of carbon tetrachloride at 0°. The time of addition was 20 minutes, but the reaction was allowed to proceed for an additional 10 minutes before products were isolated. The solution was washed with $NaHSO_3$ solution and with water and was dried over $MgSO_4$. After evaporation of the solvent, distillation of the residue afforded 23.8 g. (83%) of dibromide, a pale yellow liquid, which darkened on standing, b.p. 115–123° (0.5 mm.), $n^{25}D$ 1.5680, $d^{20}{}_4$ 1.729.

*Anal.*[19] Calcd. for $C_{10}H_{14}Br_2$: Br, 54.4. Found: Br, 54.8, 54.0.

**Reaction of Dibromide II with Sodium Iodide.**—To a solution of 80 g. (0.54 mole) of NaI in 400 ml. of acetone, 23.8 g. (0.081 mole) of the dibromide was added. The mixture was heated under reflux for 24 hr. A saturated solution of aqueous $NaHSO_3$ was then added slowly to the reaction mixture to remove iodine and acetone was removed under reduced pressure. The residue was then taken up in ether and the solution dried over $MgSO_4$. After removal of ether distillation of the residue afforded 1.87 g. (18%) of olefin I, b.p. 84–86° (30 mm.), 173° (752 mm.), $n^{25}D$ 1.4994, and 8.0 g. (33%) of starting material.

**Reaction of Dibromide II with Zinc.**—A mixture of 65.4 g. of zinc, 100 ml. of absolute ethanol and 19.3 g. (0.066 mole) of dibromide was heated under reflux for 5 days. The alcohol was then removed by evaporation under reduced pressure, the organic residue was taken up in ether and the ether solution was dried over $MgSO_4$. After evaporation of the ether, distillation of the residue yielded 2.1 g. (24%) of olefin I, b.p. 70° (25 mm.), $n^{25}D$ 1.5002, and perhaps 5 g. of tar which could not be distilled.

**Reaction of Dibromide II with Sodium Amide.**[20]—To a solution of 5.0 g. (0.21 mole) of sodium in 500 ml. of liquid ammonia was added dropwise a solution of 35 g. of *trans*-9,-10-dibromotetrahydro-*exo*-dicyclopentadiene (II). After proceding for 2.5 hr., the reaction mixture was treated with wet ether to remove excess amide ion and to extract the products. The ether solution was washed with water and then dried over $MgSO_4$. Distillation, after the removal of the solvent, gave 8.4 g. (53%) of the olefin 1,2-dihydro-*exo*-dicyclopentadiene (I) and 10.0 g. (40%) of 9-bromo-1,2-dihydro-*exo*-dicyclopentadiene (III), b.p. 112–114° (15 mm.), 64° (0.5 mm.), $n^{25}D$ 1.5380, $d^{25}{}_4$ 1.338. The latter compound was a colorless oil which slowly darkened to reddish in color on standing.

*Anal.*[19] Calcd. for $C_{19}H_{13}Br$: Br, 37.5. Found: Br, 37.8, 36.5.

**Oxidation of Bromide III.**—According to the method of Alder and Stein,[21] 30 g. of $KMnO_4$ was added in approximately 0.5-g. portions to a solution of 10 g. (0.047 mole) of the bromide III in 75 ml. of acetone in a flask fitted with a mechanical stirrer, the time of addition being about 30 minutes. The reaction mixture was allowed to stand for 12 hr., and then the precipitate of $MnO_2$ was removed by filtration. The filtrate was heated on a steam-bath for an hour. The precipitate was washed with two 50-ml. portions of 9 *M* sulfuric acid, and the acid wash solution was, in turn, twice extracted with ether. The ether extract was washed with 10% NaOH solution, and the alkaline solution was added to the filtrate from the initial separation. The combined alkaline solutions were acidified with 3 *M* sulfuric acid and extracted five times with ether. On evaporation of the ether, there was obtained a semi-solid material which was recrystallized with difficulty from nitroethane. A final recrystallization from water yielded 2.1 g. (27%) of a dibasic acid, m.p. 162–163°.

*Anal.*[22] Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.11; neut. equiv., 99. Found: C, 60.40; H, 6.98; neut. equiv., 97.

**Oxidation of Olefin I.**—The permanganate oxidation was carried in the manner described in detail above for the bromide. From 10 g. (0.075 mole) of olefin, the yield of dibasic acid was 4.4 g. (30%), m.p. 161–163°. Upon admixture with a sample of acid from the oxidation of bromide III, no depression was observed, mixed m.p. 162–162.5°.

**Action of Sodium Amide on Vinyl Bromide III.**—To a solution of sodium amide in liquid ammonia prepared by dissolving 3.45 g. (0.15 mole) of sodium in 300 ml. of liquid ammonia, there was added with stirring 10.8 g. (0.050 mole) of the unsaturated bromide III in 50 ml. of anhydrous ether. The reaction was allowed to continue until all ammonia had evaporated, and then 100 ml. of anhydrous ether was added. The mixture was allowed to stand overnight with stirring. Excess sodium amide was decomposed by addition of ammonium chloride to the ethereal solution. Water was added and the ether layer was separated, washed with water and dried. Evaporation of the ether gave an oil which on distillation yielded 10.3 g. (97%) of unreacted starting material, b.p. 62–63° (0.5 mm.), $n^{25}D$ 1.5374.

DURHAM, NORTH CAROLINA

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(10) E. v. Meyer and Th. v. Findeisen, *J. prakt. Chem.*, [2] **65**, 530 (1902).

(11) B. E. Hudson, Jr., Ph.D. Thesis, Duke University, 1941. It is worthy of mention here in the reaction of the sodium enolate of ethyl isobutyrate and benzenesulfonyl chloride that the products, ethyl α-chloroisobutyrate and sodium benzenesulfinate, were each obtained in approximately 60% yield.

(12) R. G. Jones and H. Gilman in Roger Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

(13) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

(14) R. V. Paulson and W. S. MacGregor, *ibid.*, **73**, 679 (1951).

(15) All boiling points and melting points are uncorrected.

(16) H. A. Bruson and T. W. Riener, THIS JOURNAL, **67**, 723 (1945).

(17) A sample of this material was kindly furnished by Rohm and Haas Company, Philadelphia, Penna.

(18) H. A. Bruson and T. W. Riener, THIS JOURNAL, **70**, 2809 (1948).

(19) Analysis carried out in this Laboratory by the method of Kimball and Tufts (*Ind. Eng. Chem., Anal. Ed.*, **10**, 530 (1938)).

(20) The method of preparation of sodium amide is that of Hauser, Swamer and Adams (in Roger Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 122).

(21) K. Alder and G. Stein, *Ann.*, **485**, 242 (1931).

(22) Microanalysis by Galbraith Laboratories, Knoxville, Tenn.