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REACTIONS OF BICYCLO(3.2.1)OCTENE-2

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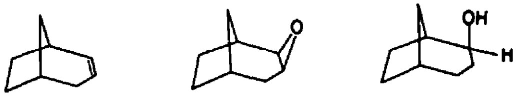
Abstract—Bromine has been shown to add to bicyclo(3.2.1)octene-2 without rearrangement. Epoxidation leads to the *exo*-epoxide.

INTRODUCTION

OWING to the close structural inter-relationships between the bicyclo(3.2.1)octyl and the norbornyl and bicyclo(2.2.2)octyl systems, it is of interest to compare and correlate the chemistry of these structures. In particular, it appeared profitable to study reactions of bicyclo(3.2.1)octene-2 (I) for comparison with corresponding reactions of norbornene and bicyclo(2.2.2)octene.

RESULTS AND DISCUSSION

Epoxidation was chosen as the simplest reaction with which the initial mode of attack on the double bond could be established. Treatment of I with buffered peracetic acid led to a crystalline epoxide in 67% yield. One major component was detected by gas chromatography. The stereochemistry of the adduct was determined by reduction to the known alcohol, *exo*-2-bicyclo(3.2.1)octanol (III) which also appeared homogeneous by IR and gas chromatography. Thus, the epoxide itself must be II and predominant *exo*-attack is established.



I II III

FIG. I

These results were expected in view of the predominant *exo*-attack on norborene itself in this reaction.[1]

Attention was then turned to bromination of I. Addition of one mole of bromine in the presence of pyridine led to an unstable oil which showed one major component on gas chromatography. The structure of this product (IV) was deduced by a consideration of the following transformations.

Treatment of IV with potassium t-butoxide in t-butyl alcohol was expected to lead to unsaturated materials which may or may not still contain bromine depending on the structure of IV. As it turned out, the product of this reaction did not contain bromine and was in fact a $C_{12}H_{20}O$ system. From the NMR spectrum, it was deduced that this substance contained an unsymmetrical double bond and a t-butoxy group. The most reasonable structure for this product seemed to be VII which could have

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[1] H. Kwart and T. Takeshita, *J. Org. Chem.* **28**, 670 (1963).

arisen by solvolysis of either V or VI.[2] The dibromides from which V and VI would be derived are VIII and IX, both of which are reasonable structures for the adduct. Since V was readily available from I, it was decided to test the stability of this compound to the conditions of the dehydrohalogenation reaction.[3] Solvolysis of V in t-butyl alcohol which contained potassium t-butoxide led exclusively to the t-butyl ether (VII). Using sodium carbonate as a base, the alcohol (X) was obtained in addition to the t-butyl ether. Thus, V is feasible intermediate in the formation of VII.

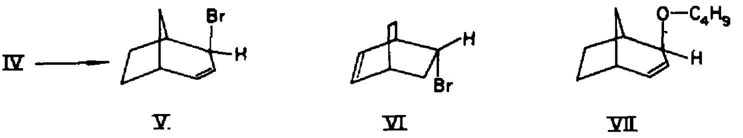

Fig. II

The decision between VIII and IX was ultimately made on the basis of the results of a sodium reduction experiment. Treatment of IV with sodium in ethanol gave a volatile hydrocarbon and a $C_{10}H_{16}O$ product. The hydrocarbon proved to be bicyclo(3.2.1)-octene-2 by IR and G.L.C. retention time comparisons.

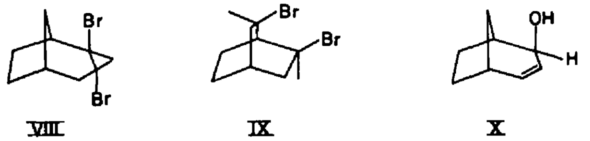

Fig. III

The other product is undoubtedly the ethyl ether (XI) as deduced from spectral data. Apparently, the sodium ethoxide produced causes elimination which is followed by ethanolysis.

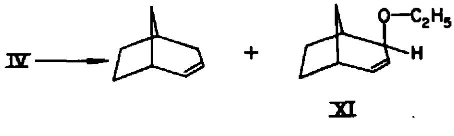

Fig. IV

Thus, the dibromide must have the unrearranged structure VIII, although the stereochemistry cannot be assigned from these experiments.[4]

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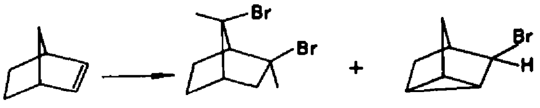
[2] H. L. Goering, R. W. Greiner and M. F. Sloan, *J. Amer. Chem. Soc.* **83**, 1391 (1961) have shown that solvolysis of the tosylate corresponding to VI leads to products analagous to VII. See also A. Gagneux and C. A. Grob, *Helv. Chem. Acta* **42**, 1753 (1959).

[3] N. A. LeBel, J. Huber and L. Zalkow, *J. Amer. Chem. Soc.* **84**, 2226 (1962). We are grateful to Prof. LeBel for information regarding this compound.

[4] While IX cannot be rigorously excluded by this experiment, rearrangement to I would require unprecedented carbanionic rearrangements. The sterochemistry assigned to VIII rests on the analogy with addition of bromine to cyclohexene and with the demonstrated epoxide formation and cleavage reactions.

It is instructive to compare these results with those with norbornene (XII) and bicyclo(2.2.2)octene (XIII). Bromination of the former leads to a 57% yield of rearranged dibromide (XIV) and a 27% yield of bromonortricyclene (XV).[5]

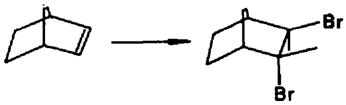


XII XIV XV

FIG. V

Bicyclo(2.2.2)octene (XIII), on the other hand, gives mainly unrearranged 2,3-dibromide (XVI) on treatment with bromine and pyridine.[3]

These results are best correlated in terms of two main factors: strain in the bromonium ions and relative rates of attack of bromide ion on the bromonium ions.

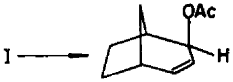


XIII XVI

FIG. VI

It is clear that the bromonium ion from norbornene is highly strained. It should be prone to rearrange to the open bromocarbonium ion. Further rearrangement or loss of a proton would then be expected to be rapid. Also, the rate of backside attack by bromide ion would be expected to be slow in the case of norbornene owing to the high degree of twisting required in the transition state.[6] The bromonium ions from bicyclo(2.2.2)octene and bicyclo(3.2.1)octene-2 would be expected to be much more flexible and hence, more readily attacked by bromide ion. Both factors favour addition to I without rearrangement.

Incidental to this work, a new synthesis of bicyclo(3.2.1)oct-3-en-2-yl acetate (XVII) was developed. Bicyclo(3.2.1.)octene-2 was acetoxylated with t-butyl peracetate catalyzed by cupric 3,3,5-trimethylhexanoate.[7]



XVII

FIG. VII

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[5] H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.* **76**, 4072 (1959).

[6] See T. G. Traylor, *J. Amer. Chem. Soc.* **86**, 244 (1964) for a discussion of this point.

[7] D. Z. Denney, A. Appelbaum and D. B. Denney, *J. Amer. Chem. Soc.* **84**, 4969 (1962). We are grateful to Prof. Denney for assistance with this reaction. Subsequent to this work, H. L. Goering and U. Mayer, *J. Amer. Chem. Soc.* **86**, 3753 (1964) performed a similar experiment with t-butyl perbenzoate and cuprous bromide.

The stereochemistry of this reaction is verified by conversion of the ester to the known alcohol (X).

EXPERIMENTAL

Analyses were performed by G. Robertson, Florham Park, N.J. and W. Manser, Switzerland. IR spectra were determined on a Perkin-Elmer 137 spectrophotometer. NMR spectra were determined on a Varian Model A-60 spectrometer in CCl_4 using tetramethylsilane as internal standard.

Epoxidation of bicyclo(3.2.1)*octene*. To a solution of 20·0 g (0·185 mole) I in 175 ml $CHCl_3$ was added 68 ml (ca. 0·4 mole) 40% peracetic acid which contained 2·4 g sodium acetate. The addition required 30 min and the temp was kept at 0°. After stirring at 0° for 2 hr the solution was kept at room temp for 4 hr. The $CHCl_3$- solution was then washed with KOHaq and water. The dried ($MgSO_4$) solution was evaporated to give 15·3 g (67%) of a white solid. After one sublimation the m.p. was 129–133°. Gas chromatography on a 5′γ-nitro-γ-methylpimelonitrile column at 110° indicated one major component (95%) which was collected and submitted for elemental analysis, m.p. 136–138°. (Found: C, 77·18; H, 9·87. $C_8H_{12}O$ requires: C, 77·42; H, 9·68%).

The NMR spectrum showed a complex absorption centered at 2·8 ppm (2 protons) a broad singlet at 2·4 ppm (1 proton) and complex absorption between 2·2 and 0·9 ppm (9 protons).

trans-*Bicyclo*(3.2.1)*octanol*-2. A solution of 10 g (0·081 mole) epoxide II in 20 ml anhydrous ether was added over 1 hr to a stirred slurry of 3·5 g (0·090 mole) LAH in 100 ml ether. The resulting mixture was stirred for 24 hr at room temp after which the complex was decomposed by cautious addition of 7 ml water. The precipitate was removed by filtration and washed with ether. The combined ether extracts were dried ($MgSO_4$) and evaporated to give 9·3 g (91%) of a white solid. After one sublimation, the m.p. was 196·7–197·1° (lit., m.p. 200–201° [8] and 199·9–200·2° [8]). The retention time of this material was identical with that of an authentic sample[8] on a 6′ Craig polyester column at 120°.

Bromination of bicyclo(3.2.1)*octene*-2 (I). Bromine (24 g, 0·15 mole) was added over 2 hr to a stirred solution of 16·2 g (0·15 mole) I in 71 ml dry CCl_4 which contained 11·9 g (0·15 mole) pyridine. The reaction temp was maintained at 0–5°. A small amount of precipitate was removed and the solution washed with HClaq, $NaHCO_3$aq and water. The dried ($CaCl_2$) CCl_4- solution was evaporated to give a dark oil weighing 22·7 g. Gas chromatography of this product on a 5′ silicone (SE–30) column at 150° indicated one major (80%) component. Attempts to collect or distill this material led to extensive decomposition.

Dehydrohalogenation. A solution of potassium t-butoxide in t-butyl alcohol was prepared by dissolving 18·6 g (0·22 mole) K in 183 ml t-butyl alcohol. The crude bromination product (26·8 g 0·1 mole) was added and the resulting solution was heated at reflux for 17 hr. An equal volume of water was added followed by ether extraction. The crude product was subjected to preparative gas chromatography whereupon one major product was observed and collected. The IR spectrum (film) of this material showed strong absorption at 7·2, 7·3, 8·3, 9·5, 9·8 μ; and medium intensity absorptions at 6·8, 6·9, 8·0, 8·1, 8·6, 11·0, 11·3, 12·9, 13·5 and 14·3 μ.

The NMR spectrum displayed a quartet (area 1) centered at 5·9 ppm, an octet (area 1) centered at 5·2 ppm, and a sharp singlet at 1·2 ppm (area 9). (Found: C, 77·93; H, 11·07. $C_{12}H_{20}O$ requires: C, 77·94; H, 11·18).

2-*Bromobicyclo*(3.2.1)*oct*-3-*ene* (V). This bromide was prepared by reaction of I with N-bromosuccinimide in CCl_4 and had b.p. 90° at 13 mm (lit.,[8] b.p. 72–74° at 6 mm). The IR spectrum was identical with that of a known sample.[8]

Reaction of 2-*bromobicyclo*(3.2.1)*oct*-3-*ene with t-butyl alcohol*. A solution of potassium t-butoxide in t-butyl alcohol was prepared by reacting 1·1 g (0·028 g atom) K with 25 ml t-butyl alcohol. Bromide (V; 4·7 g; 0·025 mole) was added and the resulting mixture was heated at reflux for 12 hr. Addition of 25 ml water was following by ether extraction. The combined extracts were dried and evaporated to give 3·5 g of an oil. Gas chromatography on either the Craig or Silicone columns indicated only one component whose retention time was identical to that of VII. The identity of this product with VII was confirmed by comparison of the IR spectra of the samples from the two sources.

Reaction of 2-*bromobicyclo*(3.2.1)*oct*-3-*ene with sodium carbonate in t-butyl alcohol*. A mixture of 2·3 g V with 2·65 g Na_2CO_3 in 9 ml t-butyl alcohol was treated as above. There was obtained 1·8 g

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[8] A. A. Youssef, M. E. Baum and H. M. Walborsky, *J. Amer. Chem. Soc.* **81**, 4709 (1959).

of product which was analyzed on the Silicone column at 130°. The main peaks were observed with area ratios of ca. 1:2. The smaller peak had a retention time and IR spectrum which were identical with those of *exo*-bicyclo(3.2.1)oct-2-en-3-ol.[9] The larger peak proved to be the t-butyl ether (VII) by comparison of retention times and IR spectra.

Reduction of dibromide with sodium. Sodium metal (4·6 g, 0·2 g atom) was added to a solution of 2·6 g (0·01 mole) crude bromination product in 60 ml EtOH. After heating under reflux for 4 hr, 30 ml water was added and the mixture extracted with pentane. The combined extracts were dried ($MgSO_4$) and evaporated to give 1·0 g of an oil. Analysis of this product on a 5′ Apiezon L column at 110° indicated two main components with relative areas 1:3. The smaller peak had a very short retention time and an IR spectrum identical with that of I. The major peak was assigned structure XI on the basis of spectral and analytical data. (Found: C, 78·91; H, 10·58. $C_{10}H_{16}O$ requires: C, 78·89; H, 10·59%).

The NMR spectrum shows two unequivalent protons due to olefinic hydrogen at 6·0 (quartet) and 5·4 (octet) ppm. Typical ethoxy group patterns appear at 1·2 and 3·5 ppm. The carbinol proton appears as a triplet (J = 3 c/s) at 3·3 ppm.

axial-*Bicyclo*(3.2.1)*oct*-3-*en*-2-*yl acetate* (XVII). A solution of I (14 g; 0·13 mole) in 35 ml benzene was treated with 18 g (0·10 mole) 75% t-butyl peracetate and a catalytic amount of cupric 3,5,5-trimethylhexanoate. The resulting solution was heated at reflux for 2·5 hr. After cooling, it was washed with water, $NaHCO_3$aq and water. Evaporation gave a viscous oil which was distilled at 25 mm. The first fraction was collected at a temp up to 105° (2 g). The main portion (9·3 g) distilled between 105° (25 mm) and 106·5° (22 mm). Redistillation of this fraction on an 18″ spinning band column gave 6·3 g (38%) pure ester (XVII), b.p. 84–85° (8 mm) (lit.,[9] b.p. 88·5–89°/11 mm). This product was essentially pure as shown by gas chromatography on an 12′ Carbowax 20M column.

The IR and NMR spectrum of this acetate were identical with those of an authentic sample. Saponification with KOH in MeOH gave the crude alcohol (X) which was converted to the p-*nitrobenzoate*. The m.p. after several recrystallizations from EtOH and pentane was 86–87° (lit., m.p. 81–81·5° [10], 86·2–86·6° [9]). (Found: C, 65·65; H, 5·54; N, 5·15. $C_{15}H_{15}NO_4$ requires: C, 65·92; H, 5·53; N, 5·13%).

Acknowledgement—We are grateful to the National Institutes of Health for financial support (GM-08701).

[9] R. R. Sauers, *Tetrahedron Letters* 146 (1961).

[10] W. C. Wildman and D. R. Saunders, *J. Amer. Chem. Soc.* 76, 946 (1954).