The oxidation product was neutralized with 20% NaOH at 0°, and water was carefully evaporated from aliquot portions. The dry salts were acidified with minimum quantities of concentrated hydrochloric acid, and then extracted with four 10-ml. portions of ether. The residues after the evaporation of ether and monobasic acids were analyzed for dibasic acids by liquid partition chromatography.[3]

GULF RESEARCH AND DEVELOPMENT COMPANY
POST OFFICE BOX 2038
PITTSBURGH 30, PA.

---

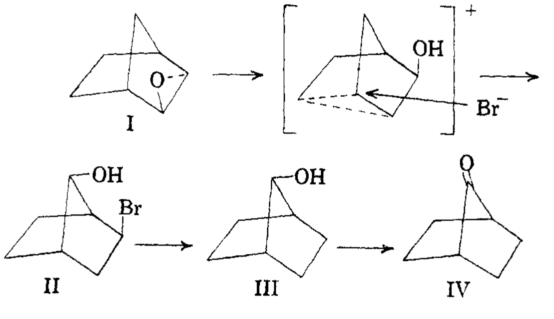
(3) T. Higuchi, N. C. Hill, and G. B. Corcoran, *Anal. Chem.*, **24**, 491 (1952).

Reaction of *Exo*-norbornylene Oxide with Hydrogen Bromide[1,2]

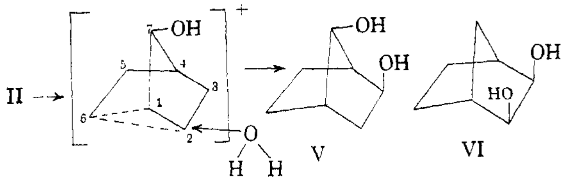
H. M. WALBORSKY AND D. F. LONCRINI

Received February 13, 1957

It has previously been demonstrated[3] that the reaction of norbornylene with peracetic acid yields the *exo*-norbornylene oxide (I). Treatment of I with hydrogen bromide produced a bromohydrin (II) as the main product.[2] The structure of II has been tentatively assigned as 2-*exo*-bromo-7-*syn*-hydroxy-norbornane based on analogy to the product formed by the hydrolysis[3] of I.



That the hydroxyl group is located at the 7-position was established by treating II with hydrogen and palladium to yield the known 7-hydroxynorbornane (III).[4] Oxidation of III yielded ketone IV which was isolated as the 2,4-dinitrophenylhydrazone.



Hydrolysis of II did not produce the rearranged product (VI) but yielded V.[2] Apparently the hydroxyl group at C-7 shields C-1 from attack by solvent so that reaction occurs at C-2. A similar observation has been made by Roberts[5] who obtained 2-*exo*-hydroxy-*syn*-7-chloronorbornane from the basic hydrolysis of *exo*-*syn*-2,7-dichloronorbornane.

EXPERIMENTAL[6]

2-exo-Bromo-7-syn-hydroxy-norbornylene (II). To 36 ml. of 48 per cent hydrobromic acid, cooled to 10°, was slowly added 20 g. (0.18 mole) of *exo*-norornylene oxide. The temperature was not allowed to rise above 15° during the addition. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium carbonate, dried over anhydrous sodium sulfate, and stripped. The residual oil was distilled to yield 13.5 g. (39%) of product, b.p. 98–100° (5 mm.), m.p. 75.5–76° from ether-pentane. An oil was also isolated but not identified.

Anal. calcd. for $C_7H_{11}BrO$: C, 43.94; H, 5.80; Br, 41.82. Found: C, 43.97; H, 6.00; Br, 41.78.

7-Hydroxynorbornane (III). Five grams (0.026 mole) of II dissolved in ethanol was hydrogenated using one gram of 10% palladium on charcoal catalyst. The reaction mixture was filtered, solvent stripped *in vacuo*, and the residue taken up in pentane. The pentane solution was dried over Drierite and stripped to yield 2.7 g. (92%) of III, m.p. 149–150° (Lit.[4] m.p. 149–150°).

The phenylurethan derivative melted at 138–139° from acetonitrile.

Anal. calcd. for $C_{14}H_7O_2N$: C, 72.72; H, 7.31; N, 6.66. Found: C, 72.78; H, 7.38; N, 6.69.

Norbornone-7. To a solution of 1 g. (0.008 mole) of III in 4 ml. of glacial acetic acid was slowly added a solution of 0.54 g. (0.0054 mole) of chromium trioxide in 10 ml. of acetic acid. The mixture was stirred for several hours at room temperature and extracted with pentane. Removal of the solvent yielded 0.2 g. (20%) of an oil with a strong camphoraceous odor. The oil was converted to the 2,4-dinitrophenylhydrazone which melted at 133–134° (Lit.[4] 133–134°).

exo-syn-2,7-Dihydroxynorbornane (V). To an aqueous solution of lithium carbonate was added 2 g. (0.001 mole) of II. The mixture was refluxed for several hours and then continuously extracted with ether. The ether extract was dried over anhydrous sodium sulfate and stripped to yield 1.1 g. (91%) of V, m.p. and mixed m.p. 180–181°. The diphenylurethan derivative m.p. and mixed m.p. 221–222°.

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLA.

---

(1) This paper is based on a portion of the thesis submitted by D. F. L. in 1956 to the Florida State University in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

(2) During the preparation of this manuscript a communication appeared describing this reaction (Winstein and Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957)).

(3) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

(4) Dissertations by P. Wilder, Jr. (1950) and R. E. Vanelli (1950) at Harvard University. S. Winstein, M. Shatovsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatovsky, **78**, 592 (1956).

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

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