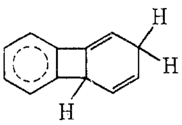
weight of 156 by mass spectral analysis. Nmr (CCl_4) indicates the following protons: four aromatic, two vinyl, two benzylic methinyl, and four allylic methylene. The benzylic hydrogens (δ 3.65) are further downfield than usual[7] for benzylic hydrogens, which is in agreement with their location on a cyclobutene ring.[7,8] Equivalency of the benzylic hydrogens is indicated, as they have the same chemical shift and do not split one another (a J of 6–10 magnitude[7] would be required). Also absence of mutual splitting and identical chemical shift indicate equivalency of the vinyl hydrogens. The absence of carbon-to-carbon double bond stretching in the 1600–1680-cm^{-1} region of the ir spectrum, as well as the overall simplicity of the ir and nmr spectra, agrees with the symmetrical structure of **2**.

The most likely structures for the dihydro intermediate which must form first and then go on to tetrahydro products **2** and **4** are 2,4a-dihydrobiphenylene (**5**), 4a,8b-dihydrobiphenylene (**6**), and 1,4-dihydrobiphenylene (**7**). **5** is the product predicted[9] by Streitwieser, who used molecular orbital theory based on protonation at sites of highest electron density in the radical anion and anion intermediates. Further reduction of **5** would be expected to form **3**. Isomerization of **5** to 1,8b-dihydrobiphenylene (**8**) by the ethoxide ion present is reasonable and further reduction would lead to **2** and **3**.



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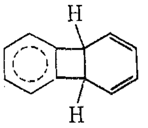

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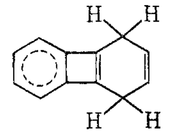

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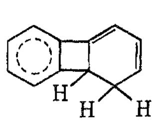

8

Experimental Section[10]

Biphenylene (**1**) was prepared in 25% yield by the procedure of Friedman,[11] mp 108–110°.

Reduction of Biphenylene (**1**).—To a stirred, refluxing (−33°) mixture of 500 ml of liquid ammonia, 150 ml of anhydrous ether, and 2.00 g of **1** (0.0132 mol) was added 0.90 g of sodium (0.039 mol). The blue solution was stirred for 15 min and then 15 ml of absolute ethanol was added over a 5-min period. The blue color disappeared and the NH_3 was allowed to evaporate. The residue was mixed with 150 ml of water and extracted with ether. Evaporation of the ether from the dried extracts ($MgSO_4$) yielded 1.70 g of a mixture of solid and liquid. Glc analysis indicated that **1**, **2**, and **4** were present in the ratio of 11:4:1 and that biphenyl was absent. Nmr confirmed the absence of biphenyl. Preparative glc gave enough material for spectral and elemental analysis.

Use of lithium instead of sodium required no ethanol but gave the same results. When the amount of sodium was increased to 4.5 equiv, then no unreacted **1** remained and the amounts of **2** and **4** were increased proportionally.

1,4,4a,8b-Tetrahydrobiphenylene (**2**): nmr (CCl_4) δ 2.35 ("filled-in" t, J = <3 Hz, 4 H), 3.65 ("filled-in" t, J = <3 Hz, 2 H), 5.60 ("filled-in" t, J = <3 Hz, 2 H), 6.95 (m, 4); ir (neat) 3.3, 3.4, 3.5, 6.9, 13.5 (ortho-disubstituted benzene), and 14.8 μ (*cis*-HC═CH); uv max (ethanol) 214 (ε 5184), 261 (ε 1410), 266.5 (ε 2150), and 273 nm (ε 2570); mol wt 156 (mass spectrum).

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.74. Found: C, 92.10; H, 7.71.

The dibromide of **2** was prepared by addition of bromine in CCl_4, mp 87–88°, recrystallized from ethanol.

Anal. Calcd for $C_{12}H_{12}Br_2$: C, 45.60; H, 3.83; Br, 50.57. Found: C, 45.37; H, 3.98; Br, 50.50.

4,5-Benzobicyclo[4.2.0]octa-2,4-diene (**4**): nmr (CCl_4) same as published spectrum[1] δ 1.8–2.7 (m, 4, two CH_2), 2.9–3.9 (m, 2, methyl CH), 5.75 (double d, 1, J_{AB} = 10 Hz, J = 3 Hz, vinyl CH), 6.30 (d, 1, J_{AB} = 10, vinyl CH), 6.93 (m, 4, aromatic CH); ir (neat) 13.2 μ; uv max (ethanol) 219.5 nm (ε 22,265), 226 (ε 17,877), 248.5 (ε 7801), 271 nm (ε 6825), lit.[1] max 248 nm (ε 8600); mol wt 156 (mass spectrum).

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.74. Found: C, 92.15; H, 7.55.

Registry No.—**1,** 259-79-0; **2,** 35031-03-9; **2** dibromide, 35031-04-0; **4**, 21367-71-5.

Acknowledgment.—The authors are indebted to the Research Corp. for a Frederick Gardner Cottrell grant, which purchased some of the equipment used, and to Dr. D. K. Wedegaertner and the University of Rochester, N. Y., for the nmr and mass spectra.

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[7] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, pp 136–145.

[8] F. A. Bovey, "NMR Data Tables for Organic Compounds," Wiley, New York, N. Y., 1967, pp 353 and 416.

[9] (a) A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley, New York, N. Y., 1961, p 429; (b) A. Streitwieser, Jr., and S. Suzuki, *Tetrahedron*, **16**, 153 (1961).

[10] Analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach uber Engelskirken, West Germany. Ir spectra were obtained on Perkin-Elmer 137B. Nmr spectra were obtained in CCl_4 on Joel JNM-C-60HL with tetramethylsilane as internal standard. Molecular weights were obtained using a Hitachi Perkin-Elmer RNV-6E mass spectrometer. Uv spectra were obtained on a Perkin-Elmer 202. Glc analysis and separations were done using Aerograph Model A-90-P instrument and a 1/4 in. × 10 ft column of 10% Carbowax on 80–100 mesh firebrick treated with HMDS at 190°. The ammonia for the reductions was distilled from its metal cylinder and condensed in the reduction flask, but not dried before use. The sodium was cut free of oxide and hydroxide just before use.

[11] F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Syn.*, **48**, 12 (1968).

Hydrogenolysis of the Acetal 6,8-Dioxabicyclo[3.2.1]octane by Aluminum Chloride Hydride. Evidence for the Preferred Direction of Ring Cleavage in the Course of α-Bromination of This Acetal

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Received April 19, 1972

A recent report[2] has suggested that bromination of acetals is acid catalyzed and that the exclusive attack of bromine on the α position of the acetal 6,8-dioxabicyclo[3.2.1]octane (**1**) is the result of initial cleavage of the protonated acetal to give the oxocarbonium ion **2** and/or **6** (path A and/or B of Scheme I) which in turn would lose a proton to form an intermediate α,β-unsaturated ether **3** and/or **7**. Bromine attack on **3** and/or **7** would produce the species **4** and/or **8** which would then suffer intramolecular attack by the hydroxyl group to re-

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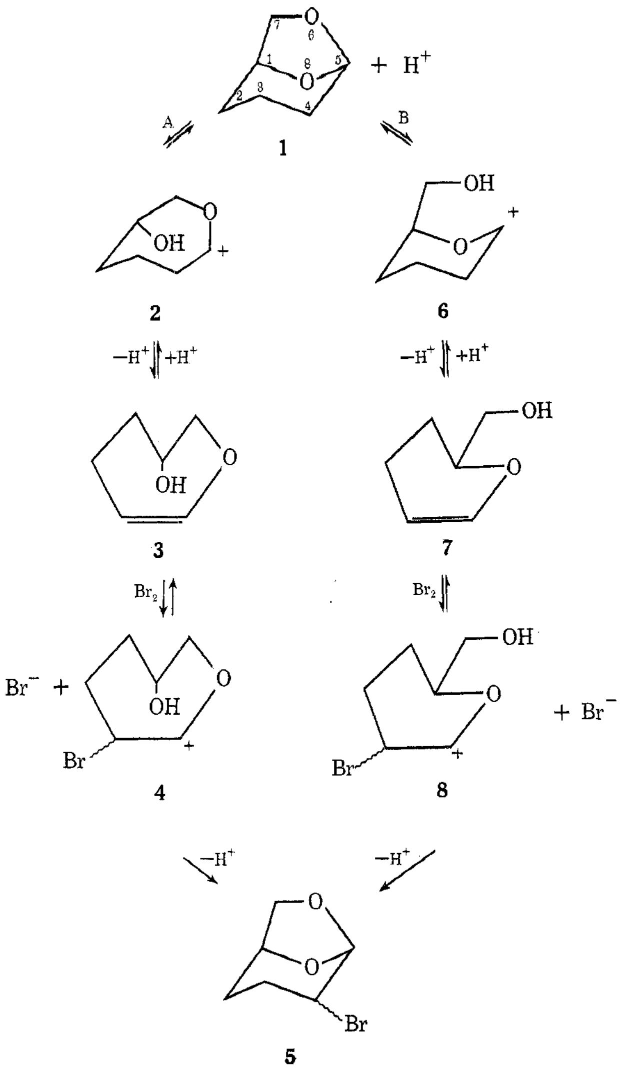
[1] Author to whom correspondence should be directed.

[2] T. P. Murray, C. S. Williams, and R. K. Brown, *J. Org. Chem.*, **36**, 1311 (1971).

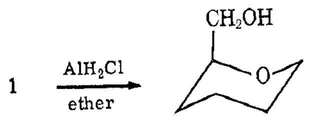
SCHEME I



generate the bicyclic molecule **5** now containing the bromine atom in the α position. Both the exo and endo monobromo isomers are obtained. No firm decision could be made as to which path of reaction (A or B) is preferred or whether both routes are followed, one giving the exo and the other the endo monobromo isomer. However, path B was considered[2] to be the preferred route on the basis of the apparent greater ease of cleavage of the C-5–O-6 bond in the hydrolysis or alcoholysis of substituted bicyclic structures such as **1**.

Work on the hydrogenolysis of acetals and ketals by mixtures of $LiAlH_4$ and $AlCl_3$ in ether[3] has indicated that, as is the case for the hydrolysis of acetals, the rate-controlling step of the hydrogenolysis reaction is the cleavage of the C–O bond, weakened by the association of its oxygen atom with the Lewis acid. However, the subsequent addition of the hydride ion to the resulting oxocarbonium ion is very fast and irreversible. Product analysis then provides clear evidence of the preferred route of bond cleavage.

We have subjected **1** to hydrogenolysis by AlH_2Cl, prepared from the appropriate quantities of $LiAlH_4$ and $AlCl_3$,[4] and found that 2-hydroxymethyltetrahydropyran (**9**, eq 1) was produced in excellent yield.



9 (1)

No other product could be detected by gas–liquid chromatography (glc) of the reaction mixture. Since the model of **1** shows that both oxygen atoms are readily accessible to the Lewis acid (AlH_2Cl), this reaction provides evidence to support our view that acid-catalyzed bromination of **1** occurs by path B.

Experimental Section

To a stirred solution of lithium aluminum hydride (0.427 g, 0.01125 mol) in 10 ml of dry ether kept at 5° by an ice bath, was added dropwise 10 ml of ether solution of aluminum chloride (1.49 g, 0.01125 mol). After the addition, the solution was stirred at room temperature for 15 min. To this stirred mixture was then slowly added a solution of 1.71 g (0.015 mol) of 6,8-dioxabicyclo[3.2.1]octane (**1**) in 10 ml of dry ether. The mixture was then stirred at room temperature for 2 hr whereupon a 15% aqueous solution of potassium hydroxide was slowly added until no further reaction occurred. The solids were removed by filtration and washed with ether. The combined ether solutions were dried (Na_2SO_4) and freed from solvent. The residue was analyzed by glc with a column of 20% butanediol succinate on Chromosorb W 60–80 mesh. The compound 2-hydroxymethyltetrahydropyran was obtained in 93% yield as the only detectable product.

Registry No.—**1,** 280-16-0.

Acknowledgment. We thank the National Research Council of Canada for financial assistance in this work.

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[3] B. E. Leggetter and R. K. Brown, *Can. J. Chem.*, **42**, 990 (1964); **43**, 1030 (1965).

[4] U. E. Diner, H. A. Davis, and R. K. Brown, *ibid.*, **45**, 207 (1967).

Alumina-Catalyzed Dehydration of Substituted Cyclohexanones. Comments on the Mechanism of Hydrocarbon Formation

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Received October 26, 1970

Over the past several years, our investigations of alumina-catalyzed dienol dehydration[1,2] have led us to investigate the formation and subsequent reactions of various 1,3-cyclohexadienes.[3] Several workers[4,5] have alluded to the possibility of the intermediacy of 1,3-cyclohexadiene in the alumina-catalyzed dehydration of cyclohexanone, even though it is found only as a minor product. Most of the reported product analyses, however, were incomplete, due mainly to difficulties in the separation of complex hydrocarbon mix-

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(1) C. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

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(5) G. Woods, *U. S. Dept. Com., Office Tech. Serv. AD 278,110*, 29 (1962).