Communications to the Editor

**Preparation and Solvolytic Behavior of a Bridgehead Birdcage Alcohol[1,2]**

Sir:

In the course of further investigations of half-cage and birdcage systems[3] we have sought derivatives of the known birdcage hydrocarbon[3] I with a functional group at a cyclobutane bridgehead position. One such derivative is the birdcage alcohol II-OH. The preparation of this alcohol and the solvolysis of the corresponding p-bromobenzenesulfonate are described in the present communication, and its homoketonization is discussed in the following one.[4]

The birdcage alcohol II-OH was derived from the hexachloro alcohol III, which in turn was prepared from the known hexachloro half-cage ketone[5] IV, m.p. 290–291° dec. Soloway, *et al.*,[5] had described isolation of a material, m.p. 330° dec., from treatment of the chlorinated half-cage ketone IV with lithium aluminum hydride (LAH) in dibutyl ether, for which the birdcage structure III was proposed. Whereas the use of a large excess of LAH under extremely vigorous conditions was reported to give rise to oxygen-inside alcohol V, m.p. 259–262° dec., in 40% yield, the use of *ca.* 1 equiv. of LAH in a large volume of solvent led to the material presumed to be III.[6]

In our hands, treatment of IV with 1 equiv. of LAH in tetrahydrofuran at 25° for 1 hr. gave the oxygen-inside alcohol[7] V, m.p. 258–261° dec., in 85% yield. On the other hand, base-catalyzed homoenolization[4] of the chlorinated half-cage ketone IV to the birdcage alcohol III could be accomplished readily by treatment of IV with alcoholic sodium hydroxide or by heating IV in pyridine solvent. Thus, in 0.1 M pyridine solution at 100.2°, ketone IV disappears with a first-order rate constant of $(2.9 \pm 0.1) \times 10^{-5}$ sec.$^{-1}$. Fairly good first-order kinetics were observed, any homoenolization–homoketonization equilibrium being well on the side of the "homoenol" III. On a preparative scale, an 80% yield of pure III[7] was obtained from heating 15 g. of half-cage ketone for 36 hr. under reflux in 50 ml. of pyridine and recrystallization of the product from methanol–water. The n.m.r. spectrum of III, *e.g.*, no α-proton, and its chemical behavior confirmed the bridgehead birdcage structure.

The hexachloro birdcage alcohol III could be successfully dechlorinated by the lithium–t-butyl alcohol–

(2) Reported at the Symposium on Cagelike Molecules, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(3) (a) S. Winstein, *Experientia, Suppl. II*, 137 (1955); (b) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, 82, 5363 (1960); (c) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405, 590 (1960); (d) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.*, 83, 2938 (1961).

(4) R. Howe and S. Winstein, *ibid.*, 87, 915 (1965).

(5) (a) S. B. Soloway, *et al.*, *ibid.*, 82, 5377 (1960); (b) C. W. Bird, R. C. Cookson, and E. Crundwell, *J. Chem. Soc.*, 4809 (1961).

(6) While the mechanism of this conversion is not clear, it probably involved base-catalyzed homoenolization of IV.

(7) This and the other indicated compounds gave good C and H analyses.

tetrahydrofuran (Li–BuOH–THF) procedure[3c] without any appreciable disturbance from homoketonization[4] of the product birdcage alcohol II-OH. Thus, the use of 25 g. of III, 30 g. of Li, 158 g. of BuOH, and 500 ml. of THF and subsequent chromatography and recrystallization of the product led to a 70% yield of pure birdcage alcohol[7] II-OH, m.p. 207–208°. The n.m.r. spectrum of the birdcage alcohol (CDCl$_3$, Varian A-60 spectrometer) is consistent with the bridgehead structure II-OH. For hydrocarbon I, the methylene proton pattern appears as an AB quartet with chemical shift values of τ 8.57 and 8.19, J_{AB} being 10.5 c.p.s. and $(\delta_A - \delta_B)$ being 23 c.p.s. For II-OH the far methylene signal occurs again as an AB quartet with chemical shift values of τ 8.52 and 8.22, J_{AB} being 10.5 c.p.s. and $(\delta_A - \delta_B)$ being 18 c.p.s. The near methylene H$_c$H$_d$ signal appears as a singlet at τ 8.28 superimposed
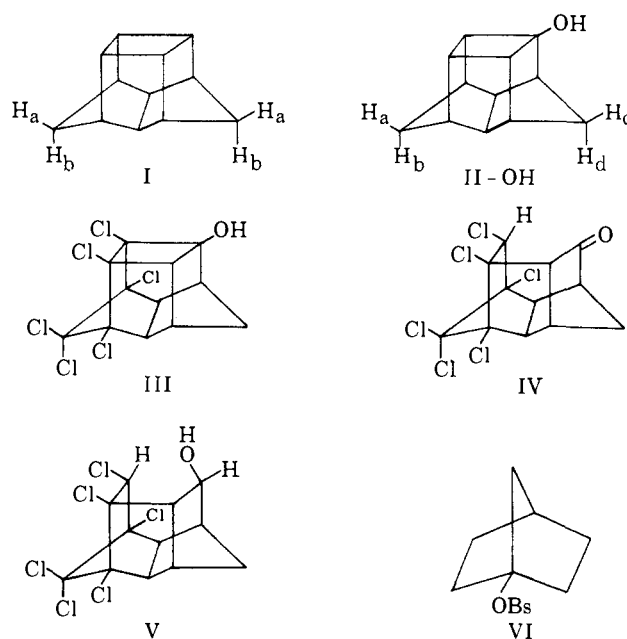
on one member of the H$_a$H$_b$ quartet. Evidently the higher field proton of a methylene group in I is deshielded in the alcohol II-OH. Presumably this is the proton labeled H$_c$. The bridgehead proton signals which occur as overlapping broad peaks at τ 7.44 (4 H) and 7.62 (6 H) in the hydrocarbon I are seen as a broad peak at τ 7.57 (8 H) and a complex multiplet at τ 7.87 (1 H).

For practical reasons the solvolysis of the p-bromobenzenesulfonate of the birdcage alcohol was of interest because this would serve as an indication of the feasibility of carbonium ion substitution reactions in this system. This solvolysis is of interest for theoretical reasons as well, since II-OBs is both cyclobutyl and bridgehead. Enhanced reactivities of cyclobutyl derivatives due to anchimeric assistance are well illustrated.[8] So are tremendously retarded ionization rates

(8) J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, 73, 5034 (1951); 81, 4390 (1959).

of bridgehead bicyclo[2.2.1]heptyl[9a] and bicyclo[2.2.2]-octyl[9b] derivatives. While the most important factor controlling bridgehead ionization rates would appear to be the one concerned with angle strain and promotion energy,[9] other factors, such as those dealing with solvation and "inside-cage" orbital overlap,[10] have been suggested.

In practice, we found that solvolytic substitution of II-OBs could be accomplished without over-all rearrangement. Thus, in acetolysis in acetic acid 0.02 M in sodium acetate, the birdcage p-bromobenzenesulfonate derivative[7] II-OBs, m.p. 81–82°, displayed a first-order solvolysis rate constant of 1.20 × 10⁻⁵ sec.⁻¹ at 195.3°. Recovery of the acetate product after a reaction time of 5 days and saponification with alcoholic potassium hydroxide led to a 92% yield of nearly pure unrearranged birdcage alcohol, m.p. 200°, undepressed on admixture with authentic II-OH, and infrared and n.m.r. spectra essentially identical with those of authentic starting alcohol.

The reactivity of II-OBs in acetolysis is nearly equal to that displayed by the bridgehead bicyclo[2.2.1]heptyl analog[11] VI. The similarity in the reactivities of II-OBs and VI-OBs is in line with a superficial resemblance between the angle strain problems encountered by bridgehead cations in the two systems, judging by the average bridgehead angles in I and in bicycloheptane.[12,13]

(9) (a) P. D. Bartlett and L. H. Knox, *J. Am. Chem. Soc.*, **61**, 3184 (1939); (b) W. von E. Doering, Abstracts, 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March 1953, p. 35M; W. von E. Doering and M. Finkelstein, Ph.D. Thesis of M. Finkelstein, Yale University, 1955.

(10) (a) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961); (b) P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 4195 (1964).

(11) C. J. Norton, Ph.D. Thesis, Harvard University, 1955. From Norton's acetolysis rate constants, 0.0339 hr.⁻¹ at 192.0° and 0.167 hr.⁻¹ at 214.0°, an interpolated value of 1.52 × 10⁻⁵ sec.⁻¹ is obtained for VI at 195.3°.

(12) V. Schomaker, A. Berndt, and C. Wong, private communication; A. Berndt and C. Wong, Ph.D. Theses, California Institute of Technology, 1957.

(13) A much more quantitative analysis of the bridgehead cation strain problem in the birdcage (II) and bicycloheptyl (VI) systems would be required to decide whether any nonclassical stabilization of the II cation is involved.

(14) N.S.F. Predoctoral Fellow, 1961–1964

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Homoenolization–Homoketonization of a Half-Cage Ketone[1,2]

Sir:

We wish to report the base-catalyzed homoenolization of the half-cage ketone I and homoketonization of the birdcage alcohol II. These transformations are of interest in connection with homoenolization–homoketonization phenomena[3] and they make available ketone III in another novel half-cage system.

(2) Reported at the Symposium on Cagelike Molecules, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(3) (a) A. Nickon and J. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); (b) A. Nickon, J. H. Hammon, J. L. Lambert, and R.O. Williams, *ibid.*, **85**, 3713 (1963); (c) C. H. DePuy and L. R. Mahoney, *ibid.*, **86**, 2653 (1964), and previous papers in the series.

Half-cage ketone[4,5a,b] I, m.p. 167–169°, is available from oxidation of the corresponding half-cage alcohol[5c,d] with chromic anhydride[5b] in pyridine, acetic acid, or ether–water.

As summarized in Table I, half-cage ketone I disappears with convenient first-order kinetics at 175–200° in t-butyl alcohol 0.9 M in potassium t-butoxide. It is

Table I. First-Order Rates[a] of Disappearance of I and II in t-BuOH, 0.898 M in KOBu-t

Substrate	Temp., °C.	k, sec.⁻¹	Rel. k
I	100.1[b]	1.0 × 10⁻⁹	1
I	172.4 ± 0.1	(7.47 ± 0.17) × 10⁻⁶	
I	172.5 ± 0.1	(7.37 ± 0.37) × 10⁻⁶	
I	196.1 ± 0.1	(7.35 ± 0.47) × 10⁻⁵	
I	195.5 ± 0.3	(7.58 ± 0.23) × 10⁻⁵	
II	100.1 ± 0.1	(3.31 ± 0.16) × 10⁻⁵	33,100

[a] Followed by v.p.c.; *ca.* 0.057 M substrate. [b] Extrapolated from data at higher temperatures.

transformed completely (>99%) to a new ketone,[4] m.p. 234–235°, less than 0.1% of birdcage alcohol II being detected. When the latter alcohol,[6] m.p. 207–208°, is treated under similar conditions, it is much more rapidly transformed (>99%) to the same new ketone.

The rearranged half-cage structure III for the new ketone is indicated by the spectral evidence and its

(4) This and other new substances here reported gave satisfactory carbon and hydrogen analyses.

(5) (a) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 2938 (1961); (b) D. Thompson and P. Bruck, unpublished work; (c) S. Winstein, *Experientia, Suppl. II*, 137 (1955); L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960); (d) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).

(6) P. Carter, R. Howe, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 914 (1965).