

of bridgehead bicyclo[2.2.1]heptyl<sup>9a</sup> and bicyclo[2.2.2]octyl<sup>9b</sup> derivatives. While the most important factor controlling bridgehead ionization rates would appear to be the one concerned with angle strain and promotion energy,<sup>9</sup> other factors, such as those dealing with solvation and "inside-cage" orbital overlap,<sup>10</sup> 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<sup>7</sup> II-OBs, m.p. 81–82°, displayed a first-order solvolysis rate constant of  $1.20 \times 10^{-5}$  sec.<sup>-1</sup> 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<sup>11</sup> 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.<sup>12,13</sup>

(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.<sup>-1</sup> at 192.0° and 0.167 hr.<sup>-1</sup> at 214.0°, an interpolated value of  $1.52 \times 10^{-5}$  sec.<sup>-1</sup> 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<sup>1,2</sup>

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<sup>3</sup> and they make available ketone III in another novel half-cage system.

(1) Research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) Reported at the Symposium on Cage-like 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<sup>4,5a,b</sup> I, m.p. 167–169°, is available from oxidation of the corresponding half-cage alcohol<sup>5c,d</sup> with chromic anhydride<sup>5b</sup> in pyridine, acetic acid, or ether–water.

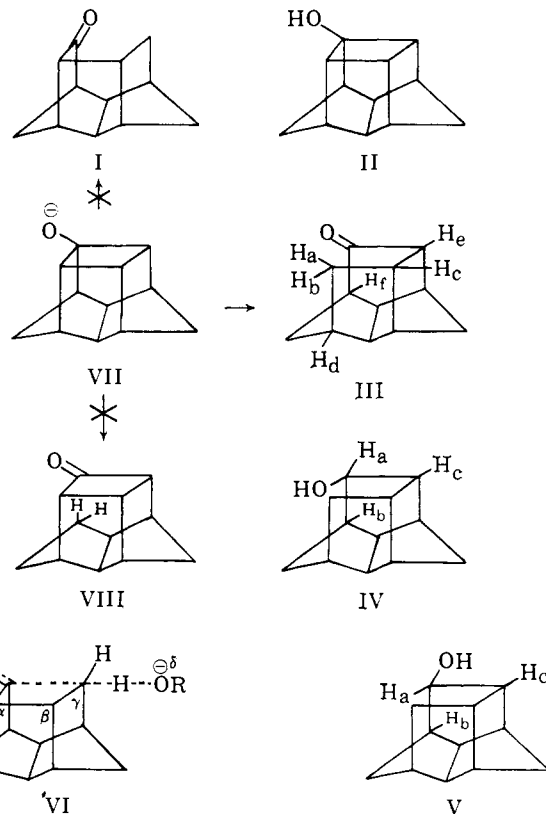
As summarized in Table I, half-cage ketone I disappears with convenient first-order kinetics at 175–200° in *t*-butyl alcohol 0.9 *M* in potassium *t*-butoxide. It is

Table I. First-Order Rates<sup>a</sup> of Disappearance of I and II in *t*-BuOH, 0.898 *M* in KOBu-*t*

Substrate	Temp., °C.	<i>k</i> , sec. <sup>-1</sup>	Rel. <i>k</i>
I	100.1 <sup>b</sup>	$1.0 \times 10^{-9}$	1
I	172.4 ± 0.1	$(7.47 \pm 0.17) \times 10^{-6}$	
I	172.5 ± 0.1	$(7.37 \pm 0.37) \times 10^{-6}$	
I	196.1 ± 0.1	$(7.35 \pm 0.47) \times 10^{-6}$	
I	195.5 ± 0.3	$(7.58 \pm 0.23) \times 10^{-6}$	
II	100.1 ± 0.1	$(3.31 \pm 0.16) \times 10^{-6}$	33,100

<sup>a</sup> Followed by v.p.c.; ca. 0.057 *M* substrate. <sup>b</sup> Extrapolated from data at higher temperatures.

transformed completely (>99%) to a new ketone,<sup>4</sup> m.p. 234–235°, less than 0.1% of birdcage alcohol II being detected. When the latter alcohol,<sup>6</sup> 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).

behavior in lithium aluminum hydride reduction. Ketone III displays an infrared carbonyl stretching frequency at 1742 and 1732  $\text{cm}^{-1}$  (split) in  $\text{CCl}_4$  solution and no absorption at 1420  $\text{cm}^{-1}$ . Thus it is not an  $\alpha$ -methylene ketone.<sup>7</sup> In its n.m.r. spectrum ( $\text{CDCl}_3$ , TMS internal standard, Varian A-60 spectrometer), ketone III displays one-half of an AB quartet ( $J_{AB} = 13$  c.p.s.) as sharp singlets at  $\tau$  8.90 (0.3 H) and 8.68 (0.7 H) ascribed to the carbonyl-shielded inside proton  $H_a$ . Proton  $H_a$  is split only by  $H_b$ , further coupling with  $H_c$  and  $H_d$  not being detected. The other half of the AB quartet ascribed to the outside proton  $H_b$  appears as a broad signal centered at  $\tau \sim 7.8$  (ca. 0.3 H) and the 0.7 proton part of a broad signal centered at  $\tau$  8.10 (4.7 H) which includes the other methylene protons. The n.m.r. spectrum of ketone III also displays broad signals centered at  $\tau$  7.33 (ca. 2 H) for the bridgehead protons  $H_e$  and  $H_f$  and at  $\tau$  7.60 (ca. 6 H) for the remaining bridgehead protons.

As expected for the half-cage structure III, lithium aluminum hydride reduction in ether proceeds with a high degree of "steric approach control" to yield an alcohol containing >97% of one epimer, assigned the oxygen-inside structure IV. Alcohol<sup>4</sup> IV, m.p. 259–260.5°, exhibits an  $\alpha$ -hydrogen  $H_a$  signal in the n.m.r. spectrum ( $\text{CCl}_4$ ) at  $\tau$  5.81 as a doublet ( $J \approx 6.5$  c.p.s.) with further unresolved splitting. The major splitting appears to be due to the coupling between the relatively eclipsed  $H_a$  and  $H_b$  protons, while the  $H_a$ – $H_c$  coupling would be expected to be smaller<sup>8</sup> since the pertinent  $H_a$ – $H_c$  dihedral angle is ca. 40°. As expected for the half-cage structure IV, aluminum isopropoxide catalyzed equilibration of the oxygen-inside alcohol IV yields an alcohol mixture containing >96% of the oxygen-outside epimer V. Pure V,<sup>4</sup> m.p. 229–229.5°, exhibits an  $\alpha$ -hydrogen  $H_a$  signal in its n.m.r. spectrum ( $\text{CCl}_4$ ) as a sharp singlet at  $\tau$  6.15. The evidently small coupling between the  $H_a$  and  $H_b$  or  $H_c$  protons is in line<sup>8</sup> with structure V since the  $H_a$ – $H_b$  dihedral angle is ca. 110° while the angle between  $H_a$  and  $H_c$  is ca. 80°.

The available evidence is that the conversion of the half-cage ketone I to the isomeric ketone III involves homoenolization to the birdcage alcohol II, the latter representing the "homoenol" common to both ketones I and III. From the general rate level observed for the disappearance of I, it seems clear that the carbonyl group aids the proton removal from I by delocalizing the developing anionic charge in proceeding to the homoenolization transition state. While we have no information on stereochemistry of the homoenolization in the present case, analogy with base-catalyzed homoenolization–homoketonization involving cyclopropanols<sup>3</sup> suggests a transition state such as VI for conversion of I to the birdcage alkoxide ion VII. This depicts homoenolization of I proceeding with inversion of configuration at  $C_5$ , an outside hydrogen being removed.

Homoketonization of the highly strained<sup>9</sup> birdcage alcohol II (by way of the anion VII) proceeds ca. 33,000 times as rapidly as does homoenolization of I at 100°. Further, the homoketonization is observed only in the direction of the new ketone III, no formation

of I being detected. It is significant also that no homo-ketonization is observed in the direction of ketone VIII containing a cyclobutanone ring. Thus the homo-ketonization of II proceeds very predominantly in the direction of the least strained ketone III. That the new ketone III is less strained than the old half-cage ketone I is apparent from inspection of models. The present observations on the homoenolization–homoketonization sequence  $I \rightarrow II \rightarrow III$  indicate substantial values of the III/I and III/II equilibrium constants.

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

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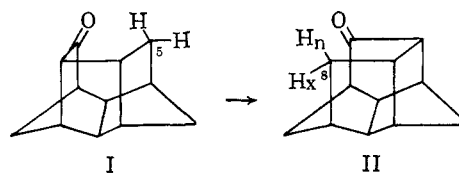
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## Isomerization via Transannular Enolate Anion

Sir:

In connection with our recent work<sup>1</sup> we became interested in the chemistry of the half-cage ketone<sup>2</sup> I, particularly with respect to transannular activation of a C-5 hydrogen atom by the closely situated carbonyl group. We wish to report a novel base-catalyzed isomerization reaction of the half-cage ketone I to the iso-half-cage ketone II.



Treatment of the half-cage ketone I, m.p. 173–175°, with potassium *t*-butoxide in *t*-butyl alcohol in a sealed tube at 250° quantitatively afforded a new isomeric ketone containing approximately 4% ketone I. The product ratio was unchanged for reaction periods of 4 and 10 hr. The isomeric ketone,<sup>3</sup> m.p. 232–234°, was assigned structure II on the following basis. The infrared spectrum of II contains a split carbonyl peak<sup>4</sup> (1733 and 1742  $\text{cm}^{-1}$ ) but lacks  $-\text{CH}_2\text{CO}-$  and  $\text{C}=\text{C}$  absorptions. The nuclear magnetic resonance spectrum has absorptions in three regions: a sharp unsymmetrical doublet centered at  $\tau$  8.80,  $J = 13$  c.p.s. (1 H), and two sets of two broad peaks centered at about 8.1 (5 H) and 7.4 (8 H). The sharp doublet at  $\tau$  8.80 is undoubtedly the upfield part of an AB pattern due to the nonequivalent methylene protons and is attributed to the *endo*-proton,  $H_n$ . Inspection of a molecular model of II suggests that  $H_n$  should be greatly shielded due to the magnetic anisotropy of the carbonyl group; on the other hand,  $H_x$  should be very little affected.<sup>5</sup>

(1) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Am. Chem. Soc.*, **86**, 3162 (1964).

(2) (a) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); (b) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 2938 (1961).

(3) Satisfactory analyses were obtained for the new compounds.

(4) The nature of this splitting has not been determined but is probably due to Fermi resonance.

(5) In contrast, however, a molecular model of I suggests that both of the protons attached to C-5 should be noticeably shielded. Thus, as expected, the n.m.r. spectrum of I shows a more complex pattern between  $\tau$  8.0 and 8.9 (6 H).

(7) S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

(8) M. Karplus, *ibid.*, **30**, 11 (1959).

(9) W. N. Hubbard, F. R. Frow, and G. Waddington, *J. Phys. Chem.*, **62**, 821 (1958).