behavior in lithium aluminum hydride reduction. Ketone III displays an infrared carbonyl stretching frequency at 1742 and 1732 cm.$^{-1}$ (split) in CCl_4 solution and no absorption at 1420 cm.$^{-1}$. Thus it is not an α-methylene ketone.[7] In its n.m.r. spectrum ($CDCl_3$, 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 τ 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 τ 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 τ 7.33 (ca. 2 H) for the bridgehead protons H_e and H_f and at τ 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[4] IV, m.p. 259–260.5°, exhibits an α-hydrogen H_a signal in the n.m.r. spectrum (CCl_4) at τ 5.81 as a doublet ($J \simeq 6.5$ 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[8] 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,[4] m.p. 229–229.5°, exhibits an α-hydrogen H_a signal in its n.m.r. spectrum (CCl_4) as a sharp singlet at τ 6.15. The evidently small coupling between the H_a and H_b or H_c protons is in line[8] 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[3] 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_γ, an outside hydrogen being removed.

Homoketonization of the hightly strained[9] 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 homoketonization is observed in the direction of ketone VIII containing a cyclobutanone ring. Thus the homoketonization 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 → II → 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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Isomerization via Transannular Enolate Anion

Sir:

In connection with our recent work[1] we became interested in the chemistry of the half-cage ketone[2] 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.

I   II
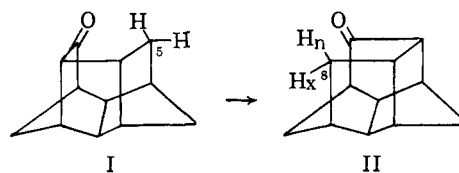
Treatment of the half-cage ketone I, m.p. 173–175°, with potassium t-butoxide in t-butyl alcohol in a sealed tube at 250° quantitatively afforded a new isomeric ketone containing approximately 4% ketone I. The product ratio was unchanged for reaction periods of 4 and 10 hr. The isomeric ketone,[3] m.p. 232–234°, was assigned structure II on the following basis. The infrared spectrum of II contains a split carbonyl peak[4] (1733 and 1742 cm.$^{-1}$) but lacks $-CH_2CO-$ and $C=C$ absorptions. The nuclear magnetic resonance spectrum has absorptions in three regions: a sharp unsymmetrical doublet centered at τ 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 τ 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.[5]

(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 τ 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).

The observed product ratio favoring II can be rationalized, at least qualitatively, in terms of less steric hindrance about the carbonyl groups with respect to solvation, fewer nonbonded hydrogen repulsions, and less ring strain. The steric hindrance about the carbonyl group in I is dramatically demonstrated by its lack of reactivity[6] toward hydroxylamine. In contrast, under normal conditions the ketone II is easily converted to the corresponding oxime,[3] 90% yield, m.p. 135–136°; ν_{Nujol} 3226, 3125, and 1667 cm.$^{-1}$. The n.m.r. spectrum shows a typical C-8 endo-proton doublet centered at τ 8.72, $J_1 = \sim 13$ c.p.s. and $J_2 = \sim 4$ c.p.s., and a broad peak at τ 6.74 (–O–H).

We visualize the isomerization reaction as a transannularly assisted abstraction of a hydrogen atom from C-5 to form the carbanion Ia. Because of the proximity, the anion adds to the carbonyl group to form the bird-cage alkoxide anion IIIa, a transannular enolate anion, which is thermally unstable at the reaction temperature with respect to the less strained species Ia and IIa. Protonation of the anions then provides the thermodynamically controlled mixture of the ketones I and II. No alcohol III could be found in the reaction products.


I ⇌ Ia

⇅

III ⇌ IIIa

⇅

II ⇌ IIa
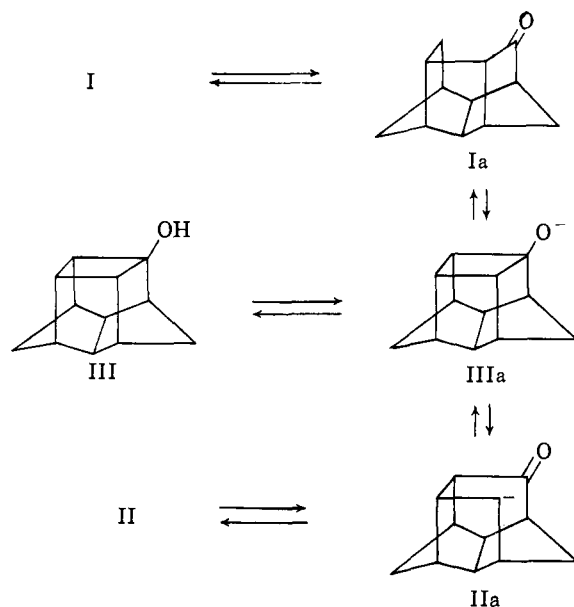
In order to test the intermediacy of the transannular enolate anion (IIIa), the bird-cage alcohol III,[3] m.p. 207–208°, was prepared (72% yield) by dechlorination of the hexachloro bird-cage alcohol V[7] with lithium and t-butyl alcohol in boiling tetrahydrofuran.[2a] The hexachloro alcohol V was in turn prepared in quantitative yield simply by heating the hexachloro half-cage ketone IV[7] in pyridine.[8]

Treatment of III with potassium t-butoxide in t-butyl alcohol at 250° readily gave the same mixture of the ketones I and II (ca. 4:96). An alternative thermal pathway for the observed isomerization reactions is

(6) For example, no oxime was formed at 10,000 atm., 75°, under which conditions di-t-butyl ketone reacted to give the corresponding oxime in 96% yield: W. H. Jones, E. W. Tristram, and W. F. Benning, J. Am. Chem. Soc., 81, 2151 (1959).
(7) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, ibid., 82, 5377 (1960).
(8) This reaction was reported in the T. W. Richard Medal Award Lecture by S. Winstein at the Massachusetts Institute of Technology, May 10, 1962.

IV → V → III
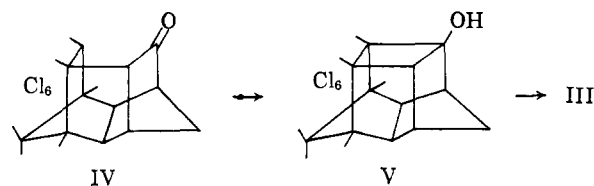
rejected since, under identical conditions in the absence of base, the ketones I and II and the alcohol III are cleanly recovered.

This reaction thus represents the first example of a transannular keto–enol isomerization involving abstraction of a γ-hydrogen atom[9] by base to give a cyclic transannular enolate anion, ketonization of which leads to carbonyl products.[10]

(9) A homoenolization process involving abstraction of a β-hydrogen atom was recently reported: A. Nickon and J. L. Lambert, J. Am. Chem. Soc., 84, 4604 (1962).
(10) The same isomerization reaction has been found independently by R. Howe and S. Winstein, ibid., 87, 915 (1965).

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Congressane

Sir:

The XIXth International Congress of Pure and Applied Chemistry, held in London on July 10–17, 1963, featured representations of the polycyclic hydrocarbon I as a decoration on the covers of abstracts, programs, and literature.[1] The Handbook of the Congress contained the following explanatory foreword: "The Congress Emblem (I) represents a beautifully symmetrical molecule which has not, so far, been described in the literature (cf. Prelog[2]). If adamantane (II) be regarded as an "adamantalogue" of cyclohexane, then the Congress Emblem is an adamantalogue of adamantane. The hypothetical process of adamantalogous expansion would provide a family of compounds all of which contain part of the diamond lattice. Indeed, diamond is an infinite adamantalogue of cyclohexane. The synthesis of the Congress Emblem, the correct name of which (kindly supplied by Dr. L. C. Cross) is pentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]tetradecane, is suggested as a challenging objective for the participants in the Congress."

I ≡ I II
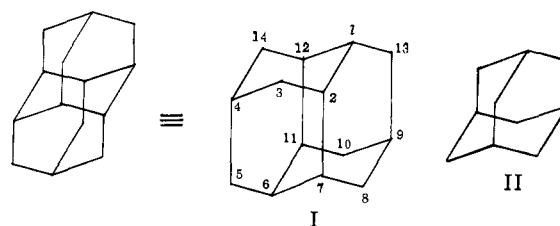
We wish to report the synthesis of "congressane"[3] (I). The method chosen was analogous to the isomeri-

(1) See also endpaper, D. J. Cram and G. S. Hammond, "Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1964.
(2) V. Prelog, Bull. soc. chim. France, 1433 (1960). (However, see cyclitol diborate, A. Weissbach, J. Org. Chem., 23, 327 (1958)).
(3) V. Prelog, Pure Appl. Chem., 6, 545 (1963); G. M. Blackburn, D. W. Cameron, A. R. Katritzky, and R. H. Prince, Chem. Inc. (London), 1349 (1963).