Although not necessarily unique, a mechanism combining least motion with the cubeoctahedron mechanism[1a] yields a very simple account of the rearrangement: (a) let the first CH_3CN add at $B_{5''}$, (b) form a B_5–$B_{5'}$ bond, (c) apply the dsd mechanism[1a,9] to the faces 5′ 4 2′ 3′, 5‴ 3′ 1′ 4′, 5 3 2 4′, and 1 2 1′ 2′, (d) break B_4–$B_{5''}$, B_3–$B_{5''}$, and B_3–B_4, (e) move H_1 into the open bridging position, and (f) add the second CH_3CN to B_1. Of course, we cannot be sure at which stage the second CH_3CN is added, but the other steps are built around the generally accepted mechanism[1a] for the rearrangement of *o*-$B_{10}C_2H_{12}$ to *m*-$B_{10}C_2H_{12}$.

Acknowledgment. We acknowledge R. E. Long and K. N. Trueblood of the University of California at Los Angeles for their computer program for the Sayre method, and Donald Voet for helpful discussions. We also wish to thank the Office of Naval Research and the Advanced Research Projects Agency for support of this research.

(9) W. N. Lipscomb, *Science*, in press.

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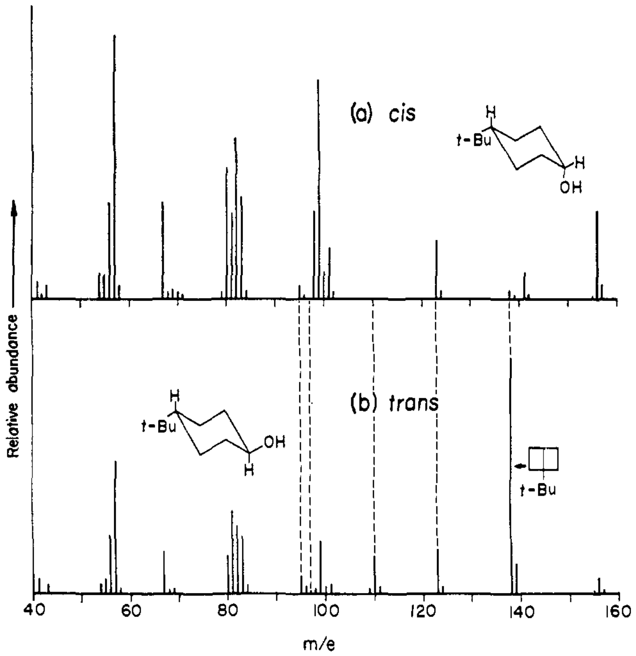

Figure 1. 4-*t*-Butylcyclohexanols; helium light source (II), 25°.

Studies of Stereoisomerism by Photoionization Mass Spectrometry. Fragmentation of *cis*- and *trans*-4-*t*-Butylcyclohexanols

Sir:

It has been suggested[1] that the process of water elimination from alcohols which occurs in the mass spectrometer shows some slight stereospecific dependence insofar that for several epimeric pairs of alcohols it has been observed that the one having the most sterically hindered hydroxyl function generally exhibits the lower intensity molecular ion (M) and the higher intensity (M − H_2O) peak. We now report a mass spectrometric investigation of the *cis* (I) and *trans* (II) isomers of 4-*t*-butylcyclohexanol[2] which reveals an unexpectedly large steric dependence for water elimination and which, furthermore, at first sight appears to contravene the generalization outlined above for this process.

Our initial study of these compounds utilized a conventional electron impact ionization source,[3] and under these conditions our results were irreproducible and inconclusive. In view of recent studies[4] it seemed highly probable that this was the result of spurious processes caused by the hot filament together with the attendant high temperature of the ion chamber (200°). Accordingly, we repeated our measurements using a modification[5] of a recently developed photoionization source[4] which operates at any desired temperature at or above room temperature. The spectra obtained were quantitatively reproducible and are shown in Figure 1. The higher mass peaks in the photoionization mass spectrum are much more intense than their electron impact counterparts. It has already been shown[4] that this is due, at least in part, to thermal effects. It is also clear that there is a most significant difference between the fragmentation patterns of the two isomers, particularly in the high mass region of the spectrum. If we assume that the molecular ions Ia and IIa adopt the same conformations in the gas phase as are believed[6] to be preferred for I and II in solution, then the *cis* isomer (I) would have the hydroxyl function in the more sterically hindered position (axial) and should thus eliminate water more readily[1] than the *trans* isomer (II). In fact the reverse is observed, with the relative (M − H_2O) peak abundances being $(M - H_2O)_{trans}:(M - H_2O)_{cis} = 38:1$. There is also a significant difference in the ratio of parent ion abundance with $M_{trans}:M_{cis} = 1:5$. A simple rationale of these findings, together with other characteristics of the spectra, can be given if we abandon the above conformational hypothesis. Previous studies[7,8] of the fragmentation of cyclohexanol have shown that water elimination occurs preferentially (83%) *via* 1,4 and 1,3 elimination processes and furthermore have led to the suggestion[8] that 1,4 elimination will occur preferentially when the substituents to be eliminated from these positions have a *trans* relationship.

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(1) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 145.

(2) These compounds were prepared according to the method of S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, 77, 5562 (1955). In the folllowing discussion roman numerals I–V refer to the parent compounds whereas Ia, etc., refer to the corresponding positive ions. After completion of the mass spectral measurements thin layer chromatography showed a single spot for each sample, and comparison with authentic material showed that the samples had not been inadvertently interchanged.

(3) An A.E.I. M.S.9 high-resolution mass spectrometer was used throughout this study.

(4) C. E. Brion *Anal. Chem.*, 37, 1706 (1965).

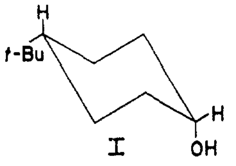
(5) Details of the improved light source will be published later. Radiation of 584 A (21.2 ev) was used and the samples were introduced at room temperature.

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

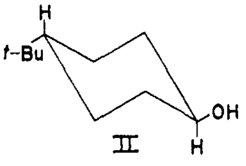
(7) H. Budzikiewicz, C. Djerassi, and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 42.

(8) C. G. MacDonald, T. S. Shannon, and G. Sugowdz, *Tetrahedron Letters*, 807 (1963).

Shannon, *et al.*,[8] have suggested the ion resulting from the 1,4 elimination may be related to the [2.2.0]bicyclohexane system (V). If this is so, and if 1,4 elimination can occur in the 4-*t*-butylcyclohexanol system, then the simple expedient of inverting the conformation of the ion (IIa) derived from the *trans* isomer (II) into the boat symmetry (IVa) would enable the 1,4 elimination of water to occur quite readily. This elimination would be far less likely to occur in the *cis* isomer (IIIa). Further evidence supporting this hypothesis follows from the work of Srinivasan,[9] who obtained the mass spectrum of [2.2.0]bicyclohexane and found major peaks at M, M − 15, M − 28, M − 41, and M − 43. If it is correct that an ion related to [2.2.0]bicyclohexane is an intermediate in the fragmentation of the *trans* isomer and not in the case of the *cis* isomer, then we should expect to see prominent peaks in the spectrum of the *trans* isomer at mass numbers 138, 123, 110, 97, and 95. These have been indicated by dotted lines in Figure 1, from which it can be seen that peaks occur as required. The fact that this rationale involves the suggestion that the *trans* isomer must assume the boat conformation for at least some excited states of its ion does not appear unreasonable to us in view of the energetics of the photoionization process.



I



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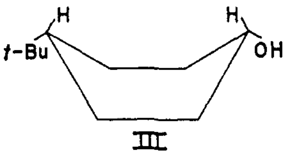

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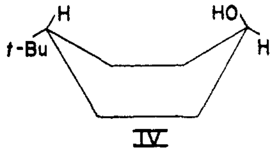
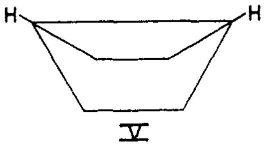


IV



V

Acknowledgment. It is a pleasure for both of us to acknowledge financial assistance from the National Research Council of Canada.

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[9] R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961).

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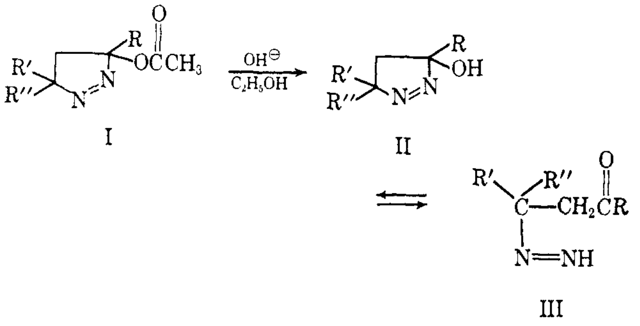
A Carbanion Rearrangement *via* a Homoenolate Ion

Sir:

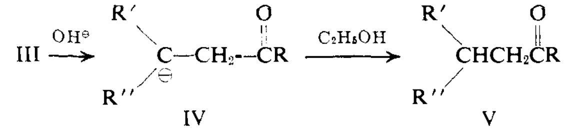
The intervention of cyclopropanol intermediates or homoenolate ions in some ketone reactions under alkaline conditions has been reported recently.[1] During an investigation of the hydrolysis of 3-acetoxy-Δ^1-pyrazolines (I)[2] we observed a carbon skeleton rearrangement that appears to involve the intermediate formation of a homoenolate ion. The alkaline hydrolysis of these pyrazolines was examined with a view to obtaining the corresponding alcohol II, the intramolecular adduct III of a ketone, and an alkyldiimide, for further study. In no cases were such compounds detected, but efforts are still being made to isolate them.



I
II
III

a, R = R′ = R″ = CH_3
b, R = $CH{=}C(CH_3)_2$; R′ = R″ = CH_3
c, R = R′ = CH_2CH_3; R″ = CH_3
d, R = CH_3; R′ = H; R″ = C_6H_5
e, R = R′ = H; R″ = C_6H_5

It would be expected on the basis of the currently accepted mode of decomposition of diimides in alkaline solution[3] that intermediate III would lose nitrogen to produce carbanion IV and ultimately ketone V. In fact, however, the major product of alkaline hydrolysis of Ia was pinacolone along with a lesser amount of the expected methyl isobutyl ketone. Hydrolysis of Ib yielded only 2,5,5-trimethyl-2-hexen-4-one, a product of carbon skeleton rearrangement, and none of the isobutyl ketone Vb. Hydrolysis of Ic yielded ethyl *t*-amyl ketone as a major product along with a small amount of the expected ketone Vc. Attempted hydrolyses of Id and Ie did not lead to nitrogen evolution but rather to loss of acetic acid and to the formation of the corresponding pyrazoles.



IV
V

It is believed that these rearrangements may be rationalized by the mechanism shown in Scheme I.[4] In support of this scheme is the fact that hydrolysis of 1,2,2-trimethylcyclopropyl acetate yields a mixture consisting of 90% pinacolone and 10% methyl isobutyl ketone,[5] and hydrolysis of 1-isobutenyl-2,2-dimethylcyclopropyl acetate yields only 2,5,5-trimethyl-2-hexen-4-one. DePuy[6] has reported that cyclopropanols open in base to give the product derived from the more stable carbanion.

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[1] A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965), and prior references; A. Nickon and J. L. Lambert, *ibid.*, **88**, 1905 (1966).

[2] J. P. Freeman, *J. Org. Chem.*, **29**, 1379 (1964).

[3] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., p 159.

[4] The equilibria represented in this scheme are written for the purpose of allowing the reader to follow the rearrangement rather than to imply anything specific about the lifetimes or individuality of the structures displayed.

[5] Interestingly, acid hydrolysis of Ia yielded exclusively methyl isobutyl ketone suggesting that, as expected, the lifetime of the carbanionic species in acid solution is very short.

[6] C. H. DePuy, Abstracts, 18th National Organic Chemistry Symposium, Columbus, Ohio, June 1963, p. 31; C. H. DePuy and F. W. Breitbeil, *J. Am. Chem. Soc.*, **85**, 2176 (1963).