difficult to prepare by conventional partial or total chemical synthesis. It should now be possible to examine whether separation of biological activities could be accomplished by suitable oxygenation of the parent hormone.[12]

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(13) Ford Foundation Fellow.

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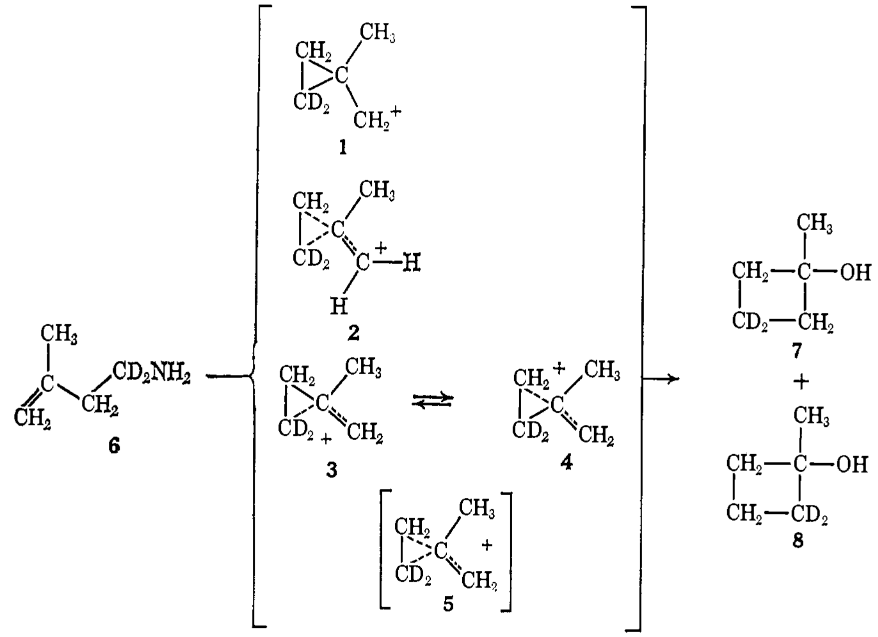
The Mechanism of Formation of 1-Methylcyclobutanol from (β-Methylallyl)carbinylamine with Nitrous Acid

Sir:

Evidence has been presented for formation of a common intermediate(s) in the carbonium ion interconversion reactions of (1-methylcyclopropyl)carbinyl, (β-methylallyl)carbinyl, and 1-methylcyclobutyl derivatives.[2] The structure(s) of the intermediate(s) is unknown but, for the corresponding unsubstituted derivatives, it has been proposed that equilibrating delocalized "bicyclobutonium" cations might provide the most economical explanation.[3] However, the stereochemical properties of the intermediate(s) derived from methylcyclopropylcarbinyl derivatives are suggestive of a "symmetrical homoallylic" structure.[4,5] Indeed, except for the extensive formation of products with the cyclobutyl structure, equilibrating "homoallylic" cations can account for the methylene shuffling, anchimeric assistance, and product distributions observed in many of the carbonium ion reactions of these systems.[6] That the dimethylcyclopropylcarbinyl cation displays nmr signals indicative of nonequivalent methyl groups has led to the postulation of a "bisected" structure for the dimethylcyclopropylcarbinyl cation,[7,8] although the bicyclobutonium structure is not rigorously excluded by the nmr spectra. In general, it seems that the properties which might be ascribed to the "bisected" cation and the "symmetrical homoallylic" cation are not in fact really different.

A possible test for the importance of cations such as the classical (1-methylcyclopropyl)carbinyl cation (**1**), the "bisected cation (**2**), a rapid equilibrating mixture of "homoallylic" cations (**3** and **4**), or the "symmetrical homoallylic" cation (**5**) as intermediates in the interconversions of (1-methylcyclopropyl)carbinyl, 1-methylcyclobutyl, and (β-methylally)carbinyl derivatives is available by investigation of the deamination of 1,1-dideuterio-3-methyl-3-butenylamine (**6**). If any of these are, in fact, intermediates in the formation of 1-methylcyclobutanol, then this product would be an equimolal mixture of **7** and **8**.

The deuterated amine was synthesized from methyl 3-methyl-3-butenoate which was reduced to 1,1-dideuterio-3-methyl-3-buten-1-ol with lithium aluminum deuteride. The alcohol was converted to the benzenesulfonate with benzenesulfonyl chloride in collidine. The azide was then obtained with sodium azide in dimethyl sulfoxide and reduced to the amine with lithium aluminum hydride. The over-all yield was 34%, based on the lithium aluminum deuteride.



The deuterated amine was deaminated with sodium nitrite in 1 *N* aqueous perchloric acid. The resulting mixture of alcohols was separated by preparative vpc on four 12-ft Carbowax columns at 120° in a Beckman Megachrom. The impure 1-methylcyclobutanol was treated with bromine at 0° in carbon tetrachloride and

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(1) Supported in part by the National Science Foundation.

(2) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961).

(3) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

(4) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).

(5) H. G. Richey and J. M. Richey, *ibid.*, **88**, 4971 (1966).

(6) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

(7) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965).

(8) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

flash distilled to remove the α,β-dimethylallyl alcohol present.

In the nmr spectrum of 1-methylcyclobutanol, the multiplets due to the protons at the 2 and 3 positions are clearly distinguishable. However, in the spectrum of the labeled 1-methylcyclobutanol from the deamination of the deuterated amine, no proton resonances were detected corresponding to the deuterated amine, no proton resonances were detected corresponding to the 3 position, and, therefore, no significant amount of **8** was found. This result *excludes* the intervention of cations **1–5** as intermediates in this reaction. It does not distinguish between classical ions and nonequilibrating nonclassical ion(s) as intermediates[9] but clearly shows that the ring closure proceeds directly to a 1-methylcyclobutyl-like cation and not a (1-methylcyclopropyl)-carbinyl-like cation.

That deamination of (1-methylcyclopropyl)carbinyl-^{14}C-amine gives 1-methylcyclobutanol with 3% of the activity in the 3 position[2] suggests that the 1-methylcyclobutyl cation is best represented as a relatively weakly delocalized bicyclobutonium ion which undergoes only slight equilibration. This interpretation is supported by the observation that 1-methylcyclobutyl methanesulfonate reacts with sodium borohydride to form a small but definite quantity of dimethylcyclopropane as well as methylcyclobutane.[10]

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(9) The argument presented for a nonclassical structure for the intermediates in these interconversions[2] has allegedly been refuted by the MO calculations of R. E. Davis, A. S. N. Murthy, and A. Ohno, *Tetrahedron Letters*, 1595 (1968). However, the substantial doubt cast on the validity of these calculations by J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, 90, 4311 (1968), would appear to leave the question still open. The delocalized structure proposed by the latter authors for bicyclobutonium cations is quite consonant with the results reported here.

(10) Z. Majerski, M. Nikoletic, S. Borcic, and D. E. Sunko, *Tetrahedron*, 23, 661 (1967).

(11) National Science Foundation Predoctoral Fellow, 1960–1962.

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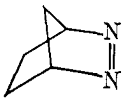
Operational Criteria for Concerted Bond Breaking in Gas-Phase Molecular Elimination Reactions

Sir:

An intriguing question often raised by mechanistically interested chemists regarding the course of molecular elimination processes concerns the details of the rate-controlling step, whether two bonds break concurrently or consecutively. A fission process is classified as stepwise or concerted depending on a postulated structure for the transition state; *i.e.*, whether at the saddle point both bonds are partially broken to a comparable degree, or whether one bond is considerably more broken than the other. Aside from the unavailability of sufficiently refined probes for exploring the structures of transition states, the relative degree of bond breaking defies quantification so that the distinction cannot be placed on an operational basis.

It is evident that the structure of any molecular species which has a lifetime of the order of a single vibration can be explored only indirectly, and it is equally clear that any result should be expressed in terms of rather broad distribution functions over distances, bond angles, and degrees of excitation about some average values. The magnitudes of the latter surely depend on the types of probes used. In contrast, highly sophisticated techniques are being developed for gas-phase reactions which permit the exploration of the states and structures of the *nascent products* as they emerge from the reaction complex, prior to their deactivation and relaxation to thermal equilibrium. The proposal presented here is that mechanistic questions should be formulated in terms of the geometric and energetic structures of these fragments. There is a correspondence, but not an equivalence, between this point of view and one in current use.

In the elimination of N_2 from **1**, of CO_2 from **2**, and of CO from **3**, one of the bonds in the ejected molecular fragment changes drastically during the transition from the parent to the product. When the process is a concerted one, prior to their deexcitation by collision, the distinctly separated species are comparable in energy to the transition state but they differ in their geometries (again keeping in mind that the transition state has a lifetime of the order of one molecular vibration). The excess energy is stored as geometric distortion in the products N_2, CO_2, and CO, which emerge vibrationally excited. Significantly, the vibrational coordinate for bond adjustment is essentially normal to the reaction coordinate along which bond breaking occurs, such that there is little coupling between them. Techniques are now available for detecting vibrationally excited species. In particular, $N_2^{(v)}$ and $CO^{(v)}$ readily transfer their vibrational energy to CO_2. Hence if CO_2 were added to the reaction mixture, under properly selected experimental conditions, and placed in a laser cavity, power gain should be observed as a consequence of the concerted elimination reaction. The ejection of vibrationally excited CO_2 from the bicyclic compound indicated above should be detectable directly as gain in a CO_2 laser cavity. On the other hand, if the elimination is a stepwise process (and this must be defined as a reaction in which the rate-controlling step involves the fission of one bond so that the intermediate specie has a lifetime of several molecular vibrations prior to the breaking of the second bond), the high efficiency for intramolecular energy transfer will permit the geometric relaxation of the fragment which is eventually ejected. Again, the argument hinges on the proposition that in a transition state which is chain-like, rather than ring-like, vibrations involving the bonds which require adjustment are appreciably coupled to those of the bond being broken. Since statistical energy redistribution occurs readily within highly excited molecules, when the final break occurs one may anticipate nearly equilibrated products and relatively little laser gain would be observed. Consideration of these and other examples suggests that attempts to establish for all cases sharp demarcations between concerted and stepwise processes may prove frustrating. Operationally, the anticipated difference between them for the fission say of cyclobutane into



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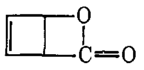

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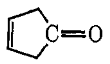

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