

The model proposed here differs from that of Huisgen¹ only trivially. Although dipole bending has not been explicitly considered here, bending may be of importance when the dipole LU-dipolarophile HO interaction is controlling, since the large central dipole coefficient will cause repulsion by the central atom for the terminal dipolarophile atoms. Steric complications have also not been considered here, although it is well known that steric repulsions can overwhelm electronic preference for one regioisomer.¹

Extensions of these qualitative arguments to the rationalization of relative reactivity, regioselectivity, and periselectivity in all 1,3-dipolar cycloadditions will appear shortly.¹⁶

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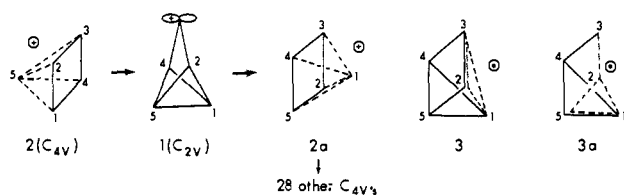
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Nature of the $(\text{CH})_5^+$ Species. I. Solvolysis of 1,5-Dimethyltricyclo[2.1.0.0^{2,5}]pent-3-yl Benzoate

Sir:

Renewed interest in the chemistry of the positively charged homotetrahedrane system (**1**)¹ is evident from the recent article by Stohrer and Hoffmann² concerning theoretical treatment of possible $(\text{CH})_5^+$ isomers. The remarkable feature of their analysis is that the ionic species of C_{4v} symmetry [square pyramid (**2**, **2a**, etc.)] represent the true energy minima on the multidimensional energy surface calculated for the $(\text{CH})_5^+$ arrangement and that other isomers such as **1** and **3**,^{3,4} are likely to be local energy minima. The transformation of one square pyramid (**2**) into another (**2a**) is suggested to proceed through **1** with low energy barriers and further, species **3**, if formed, will collapse into **2a** (Scheme I

Scheme I



(1) (a) S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *Tetrahedron Lett.*, 193 (1966); (b) S. Masamune, *J. Amer. Chem. Soc.*, **86**, 735 (1964); (c) W. von E. Doering and M. Pomerantz, *Tetrahedron Lett.*, 961 (1964); (d) G. L. Closs and R. B. Larrabee, *ibid.*, 287 (1965); (e) J. Trotter, C. S. Gibbons, N. Nakatsuka, and S. Masamune, *J. Amer. Chem. Soc.*, **89**, 2792 (1967); C. S. Gibbons and J. Trotter, *J. Chem. Soc. A*, 2027 (1972).

(2) W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972). Also see: R. E. Leone and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970); K. B. Wiberg, *Advan. Alicycl. Chem.*, **2**, 205 (1968). For $C_3\text{BH}_3$, see: R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971); R. E. Williams, *Progr. Boron Chem.*, **2**, 61 (1970).

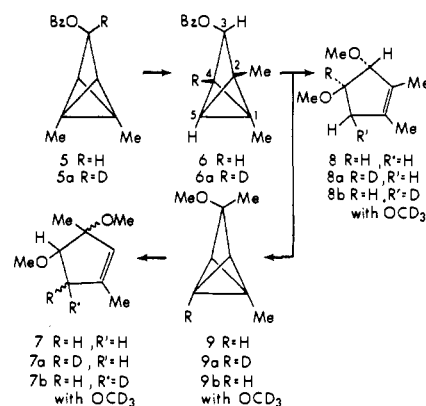
(3) Species **3** simply indicates the presence of a three-center two-electron system (Roberts' bicyclobutonium cation) and bears an obvious geometrical resemblance to **2**. However, a bicyclobutonium cation likely involved in the solvolysis of the cyclopropylcarbinyll and its related systems is now more properly represented by **3a** (see ref 4 and 11).

(4) See, for instance, J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303 (1968); V. Buss, R. Gleiter, and P. von R. Schleyer, *ibid.*, **93**, 3927 (1971), and references quoted therein.

I). Directly related to the above prediction are the rate and stereospecificity of solvolytic reactions of esters of homotetrahedran-3-ol (see **6** for numbering) and degenerate isomerizations of the tricyclo skeleton. We wish to report herein experimental data pertinent to these problems and to provide information as to the nature of the short-lived ionic species likely involved in the solvolytic reactions.

Reduction of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one^{10,5} with lithium aluminum hydride afforded a hydroxy compound **4**.⁶ The corresponding benzoate (**5**)⁶ underwent a clean first-order skeletal rearrangement in aprotic solvents to afford a new isomer (**6**)⁶ (see Scheme II). The stereochemistry of **6** is assigned on

Scheme II



the basis of the shift of $\text{H}(\text{C}-1)$ but not $\text{CH}_3(\text{C}-5)$ in the presence of $\text{Eu}(\text{fod})_3$ ⁶ and the deshielding effect of the C-O bond on $^{13}\text{C}-5$.⁷ Rates of the above rearrangement in 12 solvents at 33.0° are plotted against a solvent polarity parameter, E_T .⁸ The near perfect linear relationship between the two sets of values shows that the reaction is clearly of ionic nature and represents a typical ion-pair return. There was observed no further skeletal rearrangement and prolonged heating of **6** at elevated temperatures led to gradual destruction of the system.

Nmr spectral studies of a 0.03 *M* solution of **5** in CD_3OD showed that **5** isomerized very rapidly even at -10° ($k = 4.3 \times 10^{-4} \text{ sec}^{-1}$) to give **6** which underwent another first-order transformation at 35.0° ($k = 1.6 \times 10^{-4} \text{ sec}^{-1}$). The methanolysis products representing more than 90% of the total (glpc analysis) were compounds **7**⁶ and **8**⁶ in a ratio of 1.2:1. Compound **7** was found to be a secondary product in this solvolysis, forming as a result of acid-catalyzed ring opening of tricyclo compound **9**. Addition of 1.5 equiv of pyridine or preferably triethylamine slowed down this particular methanol addition reaction without affecting the rate of the solvolysis of **5**. The elusive intermediate **9**, isolated in pure form under proper conditions, was shown to provide mainly **7** under the sol-

(5) H. Ona, H. Yamaguchi, and S. Masamune, *ibid.*, **92**, 7495 (1970).

(6) Detailed spectral data of all new compounds were made available to the referees and can be obtained upon request. We cannot over-emphasize experimental difficulties encountered in this work. The acid sensitivity and thermal instability of virtually all the compounds described herein demanded special handling. A referee suggested acetolysis or formolysis of the present system. Obviously from the text, the tricyclo system underwent first the ring opening of the bicyclobutane moiety, providing no meaningful results.

(7) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *J. Amer. Chem. Soc.*, **94**, 8956 (1972).

(8) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

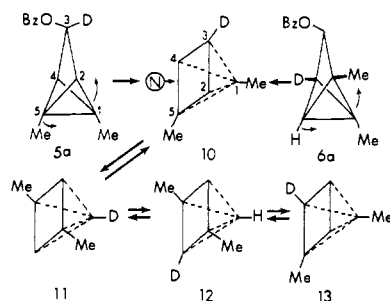
volytic condition employed. The structure of **9** formulated as shown in Scheme II stands on secure spectral evidence similar to that utilized for **6**.⁶

Use of the 3-deuterio compound **5a** in the above experiments clearly demonstrated that the label atom appeared at specific positions of the products (**6a**, **7a**, **8a**, and **9a**) as indicated and that there was no scrambling of the deuterium within the limit of the spectral analysis. Experiments employing methanol-4-*d* and **5** provided **6**, **7b**, **8b**, and **9b** and demonstrated the manner of protonation of the tricyclo system leading to the cyclopentene system, the process being analogous to that observed for protonation of the bicyclobutane system.⁹

We have established first that the solvolysis proceeds enormously fast¹⁰ *not* because of the relief of strain involved in the system, but because of the unique anchimeric assistance brought about by delocalization of the positive charge within the system. Second, we have defined the type of solvolytic rearrangement of the homotetrahedrane system. There are 18 possible isomeric monodeuteriodimethylhydroxyhomotetrahedranes of which 12 are *d,l* pairs and any types of processes leading to all the isomers must be nonstereospecific at least at some stages. In contrast, if the stereospecificity analogous to that observed for the cyclopropylcarbinyl system¹¹ is rigorously held during the formal 1,2 (but not 1,3) carbon sigmatropic rearrangement, then **5a** can lead to only two other isomers (**6a**, **9a**) which was observed.¹² The above findings appear to be explained simply by invoking well-known bicyclobutonium cations of type **3a** or their equivalents^{3,11} (without their interconversion at each step), the formation of the ions and the attack of the nucleophiles (benzoate ion and methanol) being stereospecific as defined above.

Finally, we wish to examine briefly the results in terms of Hoffmann's square pyramid intermediates by imposing some restriction to meet the observed stereochemistry. Suppose that the stereochemistry of the leaving group decides, in the manner shown in Scheme

Scheme III



(9) For instance, K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1971), and ref 1d, pp 200-201.

(10) Using the Foote-Schleyer treatment [C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854 (1964)] and proper correction factors to estimate the rate of the tosylate of **6** in acetic acid at 25° [S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961); H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); and ref 1], one obtains a factor of 21 powers of 10 in rate of acceleration attributable to the neighboring participation. While this number bears little meaning except that it is very large, it is extremely difficult to find a suitable model compound for comparison.

(11) Z. Majerski and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 663 (1971), and references quoted therein.

(12) Note that the bicyclobutonium cations formally derived from **9a** are exactly the same as those from **6a**. Therefore, **5a**, **6a**, and **9a** form a closed circuit.

III, which carbon atom will occupy the C-apical position of **10** and that the nucleophile attacks the cation from the bottom side of the pyramid. Then compounds **5a** and **6a** will lead to exactly the same square pyramid **10** which benzoate ion and methanol must attack at different positions, C-2 and C-4, in order to obtain **6a** and **9a**, respectively. Although **6a** resulted from ion-pair return and **9a** formed through capture by the solvent molecule, methanol and benzoate ion rarely choose different sites of attack, unlike methoxide and hydride. If this is the case, **10** appears unlikely to be the intermediate. On the other hand, it is not impossible that the nucleophiles may attack different sites because of the extremely high reactivity of the system and the benzoate corresponding to **9** would be too reactive to be isolated. Then the above solvolysis results are consistent with the involvement of **10**. In any event, the absence of deuterium scrambling eliminates the possibility of interconversions such as **10** → **11** → **12** → **13** during the solvolytic reaction.

In conclusion, the results obtained by the solvolytic studies tend to indicate that the mechanism similar to that now apparently accepted for the cyclopropylcarbinyl system¹¹ is operating in the present system, and whether or not C_{2v} is energetically favorable, it appears not to have fully developed. At least the experimental results using the dimethyl derivatives and the conditions specified above appear not to demand such a species.¹³

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Nature of the (CH)₅⁺ Species. II. Direct Observation of the Carbonium Ion of 3-Hydroxyhomotetrahedrane Derivatives

Sir:

Olah's remarkable success¹ in the direct observation of ionic species has led us to investigate the behavior of some 3-hydroxyhomotetrahedrane derivatives² in superacid media. We have observed well-defined ¹H and ¹³C nmr spectra of the cationic species derived from the above compounds, and wish to present extraordinary features of the long-lived carbonium ion, in contrast to those involved in the solvolysis.²

Solutions of a set of isomeric dimethylhomotetrahedranes **1**, **2**, and **3**² in a 3:2 mixture of SO₂ClF and FSO₃H at -78° all provided identical pmr and cmr spectra (Figures 1 and 2), which remained unchanged at least for several hours. An off-resonance spectrum allowed assignment of the cmr signals to two CH₃, two equivalent CH, one CH, and two quaternary carbons as indicated. Use of the specifically deuterium labeled

(1) (a) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972); (b) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972), and references quoted therein.

(2) See the preceding communication: S. Masamune, M. Sakai, and H. Ona, *ibid.*, **94**, 8955 (1972).