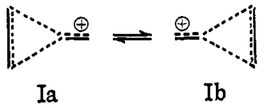
The Cyclopropylcarbinyl–Allyl Rearrangement of a Hexamethylcyclopropylcarbinyl System[1]

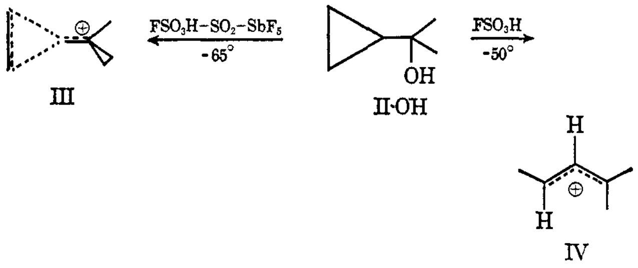
Sir:

The multiplicity and electronic structure of the nonclassical intermediates involved in the carbonium ion chemistry of cyclopropylcarbinyl, allylcarbinyl, and cyclobutyl derivatives have been of interest for some years.[2] At first, the solvolytic behavior of pertinent systems was investigated; more recently, several monocyclopropylcarbinyl cations have been directly observed by nmr in superacid media.[3a,b] The original incentive for the present investigation was the direct observation of the rate and stereochemistry of the degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement,[4] symbolized by Ia $\rightleftharpoons$ Ib, under conditions of long life of the cation in nonnucleophilic media.



Ia Ib

Cation III is representative of cyclopropylcarbinyl cations which have been generated in superacid media. It has been prepared from the corresponding alcohol II-OH in FSO_3H–SO_2–SbF_5 by Olah,[3b] and its nmr spectrum was observed at −65°. This spectrum indicated the "symmetrical homoallyl" ("bisected") structure for the cation. While stable at −65° in FSO_3H–SO_2–SbF_5, ion III was destroyed when the temperature was raised to −25°. In contrast with the observations of Olah in FSO_3H–SO_2–SbF_5 are those of Deno[5] in FSO_3H solvent. On solution of the corresponding alcohol in this solvent at −50°, there was observed only the spectrum of a species tentatively identified as the trimethylallyl cation IV. A possible mechanism[5] visualized for the formation of this allylic ion involved "dehydration of the alcohol, opening of the cyclopropane ring by protonation, and appropriate CH_3 and H shifts."



III II-OH IV

In this and the following communication, we report on the related behavior of a tetramethylcyclopropyldimethylcarbinyl system in superacid media as well as solvolytically. When α,α,2,2,3,3-hexamethylcyclopropylcarbinol (V-OH)[6] is extracted into FSO_3H–SO_2ClF (1:1, v/v)[3c] or SbF_5–SO_2ClF (1:3, v/v) at −125° and the nmr spectrum is recorded at this temperature within 2 min, the spectrum shows no evidence of the cyclopropylcarbinyl cation VI. Instead, the first and only cation observed, even at −125°, is the rearranged 1-*t*-butyl-1,3,3-trimethylallyl ion (VIII). In its nmr spectrum, singlet signals appear at τ 8.54 for the *t*-butyl group, τ 7.02 for the CH_3 group at C_1, τ 6.98 for the two CH_3 groups at C_3, and τ 2.07 for the proton at C_2.[7,8] From the manner of generation and observation of the rearranged allylic ion VIII, a conservative estimate of the rate constant of isomerization of the cyclopropylcarbinyl ion VI to its allylic isomer VIII is 10^{-2} sec^{-1} at −125°, ΔF^* being less than 9.6 kcal/mole. Extraction of V-OH into a 1:1 FSO_3D–SO_2ClF mixture at −125° gave rise to the allylic ion with no detectable deuterium incorporation, thus eliminating mechanisms for its formation which involve protonation of the cyclopropane ring. Quenching of the solution of the allylic ion in a rapidly stirred methanol–potassium bicarbonate suspension at −78° produced a 40:60 mixture of dienes IX and X, respectively.

As the temperature of the solution of allylic ion VIII was raised, the nmr spectrum remained unchanged between −125 and −10°. However, above −10° the signals for the *t*-butyl group at τ 8.54 and the C_1–CH_3 group at τ 7.02 broadened, while the other signals remained sharp. The coalescence temperature for the τ 8.54 and 7.02 signals in FSO_3H was *ca.* 75°, and at higher temperatures, *e.g.*, 90°, a broad average signal at τ 8.16 was observed with a half-width of 10 cps. The solution could be heated to 105° before noticeable decomposition occurred; however, no definite change in the spectrum of VIII could be observed. The temperature dependence of the nmr spectrum of the allylic ion is obviously associated with a four-methyl scrambling of the three methyls of the *t*-butyl group and the methyl at C_1.[9]

The application of the Saunders many-site nmr line-shape program[10] led to the rate constants listed in Table I at temperatures between 5 and 90°. These

Table I. Rates of Four-Methyl Scrambling in Allylic Ion VIII

Temp, °C	Solvent	k, sec^{-1}
5	1:3 SbF_5–SO_2ClF^a	2.5
14	1:1 HSO_3F–SO_2ClF	3.0
16	FSO_3H	4.0
24	FSO_3H	10
35	FSO_3H	27
47	FSO_3H	63
58	FSO_3H	120
90	FSO_3H	900

[a] Solution unstable above 10°.

---

(1) Research was supported in part by the National Science Foundation.

(2) (a) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (c) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); K. B. Wiberg and J. E. Hiatt, *J. Am. Chem. Soc.*, **90**, 6495 (1968); (d) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).

(3) (a) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965); (b) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965); (c) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

(4) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968), and references therein.

(5) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

(6) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **30**, 1681 (1965).

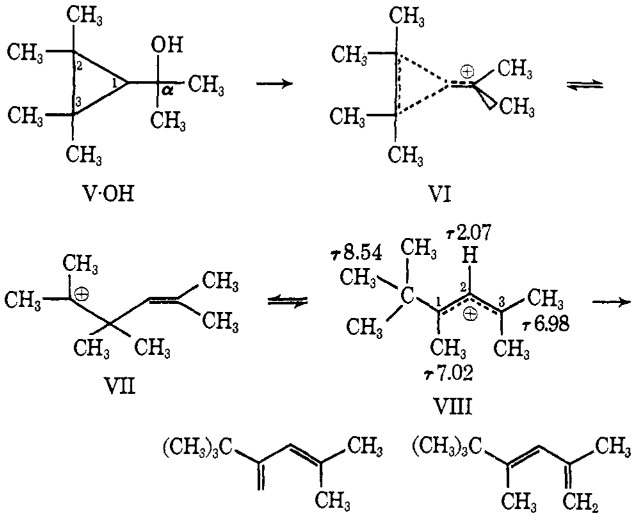
(7) Chemical shifts are reported in τ (ppm) relative to CH_2Cl_2 (4.67, internal standard).

(8) The spectrum of VIII is similar to that reported by Olah and Bollinger after this work had been completed: G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 6082 (1968).

(9) Similar rearrangements have been proposed for other allylic ions: N. C. Deno and R. R. Lastomirsky, *ibid.*, **90**, 4085 (1968); T. S. Sorensen, *ibid.*, **89**, 3794 (1967).

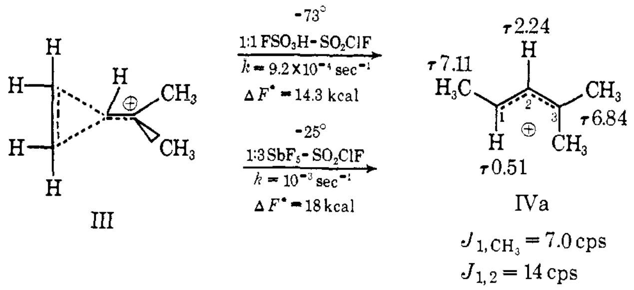
(10) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

rate constants are for exchange of the C$_1$-methyl group with one of the methyls in the *t*-butyl group. From the data in Table I, a plot of log *k* *vs.* $(1/T)$ leads to an Arrhenius activation energy of 14.3 kcal/mole and a preexponential factor of $10^{11.5}$.



For better comparison with the hexamethylcyclopropylcarbinyl case, the simpler cyclopropyldimethylcarbinyl cation III was examined in the same solvents in which carbinol V-OH was dissolved. Extraction of carbinol II-OH into 1:1 FSO_3H-SO_2ClF at $-100°$ led to cation III, with the same nmr spectrum as that reported by Olah.[3b] At $-73°$, this cation rearranged smoothly with a rate constant of 9.2×10^{-4} sec^{-1} ($\Delta F^* = 14.3$ kcal/mole) to a species whose nmr spectrum was clearly appropriate for the trimethylallyl ion IV (see IVa). When FSO_3D-SO_2ClF was employed as the solvent, the rearranged allylic ion IV contained no deuterium, as judged by the observed 1.0:1.0:6.0:3.0 area ratios for the 1-H, 2-H, 3-CH$_3$, and 1-CH$_3$ proton signals, respectively. In the 1:3 SbF_5-SO_2ClF solvent, cation III is considerably more stable, the rate constant for its disappearance being *ca.* 10^{-3} sec^{-1} at $-25°$ (ΔF^* = *ca.* 18 kcal/mole). At least some allylic ion IV is observed, but the latter is also not stable and is fairly rapidly destroyed.

The four additional methyl substituents in VI compared to the simpler cyclopropylcarbinyl cation III have made the rate of isomerization of VI to the allylic isomer so much larger than that of III that it has been impossible so far to observe VI.[11] The simplest way to represent the rearrangement of VI to VIII is by way of the open classical homoallyl ion VII which isomerizes to VIII by a 1,2-methyl shift. Alternatively, it is just as conceivable that the isomerization of VI to VIII avoids VII as an intermediate and proceeds *via* a nonclassical transition state between a homoallyl ion and VIII. In the case of the simpler cyclopropyldimethylcarbinyl cation III, it is evident that the rate of isomerization to the allylic isomer IV is very solvent sensitive. This suggests a mechanism for the isomerization, at least under some conditions, which involves a covalent homoallylic intermediate, *e.g.*, the fluorosulfonate II-OSO_2F. Ionization of the latter with hydrogen participation could lead to the allylic ion IV.



The rearranged allylic ion VIII is obviously more stable ($K > 100$) than any other ion through which V-OH is converted to VIII. However, equilibrations of VIII with its predecessor species present in low concentrations can be expected to be associated with characteristic rate constants. The four-methyl scrambling of VIII which has been observed is due to one of these equilibrations occurring sufficiently rapidly to be measured on the nmr time scale. If the originally sought cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement were also to occur by way of a small proportion of ion VI in equilibrium with VIII, the net result would be a six-methyl scrambling in VIII. This additional scrambling of two more methyl groups in VIII is obviously too slow to be observed on the nmr time scale.[12] However, as reported in the following communication,[13] it can be studied on the ordinary time scale by deuterium labeling.

---

(11) For contrast with the hexamethylcyclopropylcarbinyl system V-OH, we studied also the behavior of the related tetramethylcyclopropanecarboxylic acid in FSO_3H. In this case, the expected carbonium ion from protonation of the carboxyl group has two powerfully electron-donating hydroxyl groups at the α-cation center. Thus, we could expect the type of rearrangement which VI undergoes to be retarded. In actual fact, we were able to observe the protonated carboxylic acid, as well as the derived acylium ion, and finally the conversion of the latter species to the acylium ion of a rearranged α,β-unsaturated acid. Also, Deno and coworkers[8a] have reported the direct observation of a tetramethyltricyclopropylcarbinyl cation in CF_3CO_2H, where electron-donating groups have again retarded the cyclopropylcarbinyl → allyl rearrangement.

(12) At 90° the nmr spectrum of VIII does show some evidence of six-methyl scrambling in that the singlet at τ 6.98 is broadened slightly with respect to the sharp singlet at τ 2.07.

(13) C. D. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **91**, 3650 (1969).

(14) National Institutes of Health Postdoctoral Fellow, 1967–1969.

C. Dale Poulter,[14] S. Winstein
Contribution No. 2397, Department of Chemistry
University of California, Los Angeles, California 90024
Received March 29, 1969

Solvolysis and Degenerate Cyclopropylcarbinyl–Cyclopropylcarbinyl Rearrangement of a Hexamethylcyclopropylcarbinyl System[1]

Sir:

As reported in the preceding communication,[2] solution of α,α,2,2,3,3-hexamethylcyclopropylcarbinol (V-OH)[3] in FSO_3H-SO_2ClF or SbF_5-SO_2ClF gives rise to the rearranged allylic ion VIII, even at $-125°$. The rate of isomerization of cyclopropylcarbinyl cation VI to the allylic isomer VIII is sufficiently large to prevent direct observation of VI. Also, it has been im-

---

(1) This research was supported in part by the National Science Foundation.

(2) C. D. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **91**, 3649 (1969).

(3) The same numbering system used in the previous communication[2] is employed in this paper.