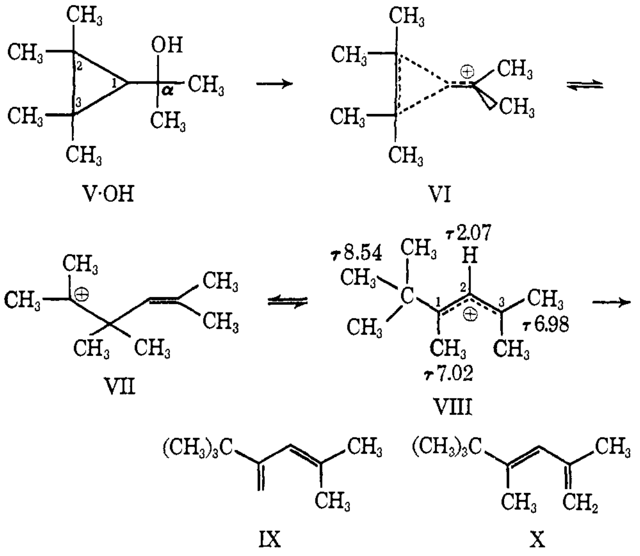
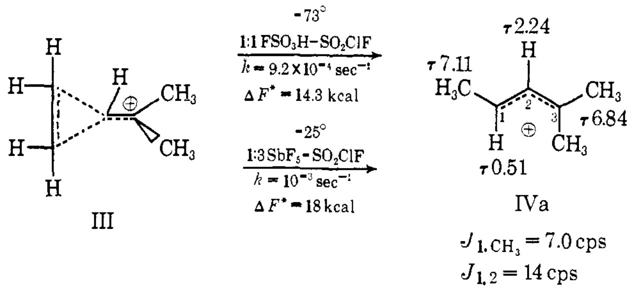
rate constants are for exchange of the C_1-methyl group with one of the methyls in the *t*-butyl group. From the data in Table I, a plot of log *k vs.* $(1/T)$ leads to an Arrhenius activation energy of 14.3 kcal/mole and a preexponential factor of $10^{11.5}$.



V·OH VI VII VIII IX X

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.



III IVa

$J_{1,CH_3} = 7.0$ cps
$J_{1,2} = 14$ cps

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).

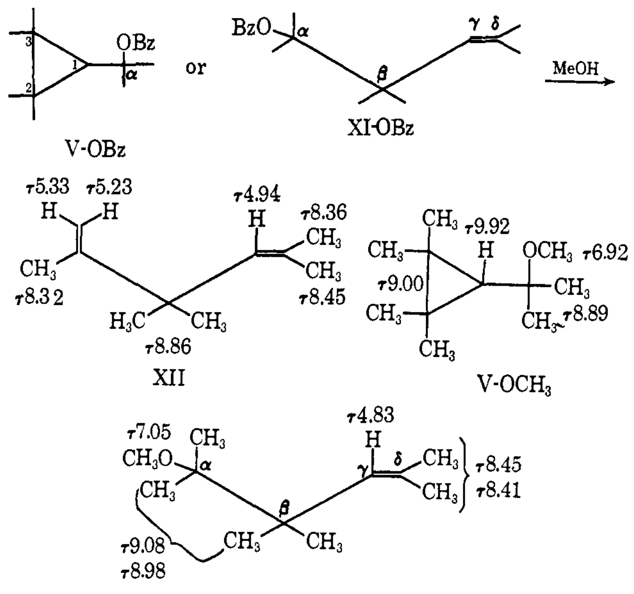
(3) The same numbering system used in the previous communication[2] is employed in this paper.

possible to observe the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement for cation VI on the nmr time scale. In this communication we report additional observations on the hexamethylcyclopropylcarbinyl system under conventional solvolytic conditions as well as in strong acid media, which provide information regarding the degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.[4] Hexamethylcyclopropylcarbinyl benzoate V-OBz, prepared from the alcohol by the method of Hart and Law,[5,6] is quite reactive in solvolysis; the first-order solvolysis rate constant at 25.0° is 4.6×10^{-4} sec^{-1} in 80% aqueous acetone and 8.8×10^{-4} sec^{-1} in methanol. At 25° the products of methanolysis[7] consist of 41% cyclopropylcarbinyl ether[6] V-OCH_3, 55% homoallylic ether[6] XI-OCH_3, and 4% diene[6] XII. No products were detected which might arise from the rearranged allylic ion VIII. For example, no allylic ethers and neither of the two dienes obtained previously[2] from the quench of VIII were observed from solvolysis of V-OBz. Hydrolysis of V-OBz in 80% aqueous acetone gave diene XII and alcohols V-OH[6] and XI-OH.[6]

Homoallylic benzoate[6] XI-OBz has a first-order methanolysis rate constant of 4.0×10^{-6} sec^{-1} at 75° and 5.2×10^{-5} sec^{-1} at 100°. The extrapolated rate constant at 25° is 6.3×10^{-9} sec^{-1}, so that the V/XI rate ratio is 7.3×10^4. At 100° after three reaction half-lives, the products from XI-OBz consist of diene XII (45%), cyclopropylcarbinyl ether V-OCH_3 (3%), and homoallylic ether XI-OCH_3 (52%). Cyclopropylcarbinyl ether V-OCH_3 is not stable under the conditions required for methanolysis of XI-OBz and gives diene XII (13%) and homoallylic XI-OCH_3 (87%) ($k = 1.0 \times 10^{-4}$ sec^{-1} at 100°). Also, methanolysis of V-OBz at 65° gives 21% XII, 32% V-OCH_3, and 47% XI-OCH_3. If one corrects for subsequent reaction of V-OCH_3, a plot of log (% ether/% diene) *vs.* ($1/T$) for V-OBz (25 and 65°) and XI-OBz (100°) gives a fair straight line. This is consistent with both V-OBz and XI-OBz ionizing to common intermediates which then give both diene and ethers.

For comparison purposes, the solvolysis of cyclopropyldimethylcarbinyl *p*-nitrobenzoate[8] (II-OPNB) was also examined in 80% acetone. The solvolysis rate constant in this medium is 3.34×10^{-5} sec^{-1}, and the product is >98% cyclopropylcarbinol II-OH.

In order to check whether the degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement of VI accompanies solvolysis of the V system, V-OH containing α-CD_3 groups was prepared. Hydrolysis and methanolysis of deuterated V-OBz led to corresponding product mixtures which showed no evidence of any deuterium scrambling. For example, after hydrolysis in 80% acetone, the deuterated V-OH product showed less than 1% protium incorporation into the α-methyl groups, judging by the absence of the τ 8.73 signal in its nmr spectrum. Similarly, the XI-OH product also showed less than 1% protium incorporation into the δ-methyl groups, judging by the absence of τ 8.41 and 8.45 signals in its nmr spectrum. Since the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement VIa $\rightleftharpoons$ VIb would scramble the α-methyls with the 2- and 3-methyl groups in the eventual V-OH product, and the δ-methyls with the α- and β-methyl groups in the eventual XI-OH product, it is clear that such rearrangement does not compete with solvent capture in 80% aqueous acetone or methanol.



V-OBz

XI-OBz

XII

V-OCH_3

XI-OCH_3

In order to probe for evidence of the VIa $\rightleftharpoons$ VIb rearrangement in the superacid media which permit long carbonium ion life and direct observation of the rearranged allylic ion VIII from V-OH, the hexadeuterio-V-OH containing two α-CD_3 groups was extracted into FSO_3H-SO_2ClF (1:1, v/v) at −125°. At this temperature, we observed the nmr spectrum of allylic ion VIII, which contained the *t*-butyl (τ 8.54), 1-methyl (τ 7.02), and 2-H (τ 2.07) proton signals, but less than 1% of the 3-methyl signal (τ 6.98). Thus, no detectable cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement occurs prior to rearrangement of VI to allylic ion VIII at −125°.

When the solution of allylic ion VIII with two 3-CD_3 groups was warmed, the previously described[2] four-methyl scrambling of the 1-methyl with the three in the *t*-butyl group was observed on the nmr time scale. Much more slowly, the CD_3 groups at C_3 became equilibrated with the four unlabeled methyl groups, as shown by the development of the 3-methyl signal (τ 6.98). The nmr spectrum of the fully equilibrated allylic ion VIII showed six *t*-butyl protons and six 1-methyl plus 3-methyl protons relative to one 2-proton, all six methyl groups now being statistically scrambled. By following the growth of the 3-methyl signal relative to the 2-H signal from zero to the final equilibrium value, a first-order rate constant of 3.1×10^{-3} sec^{-1} ($\Delta F^* = 20.2$ kcal/mole) was obtained for the approach to equilibrium at 16°; in other words the six-methyl scrambling of the two 3-methyl groups with the four others.

The solvolytic reactivity of V-OBz is very high relative to other tertiary cyclopropylcarbinyl systems which have been studied. For example, in 80% acetone at 25°, V-OPNB is more reactive than II-OPNB by a factor[9]

---

[4] K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, **90**, 4195 (1968).

[5] H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964).

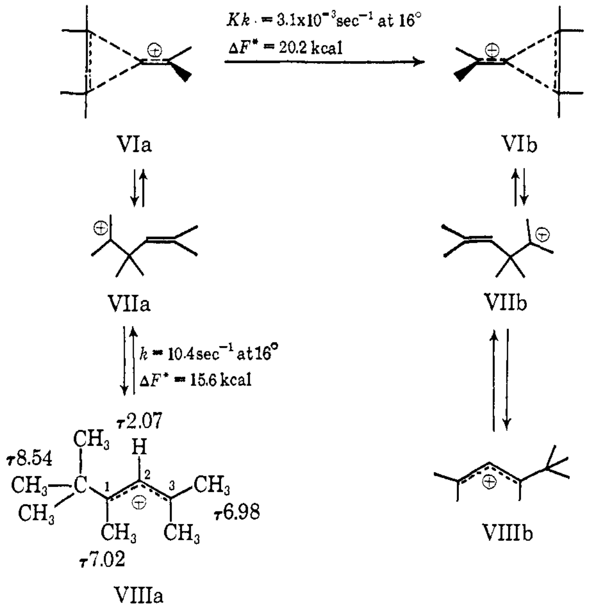
[6] All new compounds gave satisfactory infrared and nmr spectra and C–H analyses, except for V-OBz and XI-OBz. The noncrystalline benzoate esters could not be obtained sufficiently pure for C–H analysis.

[7] 2,6-Lutidine was used to buffer all preparative solvolyses.

[8] M. Hanack and K. Goerler, *Ber.*, **96**, 2121 (1963).

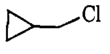
[9] This assumes $(k_{\text{V-OPNB}}/k_{\text{V-OBz}}) = 22.$[5]

of 300. It is obvious that the cyclopropane ring is heavily involved in electron delocalization during the ionization of V-OBz. All the solvolysis products could be formulated as arising from the "symmetrical homoallyl" ("bisected") cation[10] VI. In solvolysis, the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement is not competitive, and neither is the rearrangement to the allylic ion VIII.

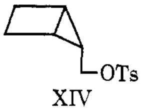


Under conditions of long carbonium ion life in FSO_3H–SO_2ClF or related solvents, the first and only ion visible, even at −125°, is the rearranged allylic ion VIII. For simplicity, this rearrangement may be formulated *via* the classical open ion VII; however, other alternatives are conceivable, for example, *via* a nonclassical transition state between a nonclassical homoallyl ion and VIII. The allylic ion VIII is obviously more stable than VI or any other ion through which the rearrangement from VI to VIII occurs. At higher temperatures, *e.g.*, 16°, the four-methyl scrambling of the *t*-butyl and C_1-methyl groups occurs with a rate constant of *ca.* 5 sec^{-1}. Since four-methyl scrambling represents the exchange of the methyl group at C_1 with a methyl in the *t*-butyl group, the rate of VIII → VII is $2k_{4\text{-CH}_3}$. For example, at 16° $k = 10.4\ \text{sec}^{-1}$, ΔF^* being 15.6 kcal/mole. This process is obviously related to the cyclopropylcarbinyl → allyl rearrangement and it may proceed through the same rate-determining transition state, but not necessarily.[11] If classical homoallylic ion VII is an intermediate in the cyclopropylcarbinyl → allyl rearrangement, we cannot determine from the available data whether VII → VIII or VII → VI has a higher transition state. We do know,[2] however, that the rate-determining transition state from VI → VIII is less than 9.6 kcal/mole above VI and the rate-determining transition state for VIII → VI must be at least 15.6 kcal/mole above VIII. Thus, VI must be at least 6.0 kcal/mole less stable than VIII and would obviously not be observed by nmr. Considerably slower than four-methyl scrambling is the observed six-methyl scrambling process. This is best accounted for by way of the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement (VIa $\rightleftarrows$ VIb; rate constant k_r) superimposed on the four-methyl scrambling. The apparent rate constant for six-methyl scrambling ($k = 3.1 \times 10^{-3}\ \text{sec}^{-1}$ at 16°; $\Delta F^* = 20.2$ kcal/mole) is k_rK, where K, the equilibrium constant for VIII $\rightleftarrows$ VI, corresponds to a free-energy difference equal to or greater than 6.0 kcal/mole. Thus, the actual value of k_r is still not available.

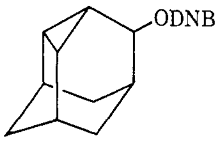
It is quite clear that with the hexamethylcyclopropylcarbinyl ion VI, the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement is much slower than with previously studied symmetrically substituted primary and secondary cyclopropylcarbinyl systems[4,12] such as XIII, XIV, and XV, which rearrange during solvolysis. With ion VI, the present work shows that in the solvolyzing solvents solvent capture is faster than rearrangement to the allylic ion by at least a factor of 50. Similarly, in the FSO_3H–SO_2ClF type of solvent, rearrangement to allylic ion is at least 50 times as rapid as the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement. With ions from XIII, XIV, and XV, the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement and solvent collapse occur at comparable rates.[13] Since we would judge solvent capture of the ions from XIII, XIV, and XV to be at least as rapid as that of VI, we arrive at the conclusion that the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangements of the ions from XIII, XIV, and XV are faster than that of VI by at least a factor of 10^3. Additional work is needed to reconcile the remarkable retardation of the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement for VI with current mechanistic proposals.[4]



XIII



XIV



XV

---

[10] Actually, no evidence is available that the products do not arise at least partially from another species, such as an unsymmetrical homoallylic ion.

[11] Alternatively, if VII → VI is faster than VII → VIII or if four-methyl scrambling proceeds directly between VI and VIII, k could be as low as $^4/_3k_{4\text{-CH}_3}$ ($k = 6.9\ \text{sec}^{-1}$) and ΔF^* could be as high as 15.8 kcal/mole. The variation in k results from statistical factors for each mechanism.

[12] (a) R. H. Mazur, W. H. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959); (b) K. B. Wiberg and A. J. Ashe, III, *ibid.*, **90**, 63 (1968); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968).

[13] In some solvents, the rate of reaction with solvent may be two to three times as fast as that of the cyclopropylcarbinyl rearrangement for the ion in the simple XIII system.[4,12a]

[14] National Institutes of Health Postdoctoral Fellow, 1967–1969.

C. Dale Poulter,[14] S. Winstein
Contribution No. 2398, Department of Chemistry
University of California, Los Angeles, California 90024
Received March 29, 1969

The Stereochemistry of the Reactions of Secondary Cyclopropyl Bromides with Lithium[1]

Sir:

The mechanism of the reactions of alkyl halides with metals to form metal alkyls, and the geometry of the cyclopropyl radical, are problems of current in-

---

[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.