The α,α,2,2,3,3-Hexamethylcyclopropylcarbinyl System. A Study of Carbonium Ion Behavior in Nucleophilic and Superacid Solvents[1,2]

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Abstract: The behavior of α,α,2,2,3,3-hexamethylcyclopropylcarbinyl derivatives was investigated in both normal, nucleophilic solvolysis solvents and in superacid media. In methanol at 25°, α,α,2,2,3,3-hexamethylcyclopropylcarbinyl benzoate (**1**-OBz) gave 2,3,3,5-tetramethylhexa-1,4-diene (**4**), 4%, cyclopropylcarbinyl methyl ether (**1**-OCH_3), 41%, and 2,3,3,5-tetramethyl-2-methoxyhex-4-ene (**3**-OCH_3), 55%. Methanolysis of homoallylic benzoate **3**-OBz at 100° yielded the above products; however, **1**-OCH_3 was shown to be unstable to the reaction conditions, producing **3**-OCH_3 and **4**. The solvolytic results are explained in terms of a single cyclopropylcarbinyl intermediate **6**. In superacid solvents, **1**-OH cleanly gave 1-*tert*-butyl-1,3,3-trimethylallylic cation (**7**). At elevated temperatures, the three *tert*-butyl methyl groups and the methyl group at C_1 became equivalent on the nmr time scale. Isotopic labeling revealed an additional isomerization which scrambled all six methyl groups. Four-methyl scrambling is accounted for by a reversible isomerization between allylic and cyclopropylcarbinyl cations. The slower six-methyl scrambling is believed to involve a degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement. The results in nucleophilic and superacid solvents are compared.

Experimental[4-6] and theoretical[7] studies have shown cyclopropylcarbinyl cations to be unusually stable. In nucleophilic solvents skeletal isomerizations to give cyclobutyl and homoallylic products are commonly observed.[4,5] An additional rearrangement of one cyclopropylcarbinyl cation to another has also been reported in nucleophilic solvents for several different systems.[5h,i,k,l,v,y] Olah and coworkers[6e] observed the degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement in SbF_5–SO_2ClF at −80° by nmr. At that temperature the equilibration was so fast that only a time-averaged spectrum consisting of the endo methylene protons, the exo methylene protons, and the methine proton was recorded.

The long lifetime of a cation in superacid media also allows one to uncover rearrangements with relatively high activation energies that cannot compete with solvent collapse in more nucleophilic solvent systems. For example, hydrogen migrations are not normally observed during cyclopropylcarbinyl, cyclobutyl, or homoallylic solvolysis reactions, but recently Saunders and Rosenfeld[6f] reported that the 1-methylcyclobutyl and the α-methylcyclopropylcarbinyl cations are in dynamic equilibrium at −25° in SbF_5–SO_2ClF, presumably through an intramolecular 1,2-hydride shift. There are several nmr reports[8] of hydride or alkyl shifts in allylic cations which can be most easily described as proceeding through less stable homoallylic or cyclopropylcarbinyl intermediates. In 1965, Deno and coworkers[6c] attempted to generate dimethylcyclopropylcarbonium ion from α,α-dimethyl-

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(2) A preliminary account of this work has been reported: (a) C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 3649; (b) C. D. Poulter and S. Winstein, *ibid.*, **91**, 3650 (1969).

(3) (a) This investigation was supported in part by National Institutes of Health Postdoctoral Fellowships 1-F2-GM-29,317-01, and 1-F2-GM-29,317-02, from the Institute of General Medical Sciences; (b) address correspondence to this author at the University of Utah; (c) deceased, Nov 23, 1969.

(4) Recent reviews include: (a) H. J. Richey, Jr., in "Carbonium Ions," Vol. 3, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1972; (b) K. B. Wiberg and A. J. Ashe in "Carbonium Ions," Vol. 3, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1972; (c) M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967).

(5) (a) S. Winstein and R. Adams, *J. Amer. Chem. Soc.*, **70**, 838 (1948); (b) C. W. Shoppe, *J. Chem. Soc.*, 1147 (1946); (c) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4275 (1970); (d) C. D. Poulter and S. Winstein, *ibid.*, **92**, 4282 (1970); (e) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, **89**, 6382 (1967); (f) D. Whalen, M. Gasic, B. Johnson, H. Jones, and S. Winstein, *ibid.*, **89**, 6384 (1967); (g) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959); (h) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (i) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961); (j) P. von R. Schleyer and G. W. van Dine, *ibid.*, **88**, 2321 (1966); (k) J. E. Baldwin and W. D. Foglesong, *ibid.*, **89**, 6372 (1967); (l) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **90**, 5324 (1968); (m) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (n) J. C. Martin and B. R. Ree, *ibid.*, **92**, 1660 (1970); (o) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2317 (1966); (p) W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969); (q) K. B. Wiberg and J. E. Hiatt, *ibid.*, **90**, 6495 (1968); (r) K. B. Wiberg, J. E. Hiatt, and K. Hseih, *ibid.*, **92**, 544 (1970); (s) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **92**, 553 (1970); (t) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *ibid.*, **92**, 564 (1970); (u) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *ibid.*, **92**, 568 (1970); (v) K. B. Wiberg and G. Szeimies, *ibid.*, **92**, 571 (1970); (w) K. B. Wiberg and T. Nakahira, *ibid.*, **93**, 5193 (1971); (x) P. G. Gassman, E. A. Williams, and F. J. Williams, *ibid.*, **93**, 5199 (1971); (y) Z. Majerski and P. von R. Schleyer, *ibid.*, **93**, 665 (1971).

(6) (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) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965); (d) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967); (e) G. A. Olah, D. P. Kelley, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970); (f) M. Saunders and J. Rosenfeld, *ibid.*, **92**, 2548 (1970); (g) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970).

(7) (a) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (b) R. Hoffman, *J. Chem. Phys.*, **49**, 2480 (1964); (c) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); (d) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 2788 (1966); (e) K. B. Wiberg, *Tetrahedron*, **23**, 1083 (1968); (f) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968); (g) C. Trindle and O. Sinanoglu, *ibid.*, **91**, 4054 (1969).

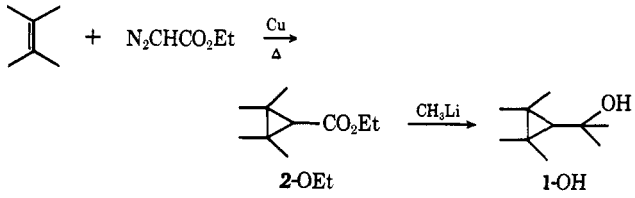
(8) (a) N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1970; (b) T. S. Sorensen in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Wiley, New York, N. Y., 1970.

cyclopropylcarbinol in neat HSO_3F at $-50°$ and only observed a species tentatively identified as 1,1,3-trimethylallylic cation. A possible mechanism 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." We[2] were subsequently able to demonstrate that intramolecular H shifts were responsible for the cyclopropylcarbinyl–allyl rearrangement. In this paper we compare the behavior of a cyclopropylcarbinyl cation in nucleophilic solvolysis and nonnucleophilic superacid solvents.

Results and Discussion

Solvolysis in Nucleophilic Solvents. α,α,2,2,3,3-Hexamethylcyclopropylcarbinol (**1-OH**) was prepared by the procedure of Wharton and Bair (Scheme I).[9]

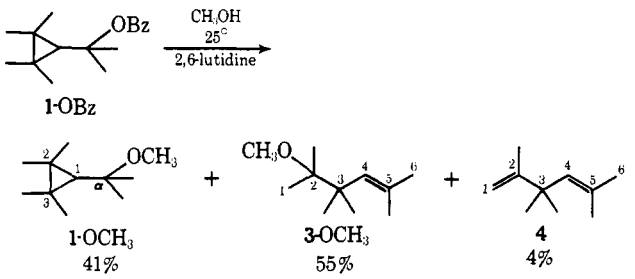
Scheme I. Preparation of α,α,2,2,3,3-Hexamethyl-1-hydroxymethylcyclopropane



Several attempts to prepare a *p*-nitrobenzoate ester from **1-OH** for solvolysis studies were unsuccessful, presumably because of the highly hindered hydroxyl group and the reactivity of the cyclopropylcarbinyl system. The benzoate derivative (**1-OBz**), prepared by the method of Hart and Law,[10] was found to be quite satisfactory for solvolysis studies. The reactive noncrystalline benzoate could not be obtained sufficiently pure for combustion analysis, and nmr was used to provide a check on sample purity prior to all product and kinetic studies.

Methanolysis of **1-OBz** in the presence of 2,6-lutidine (Scheme II) was rapid at 25° (Table I), giving 41% cyclopropylcarbinyl methyl ether (**1-OCH$_3$**), 55% homoallylic methyl ether (**3-OCH$_3$**), and 4% 2,3,3,5-tetramethylhexa-1,4-diene (**4**). The structures of **1-OCH$_3$**, **3-OCH$_3$**, and **4** were easily established from their ir and nmr spectra (see Experimental Section).

Scheme II. Methanolysis of **1-OBz**



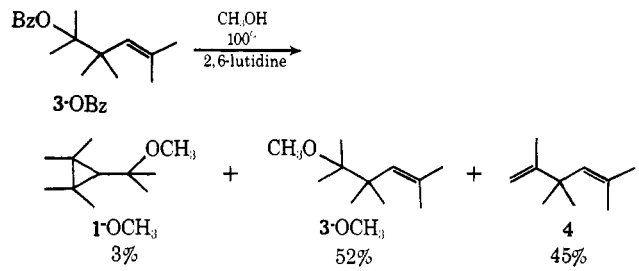
The same products were also obtained from methanolysis of homoallylic benzoate **3-OBz**. 2,3,3,5-Tetramethylhex-4-en-2-ol (**3-OH**) was obtained in 95% yield by treating cyclopropylcarbinol **1-OH** with dilute perchloric acid in dioxane, and the benzoate derivative (**3-OBz**) was prepared as previously described. Methanolysis of **3-OBz** was slower than its cyclopropylcarbinyl isomer by a factor of 1.5×10^5 (Table I). At 100° after 3 reaction half-lives, the products from **3-OBz** consisted of diene **4** (45%), cyclopropylcarbinyl ether **1-OCH$_3$** (3%), and homoallylic ether **3-OCH$_3$** (52%). Ether **1-OCH$_3$** was not stable to the reaction conditions required for methanolysis of **3-OBz** and gave diene **4** (13%) and homoallylic ether **3-OCH$_3$** (87%) ($k \cong 1.0 \times 10^{-4}$ sec^{-1} at 100°). We found that methanolysis of **1-OBz** at 65° produced 21% **4**, 31% **1-OCH$_3$**, and 47% **3-OCH$_3$**. If one corrects for further reaction of **1-OCH$_3$** at 100°, a plot of log (per cent ether/per cent diene) *vs.* $1/T$ is linear for the product distributions obtained at 25, 65, and 100°. This is consistent with both **1-OBz** and **3-OBz** ionizing to a common intermediate (or intermediates) that gives both diene and ethers.

Table I. Solvolysis Rate Constants

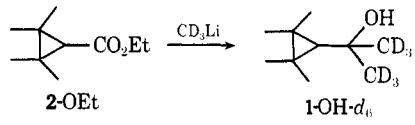
Compd	Solvent	Temp, °C	10^5k, sec^{-1}
1-OBz	Methanol	25	87.9
	80% aqueous acetone	25	46.2
3-OBz	Methanol	100	5.23
	Methanol	75	0.395
	Methanol	25	6×10^{-4} [a]
5-OPNB	80% aqueous acetone	25	3.34

[a] Extrapolated from rate at 75 and 100°; $\Delta H^{\ddagger} = 25.9$ kcal/mol, $\Delta S^{\ddagger} = -9.0$ eu.

Scheme III. Methanolysis of **3-OBz**



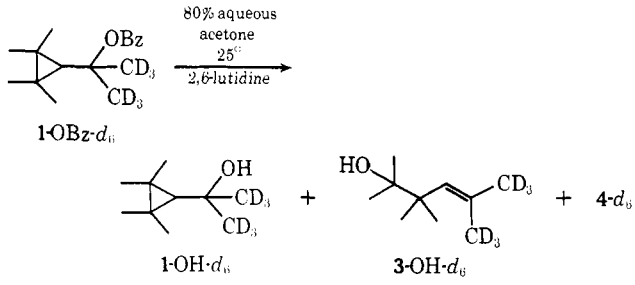
The symmetric substitution pattern of **1-OBz** would obscure carbon scrambling during solvolysis by a cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement similar to that observed for the parent cation. In order to remove the degeneracy of the disubstituted cyclopropylcarbinyl carbons, we prepared **1-OH-d_6**



with deuterium-labeled α-methyls by allowing ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate to react with methyllithium-d_3 (<1% H).[11] Solvolysis of **1-OBz-d_6** in methanol or aqueous acetone gave cyclopropylcarbinyl and homoallylic substitution products which showed no evidence of deuterium scrambling (Scheme IV). After hydrolysis in 80% aqueous acetone, deuterated cyclopropylcarbinol showed less than 1% protium incorporation into the α-methyl groups, judging by the absence of a signal at 1.27 ppm in its nmr spectrum. Similarly, the **3-OH-d_6** product also had less than 1% protium incorporation into the olefinic methyl groups, as evidenced by the absence of

(9) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **30**, 1681 (1965).
(10) H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, **86**, 1957 (1964).
(11) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

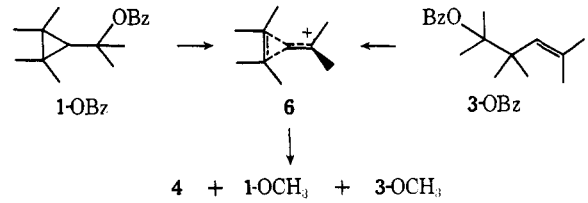
Scheme IV. Solvolysis of 1-OBz-d_6



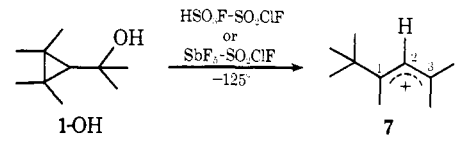
1.59- and 1.55-ppm signals in its nmr spectrum. Parallel results were found for methanolysis of 1-OBz-d_6. The α-methyl groups and either the cis or trans C_2 and C_3 methyl groups of 1-OCH_3 appear as a 12-proton singlet at 1.11 ppm. Therefore, the estimated minimum value for deuterium scrambling is high (<10%). However, we are confident that this value should be less than 1% since homoallylic ether 3-OCH_3-d_6 has no nmr detectable signals for its olefinic methyl groups. From these experiments it is clear that deuterium scrambling, presumably by a degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement, cannot compete with solvent capture in 80% aqueous acetone or methanol.

Kinetic and product studies of 1-OBz and 3-OBz in "normal" solvolysis solvents provide a considerable amount of information about the cationic intermediate generated upon ionization. The solvolytic reactivities of 1-OBz and 3-OBz are high when compared to other tertiary cyclopropylcarbinyl and tertiary alkyl systems, respectively. For example, in 80% aqueous acetone at 25°, 1-OBz is more reactive than α,α-dimethylcyclopropylcarbinyl benzoate (5-OBz)[12] by a factor of 300. Steric acceleration cannot adequately account for the kinetic results since the highly hindered *p*-nitrobenzoate ester of 2,2,3,4,4-pentamethylpentan-3-ol is only 18.4 times more reactive than *tert*-butyl *p*-nitrobenzoate,[13] and by comparison 1-OBz is considerably less hindered. Schleyer and van Dine[5j] have demonstrated that alkyl groups at C_2 and C_3 of a cyclopropane ring accelerate ionization at the carbinyl position, and reported the primary 2,2,3,3-tetramethylcyclopropylcarbinyl system to be 1570 times more reactive than cyclopropylcarbinyl *p*-nitrobenzoate. The rate difference of 300 between 1-OBz and 5-OBz when compared with the above difference of 1570 can best be accounted for by a diminished, but still considerable, demand by the developing tertiary positive center for cyclopropane participation. On the basis of ^1H and ^{13}C chemical shifts obtained by direct observation, Olah and coworkers[6e] also concluded that charge delocalization into the cyclopropane ring decreases significantly when methyl substituents are added to the carbinyl position. Homoallylic benzoate 3-OBz also showed a significant enhancement relative to the expected solvolysis rate of 2,3,3-trimethylbutan-2-yl benzoate,[13] indicative of double bond participation.

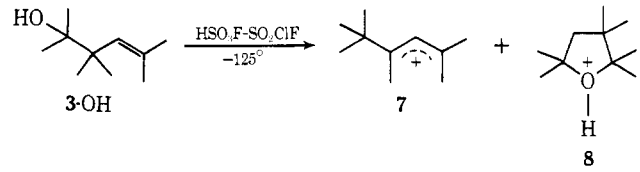
All of the solvolysis products from 1-OBz and 3-OBz could most economically be formulated as arising from a common symmetric homoallylic (or bisected cyclopropylcarbinyl) cation (6). Deuterium labeling using 1-OBz-d_6 clearly demonstrates that 6 does not rearrange to cyclobutyl, "bisected" bicyclobutonium,[6f] or degenerate cyclopropylcarbinyl cations prior to reaction with methanol or water. In fact, the stability of 6, with regard to rearrangement when compared to other cyclopropylcarbinyl species, is striking and will be discussed shortly in connection with data obtained in superacid solvents by nmr.



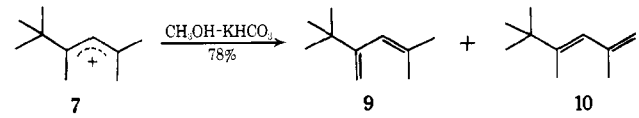
Direct Observation in Superacid Solvents. When 1-OH was extracted into HSO_3F–SO_2ClF (1:1, v/v) or SbF_5–SO_2ClF (1:3, v/v) at −125° and the spectrum recorded within 2 min, the only major signals observed were those characteristic of 1-*tert*-butyl-1,3,3-trimethylallyl cation (7) (see Figure 1). At −50°,



the nmr spectrum of 7 was similar to that recorded by Olah and Bollinger,[14] who also reported that 7 was generated from 1-OH in superacid solvents. Allylic cation 7 was produced in minor amount when 3-OH was extracted into HSO_3F–SO_2ClF at −125°, along with a protonated tetrahydrofuran (8). Our nmr



spectrum for 8 was similar to that described by Sorensen and Ranganayakulu,[15] who reported that 8 was the exclusive product of addition of allylic alcohol 3-OH to fluorosulfuric acid at −80°.[16] The structure of 7 is further substantiated by dienes 9 and 10, prod-



ucts from quenching cation 7 in a rapidly stirred methanol–potassium bicarbonate suspension at −78°.

As the temperature of a solution of allylic ion 7 was raised, the nmr spectrum remained unchanged between −125 and −10°. Above −10° the signals for the tertiary butyl group at 1.46 ppm and the C_1 methyl group at 2.98 ppm broadened, while other signals

(12) This assumes ($k_{5\text{-OBz}}/k_{5\text{-OPNB}}$) = 0.045.[10]

(13) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968).

(14) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 6082 (1968).

(15) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 659 (1970).

(16) Small amounts of protonated tetrahydrofuran 8 were also formed from 1-OH if care was not taken to keep the solution cold during mixing. Cation 8 could be generated by protonation at the hindered C_1 position and subsequent ring closure, or more likely 3-OH is produced from 1-OH by internal return, followed by protonation at C_4 and cyclization to give 8.

Table II. Rate Constants Associated with Four-Methyl Scrambling

Temp, °C	Solvent	$k_{4\text{-}CH_3}$, sec^{-1}	$k_{7\rightarrow 6}$, sec^{-1}
−70	HSO_3F	5×10^{-5} [a]	6.7×10^{-5}
−66	HSO_3F	9.5×10^{-5} [a]	1.3×10^{-4}
−62	HSO_3F	2.1×10^{-4} [a]	2.8×10^{-4}
−58	HSO_3F	5.1×10^{-4} [a]	6.8×10^{-4}
−55	HSO_3F	6.4×10^{-4} [a]	8.5×10^{-4}
−51	HSO_3F	1.5×10^{-3} [a]	2.0×10^{-3}
−46.5	HSO_3F	2.1×10^{-3} [a]	2.8×10^{-3}
−44.5	HSO_3F	3.35×10^{-3} [a]	4.5×10^{-3}
−41.5	HSO_3F	5.5×10^{-3} [a]	7.3×10^{-3}
5	1:3 SbF_5–SO_2ClF	2.5	3.3
14	1:1 HSO_3F–SO_2ClF	3.0	4.0
16	HSO_3F	4.0	5.3
24	HSO_3F	10.0	13.3
35	HSO_3F	27.0	36.0
47	HSO_3F	63.0	84.0
58	HSO_3F	120.0	160.0
90	HSO_3F	900.0	1200.0

[a] Reference 13.

remained sharp (Figure 1). The coalescence temperature for the 1.46- and 2.98-ppm signals was *ca.* 75°, and at higher temperatures, *e.g.*, 90°, a broad average signal at 1.84 ppm with a half-width of 10 Hz was observed. The original spectrum was regenerated when the sample was cooled to −10°. The solution could

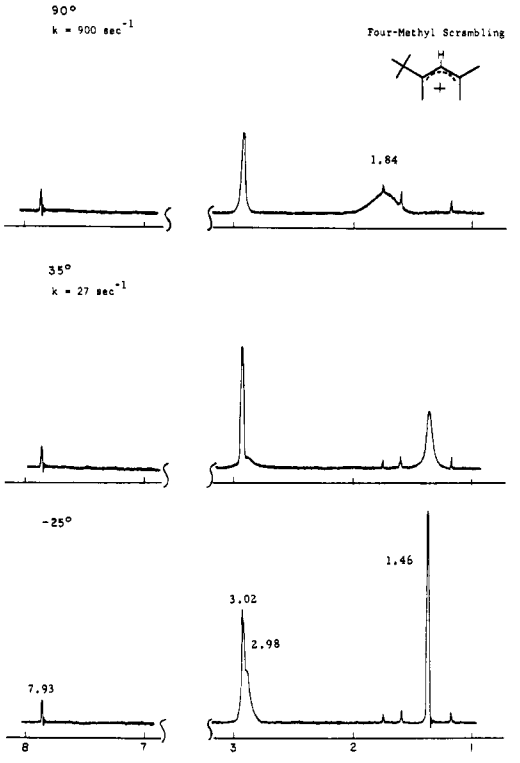


Figure 1. Temperature dependence of the nmr spectrum of 1-*tert*-butyl-1,3,3-trimethylallyl cation (**7**).

be heated to 105° before decomposition occurred. The temperature-dependent nmr spectrum is obviously associated with a four-methyl scrambling of the three methyls of the tertiary butyl group and the methyl group at C_1. Application of Saunders' many-site nmr line-shape program[17] gave the rate constants listed in Table II. These constants represent the exchange of the C_1 methyl group with one of the methyls in the tertiary butyl group. Rate constants for four-methyl scrambling have been obtained over a range of 160° by using line-broadening techniques in the high-temperature range and isotopic scrambling data for the low-temperature range.[13] A plot of ln $k_{4\text{-}CH_3}$ *vs.* $1/T$ is linear with E_a = 15.4 kcal/mol, which can be compared with E_a^{low} = 14.5 kcal/mol and E_a^{hi} = kcal/mol for low- and high-temperature data, respectively. Considering the problems normally associated with temperature regulation, the values for E_a, E_a^{low}, and E_a^{hi} are within experimental error of one another.

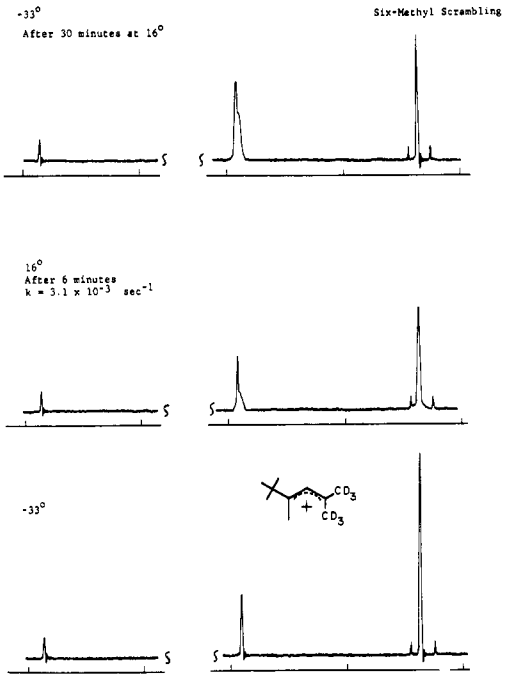
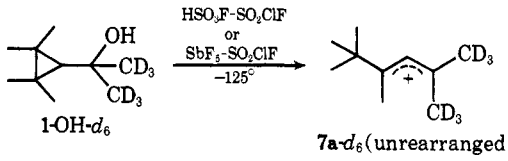


Figure 2. Temperature dependence of the nmr spectrum of 1-*tert*-butyl-1,3,3-trimethylallyl *3,3-dimethyl-d*$_6$ cation (**7**-d_6).

At 90° the six-proton singlet at 3.02 ppm had broadened noticeably with respect to the sharp resonance at 7.93 ppm. This broadening suggests an additional scrambling which involved all six methyls.

(17) M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

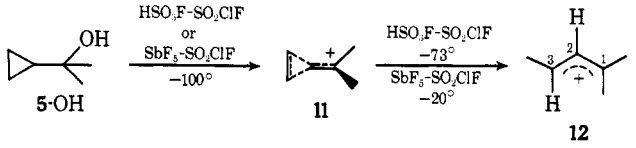
Since cation **7** was destroyed at temperatures above 105°, conclusive evidence for 6-methyl scrambling was obtained by isotopic labeling. When **1-OH-d_6** is extracted into 1:1 HSO_3F–SO_2ClF (v/v) or SbF_5–SO_2ClF (1:3, v/v) at −125° and the spectrum is recorded within 2 min, only unrearranged **7a-d_6** is observed. The spectrum of **7a-d_6** (see Figure 2) is identical with



1-OH-d_6 → 7a-d_6 (unrearranged)

that of undeuterated cation **7**, except for the absence of any detectible absorption (<1% protium) at 3.02 ppm for the methyl groups at C_3. When the solution of unrearranged **7a-d_6** was warmed to 16° (Figure 2), the previously described four-methyl scrambling of the methyl group at C_1 with the three in the tertiary butyl group was observed, as evidenced by line broadening. Much more slowly, the perdeuteriomethyl groups at C_3 were scrambled with the four unlabeled methyl groups, as shown by the development of a signal at 3.02 ppm. The nmr spectrum of fully equilibrated allylic cation **7b-d_6** showed six tertiary butyl protons and six protons for methyls at C_1 and C_3 relative to the one proton at C_2, all six methyl groups now being statistically scrambled. By following the growth of the methyl signal at C_3, relative to the signal for the proton at C_2, from zero to the final equilibrium value, a first-order rate constant of 3.1×10^{-3} sec^{-1} was obtained for the approach to equilibrium at 16°.

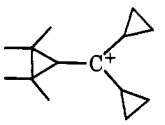
Both **7** and **7a-d_6** were prepared by extracting the corresponding alcohols into DSO_3F–SO_2ClF at −125°. The proton nmr spectra were *identical* with those for the same allylic ions generated in HSO_3F, indicating that a mechanism involving protonation of the cyclopropane ring[7c] is unlikely. We then decided to reinvestigate the cations generated from α,α-dimethylcyclopropylcarbinol (**5-OH**) in superacid media. Extraction of **5-OH** into either 1:1 HSO_3F–SO_2ClF or 1:3 SbF_5–SO_2ClF at −100° gave cyclopropylcarbinyl cation **11**.[2b,7b,e,g] At −73° in HSO_3F–SO_2ClF, **11** cleanly isomerized to 1,1,3,-trimethylallyl cation **12**.



5-OH → 11 → 12

The proton at C_2 gave a doublet ($J_{2,3}$ = 14 Hz) at 7.76 ppm and the proton at C_3 appeared as a sextet (an overlapping doublet of quartets, J = 7 Hz and J = 14 Hz) at 9.49 ppm. The trans stereochemistry between C_2 and C_3 is based on a comparison of $J_{2,3}$ (14 Hz) with similar coupling constants in *cis,cis*-1,3-dimethylallyl cation (J = 9.0 Hz) and *trans,trans*-1,3-dimethylallyl cation (J = 14.0 Hz).[18] A higher temperature (*ca.* −20°) was required for isomerization of **11** to **12** in SbF_5–SO_2ClF. At that temperature only minor amounts of **12** appeared to be formed as **11** was being destroyed. When DSO_3F–SO_2ClF was employed as a solvent, rearranged allylic ion **12** contained no deuterium, as judged by the observed 1.0:1.0:6.0:3.0 area ratios for the protons at C_2 and C_3 and the methyl groups at C_1 and C_3, respectively.

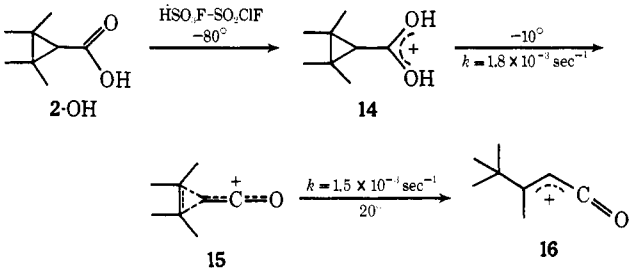
In analogy with the rearrangement of **11** to **12**, one would expect allylic cation **7** to be produced by a cyclopropylcarbinyl–allyl rearrangement. Since Deno and coworkers[6a] have reported the direct observation of cyclopropyl cation **13**, in trifluoroacetic acid, it



13

appeared likely that electron-donating groups (*e.g.*, cyclopropane) can retard the cyclopropylcarbinyl–allyl rearrangement. Verification of this hypothesis was sought by studying 2,2,3,3-tetramethylcyclopropanecarboxylic acid (**2-OH**) in HSO_3F–SbF_5–SO_2. The expected cation from protonation of the carbonyl group has two powerful electron-donating hydroxyl groups at the α carbon atom (see Scheme V). When

Scheme V. Rearrangements of Protonated 2,2,3,3-Tetramethylcyclopropanecarboxylic Acid



2-OH → **14** → **15** → **16**

acid **2-OH** was extracted into HSO_3F–SbF_5–SO_2 at −78°, protonation occurred at carbonyl to give **14**. The nmr spectrum of **14** had a 12-proton singlet ($W_{1/2}$ ~ 3 Hz) at 1.41 ppm and a one-proton singlet at 1.53 ppm. We did not observe distinct peaks which could unambiguously be assigned to the hydroxyl protons; however, a one-proton resonance was observed at 10.99 ppm (in addition to the H_3O^+ peak) next to the intense HSO_3F peak at 11.2 ppm. Between −40 and −50° the 10.99-ppm peak broadened and disappeared, merging with the solvent peak. Presumably the second OH resonance was obscured by the solvent.

Above −40° **14** cleanly eliminated a molecule of water to give acylium ion **15**, as evidenced by an increase in the intensity of the H_3O^+ peak at 10.1 ppm. The methyl groups of **15** appeared as two six-proton singlets at 1.41 and 1.53 ppm, and the proton at C_1 gave a singlet at 2.60 ppm. As the sample of **15** was warmed to 0°, a final isomerization, **15** to **16**, was observed. The structure of allylic acylium ion **16** could be deduced from its nmr spectrum (see Experimental Section). When cation **16** was quenched in methanol–potassium bicarbonate at −78°, a mixture of methyl ethers, *trans*-**17** and *cis*-**17**, was obtained.[19,20]

(18) P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

(19) Since both *cis*- and *trans*-**18** are formed from **16** and since the nmr spectrum of **16** shows only "one" isomer, it is possible that the observed spectrum is the time average of cis and trans isomers. This point is being investigated.

(20) The nmr spectrum of *trans*-**17** is identical with that previously reported: C. Metzger, D. Borrmann, and R. Wegler, *Chem. Ber.*, **100**, 1817 (1967).

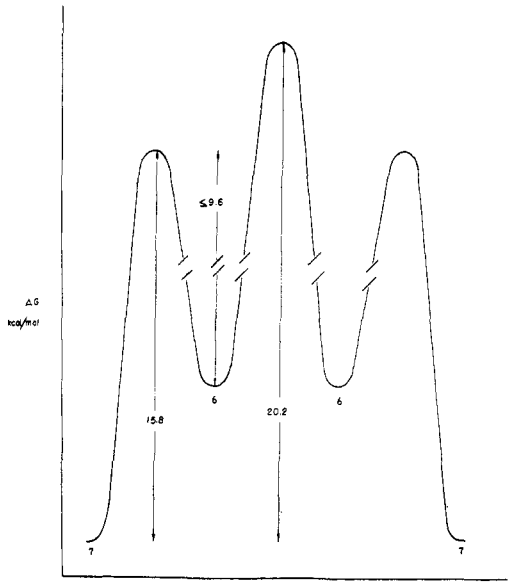
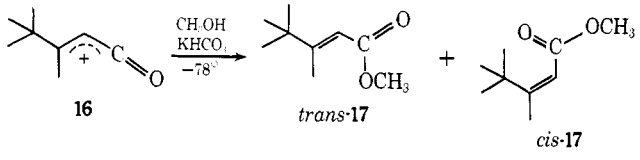


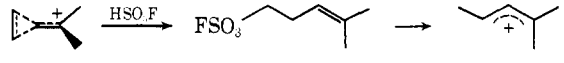
Figure 3. Free-energy diagram for isomerizations of cyclopropylcarbinyl and allyl cations **6** and **7**.

In superacid media new higher energy reaction paths not available in nucleophilic solvents are opened. Our results show that dimethylcyclopropylcarbonium ion



(**11**) undergoes a solvent dependent intramolecular hydrogen shift to give allylic ion **12** (Scheme VI), as evi-

Scheme VI. Cyclopropylcarbinylallyl Rearrangement of **11**

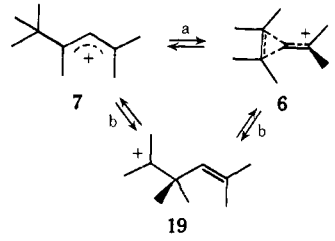


denced by the rate difference between HSO_3F–SO_2ClF and SbF_5–SO_2ClF. This suggests a mechanism for the isomerization, at least under some conditions, which involves a covalent homoallylic intermediate, *e.g.*, fluorosulfonate **18**-SO_3F.[21] Repeated ionization of **18**-SO_3F with some hydrogen participation could lead directly to allylic ion **12**. An analogous intramolecular rearrangement for hexamethylcyclopropylcarbinyl cation **6** is so rapid that only allylic ion **7** can be directly observed in either HSO_3F–SO_2ClF or SbF_5–SO_2ClF. However, the insensitivity of the rate of four-methyl scrambling to solvent (see Table II) suggests that isomerization of **7** to **6**, and therefore by the principle of microscopic reversibility, **6** to **7**, does not proceed through a covalent homoallylic intermediate.

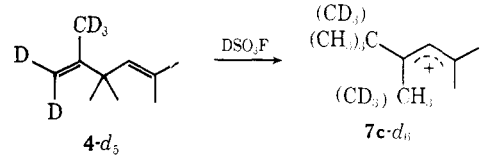
Strong electron-donating substituents at the carbinyl position are sufficient to retard the cyclopropylcarbinyl–allyl rearrangement, as evidenced by the direct observation of **13**,[7a] **14**, and **15**. Observed downfield shifts for the methyl groups and the C_1 proton of protonated acid **14** indicate some charge delocalization into the cyclopropane ring. When **15** is generated (by elimination of water) at higher temperature, the cyclopropane ring becomes more heavily involved in charge delocalization, as evidenced by further downfield shifts.[22] Obviously, migration of a methyl group from C_2 to C_3 (or *vice versa*) requires that C_3 (or C_4) be electron deficient. Acylium ion **15** appears to be intermediate between **14** and **6** as far as charge delocalization into the cyclopropane ring is concerned, on the basis of nmr shifts and the rates of cyclopropylcarbinyl-allyl isomerizations.

Four-methyl scrambling can most easily be accommodated by the reaction sequence outlined in Scheme VII, with direct interconversion of **7** and **6** (path a).

Scheme VII. Possible Mechanisms of Four-Methyl Scrambling



It is attractive to propose a mechanism in which **7** and **6** are separated by a classical homoallylic cation **19** (path b). However, Sorensen and Ranganayakulu[15] attempted to prepare **19**-d_6, by protonation of diene **4**-d_5 in DSO_3F at −80°, and the initially formed allylic ion **7c**-d_6 had deuterium label statistically scrambled be-



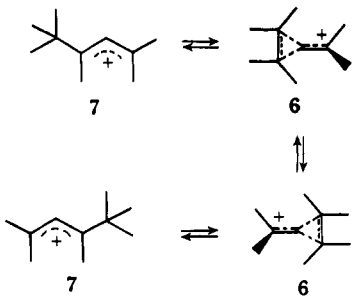
tween the three methyls of the tertiary butyl group and the C_1 methyl group. If **19** is an intermediate, then cyclization to **6** must be much faster than isomerization to **7**, and **19** must be less stable than **6** in order to account for the solvolytic rate enhancement of **3**-OBz. Granting these two restrictions, we cannot distinguish between **7** ⇄ **6** and **7** ⇄ **19** ⇄ **6**. The rate constants for four-methyl scrambling presented in Table II represent the exchange of the methyl group at C_1 with a methyl in the tertiary butyl group. Therefore, $k_{7\rightleftarrows6}$ is $^4/_3k_{4\text{-}CH_3}$ and at −16°, $\Delta F_{7\rightleftarrows6}^{\ddagger}$ is 15.8 kcal/mol. Since allylic cation **7** is the only carbonium ion observed at −120° within 2 min of mixing at −130°, the rate-determining transition state for **7** ⇄ **6** is less than 9.6 kcal/mol. Thus, cyclopropylcarbinyl cation **6** must be at least 6.2 kcal/mol less stable than allylic cation **7** (Figure 3) and would obviously not be observed by nmr.

Considerably slower than four-methyl scrambling is observed six-methyl scrambling process. This is best accounted for by way of a degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement **6** ⇄ **6**, superimposed on four-methyl scrambling (Scheme VIII). The apparent rate constant for six-methyl scrambling, $k_{6\text{-}CH_3} = 3.1 \times 10^{-3}$ sec^{-1} at 16° ($\Delta F_{6\text{-}CH_3}^{\ddagger} = 20.2$ kcal/mol), is $k_{6\rightleftarrows6}K$, where $k_{6\rightleftarrows6}$ is the rate constant for degenerate cyclopropylcarbinyl rearrangement and K is the equilibrium constant for **7** ⇄ **6**. Since the free-

(21) Similar covalent intermediates may explain the rate differences for cis–trans isomerization of allylic cations in HSO_3F–SbF_5–SO_2 and SbF_5–SO_2ClF solvents.[18]

(22) Similar results are found for cyclopropanecarboxylic acid: N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **86**, 2531 (1964).

Scheme VIII. A Mechanism for Six-Methyl Scrambling

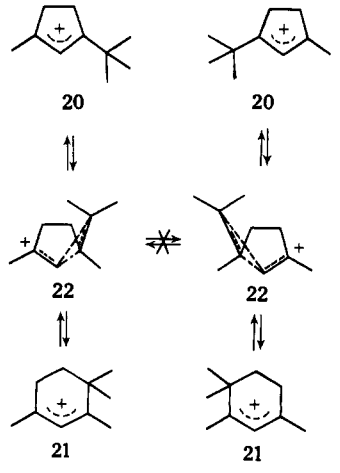


energy difference between **7** and **6** is not known, a value for $k_{6\rightleftarrows 6}$ cannot be accurately determined.

It is quite clear that the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement is much slower for hexamethyl cation **6** than previously studied symmetrically substituted primary and secondary cyclopropylcarbinyl systems, which rearrange extensively during solvolysis. The rate of rearrangement must be significantly higher than that of reaction with solvent in these latter systems.

The present work shows that solvent capture of **6** is at least 50 times faster then rearrangement of **6** to **7**, and in HSO_3F–SO_2ClF rearrangement of **6** to **7** is at least 50 times faster than degenerate rearrangement of **6**.[23] Thus, cyclopropylcarbinyl–cyclopropylcarbinyl rearrangements for **6** are at least 10^8 times slower than symmetrically substituted primary and secondary systems.

Sorensen and Ranganayakulu[24] have reported detailed nmr studies of the equilibrium between cyclopentenyl and cyclohexenyl cations **20** and **21**, and a brief summary of their conclusions is shown below. By a process analogous to our four-methyl scrambling, **20** and **21** isomerize through a common cyclopropylcarbinyl intermediate **22**. However, they did not ob-



serve any degenerate rearrangement of cation **21** after 48 hr at 25°. If one assumes that at least 10% rearrangement would have been detectable, then $k_{22\rightleftarrows 22}$ is less than 6×10^{-7} sec^{-1}, or $k_{22\rightleftarrows 22}$ is at least 10^4 times slower than $k_{6\rightleftarrows 6}$ and at least 10^7 times slower than the unsubstituted parent cation. Thus, steric constraints as well as the overall substitution pattern of a cyclopropylcarbinyl cation exert a marked influence on the rate of rearrangement.

(23) The transition state between **7** and **6** is *ca.* 4.8 kcal/mol below that for $6 \rightleftarrows 6$.

(24) T. S. Sorensen and K. Ranganayakulu, *J. Amer. Chem. Soc.*, **92**, 6539 (1970).

The cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement is generally viewed in terms of two possible mechanisms, one which involves direct isomerization of two cyclopropylcarbinyl cations and one which proceeds through a cyclobutyl intermediate. However, one might expect parallel electronic and steric requirements for either pathway and a distinction between the two possibilities cannot be made on the basis of our results.

According to theoretical considerations,[5v] allylcarbinyl products may originate from either cyclopropylcarbinyl or cyclobutyl cationic intermediates. Majerski and Schleyer's work[5y] on the stereochemistry of cyclopropylcarbinyl rearrangements suggested (but did not demand) that homoallylic and cyclobutyl products share a common cationic precursor. On the other hand, it is clear than homoallylic derivatives **3**-OCH_3 and **3**-OH were not formed from a cyclobutyl cation. Isomerization of **6** to a cyclobutyl isomer prior to formation of homoallylic substitution products would scramble deuterium label in **3**-OCH_3-d_6 and **3**-OH-d_6. Not only was no scrambling observed in nucleophilic solvents, but the barrier for deuterium scrambling was found to be 4.4 kcal/mol above that for $6 \rightleftarrows 7$ and even the latter rearrangement was too slow to compete with solvent collapse. Only by employing a solvent with high ionizing power and extremely low nucleophilicity could one hope to determine how much the rearrangement of **6** had been retarded with respect to its less substituted counterparts. These are the specific properties with which superacid solvents complement what are considered standard solvolysis solvents.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. Elemental analyses were performed by Miss Heather King, University of California, Los Angeles, Calif. Ir spectra were recorded with 10% solution on a Perkin-Elmer Model 421 grating spectrometer, and nmr spectra were obtained on a Varian A-60 or HA-100 spectrometer with chemical shifts measured downfield from internal tetramethylsilane (δ, parts per million) in CCl_4 or $CDCl_3$ and with respect to internal methylene chloride (assume δ = 5.33 ppm) in acidic solvents. All preparative glpc separations were carried out with a 5 ft × 1/4 in. 5% Carbowax 20M column (60–80 Chromosorb W) on an Aerograph A-90 gas chromatograph. Analytical glpc analyses were performed with a 10 ft × 1/8 in. 5% Carbowax 20M column (80–100 Chromosorb W) on an Aerograph Hy-Fi Model 600D.

Solvents. The purification of fluorosulfuric acid and antimony pentafluoride has been previously described.[25] Deuteriofluorosulfuric acid was used as received[26] as was sulfuryl chlorofluoride.

Ethyl 2,2,3,3-Tetramethylcyclopropanecarboxylate.[27] Following the previously described procedure, 20.0 g (0.197 mol) of ethyl diazoacetate was decomposed in the presence of 20.0 g (0.238 mol) of 2,3-dimethyl-2-butene to give 9.4 g (30%) of the desired ester, bp 71–73° (12 mm); lit.[27] 76–77° (15 mm).

α,α,2,2,3,3-Hexamethyl-1-hydroxymethylcyclopropane.[9] Following the previously reported procedure, 10 ml of a 1.3 *M* solution of methyllithium in diethyl ether (13 mmol) was used to convert 600 mg (3.7 mmol) of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate to the desired alcohol. Distillation of the product (molecular still, pot 130° (15 mm)) gave 410 mg (77%) of the desired product: ir (CCl_4) 3620, 3500, 3020, 2960, 2920, 1460, 1450, 1375, 1360, 1195, 1115, and 945 cm^{-1}; nmr (CCl_4) 0.10 (1, s, H at C_1), 0.67 (1, s, hydroxyl group), 1.06 (6, s), and 1.27 (6, s).

(25) M. Brookhart, Ph.D. Thesis, University of California, Los Angeles, 1968.

(26) Diaprep Corporation.

(27) A. P. Meshcheryakov and I. E. Dolgii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 931 (1960).

2,2,3,3-Tetramethylcyclopropanecarboxylic Acid. A solution of 259 mg (1.52 mmol) of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate and 7 pellets of potassium hydroxide in 6 ml of methanol was heated at reflux for 5 hr. The mixture was poured into a separatory funnel containing 100 ml of water, and the aqueous solution was washed with four 30-ml portions of ether. The aqueous layer was acidified with concentrated hydrochloric acid (using pH paper), and the resulting milky solution was extracted with four 25-ml portions of ether. The combined ether layers were washed with 25 ml of saturated sodium chloride solution and dried over magnesium sulfate to give 172 mg (80%) of a light yellow solid: mp 113–116°; nmr ($CDCl_3$) 1.20 and 1.27 (13, s, methyl groups and H at C_1) and 10.8 ppm (1, broad, carboxyl proton).

2-(2′,2′,3′,3′-Tetramethyl-1′-cyclopropyl)propan-2-yl Benzoate. Following the procedure of Hart and Law[10] and using Schlenk tubes, 515 mg (3.03 mmol) of α,α,2,2,3,3-hexamethyl-1-hydroxymethylcyclopropane in 10 ml of pentane was heated at reflux with 302 mg (7.76 mmol) of potassium. The slightly turbid solution was filtered and cooled in an ice bath. Benzoyl chloride, 464 mg (3.30 mmol), was added by syringe, and potassium chloride began to precipitate within 30 sec. The solution was stirred at room temperature for 4 hr before solvent was removed at reduced pressure to give a pale yellow oil: ir (CCl_4) 3060, 3010, 2980, 2930, 2860, 1713, 1600, 1580, 1450, 1380, 1310, 1280, 1100, 710 cm^{-1}; nmr (CCl_4) 0.60 (1, s, H at C_1), 1.11 (6, s), 1.22 (6, s), 1.63 (6, s), and 7.3–8.0 ppm (5, m, aromatic H).

2,3,3,5-Tetramethylhexa-1,4-diene. Passage of 530 mg (204. mmol) of 2-(2′,2′,3′,3′-Tetramethyl-1′-cyclopropyl)propan-2-yl benzoate through 30 g of activity II alumina, eluting with pentane, gave 228 mg (81%) of a colorless oil. Samples for spectral and combustion analyses were purified by glpc: ir (CCl_4) 3080, 2960, 2920, 2860, 1630, 1370, 890 cm^{-1}; nmr (CCl_4) 1.14 (6, s, methyl groups at C_3), 1.55 (3, d of q, methyl group at C_5 trans to H at C_4, J = 0.3 Hz (q), J = 1.5 Hz (d)), 1.64 (3, d of q, methyl group at C_5 cis to H at C_4, J = 0.3 Hz (q), J = 1.4 Hz (d)), 1.68 (3, d of d, methyl group at C_2, J = 0.7 Hz, J = 1.4 Hz), 4.67 (1, d of q, H at C_1 cis to methyl group at C_2, J = 1.4 Hz (q), J = 1.7 Hz (d)), 4.77 (1, d of q, H at C_1 trans to methyl group at C_2, J = 0.7 Hz (q), J = 1.7 Hz (d)), and 5.06 ppm (1, superimposed q, H at C_4, J = 1.4 Hz, J = 1.5 Hz).

Anal. Calcd for $C_{10}H_{18}$ (138.25): C, 86.88; H, 13.12. Found: C, 87.03; H, 13.19.

2,3,3,5-Tetramethylhex-4-en-2-ol. A solution of 490 mg (3.14 mmol) of α,α,2,2,3,3-hexamethyl-1-hydroxymethylcyclopropane in 4.0 ml of dioxane and 1.0 ml of 0.00645 N perchloric acid was allowed to stand at room temperature (22°) for 22 hr. A 300-ml portion of the solution was allowed to equilibrate at nmr probe temperature (33°) for 5 min, and the spectrum was repeatedly scanned. The rate of change of the signals at 1.27 (cyclopropylcarbinol) and 1.66 (homoallylic alcohol) was used to calculate the first-order rate constant for the isomerization, $k^{33°} = (1.23 \pm 0.03) \times 10^{-3}$ sec^{-1}. Both the bulk and nmr samples were poured into a separatory funnel which contained 75 ml of ether. The resulting mixture was washed with four 20-ml portions of water and dried over sodium carbonate. Solvent removal at reduced pressure and molecular distillation of the residue (130° (15 mm)) gave 465 mg (95%) of a colorless oil: ir (CCl_4) 3620, 3560, 3480, 2960, 2920, 2870, 1650, 1440, 1390, 1370, 1360, 1320, 1140, 940 cm^{-1}; nmr (CCl_4) 1.10 (12, s, methyl groups at C_4), 1.24 (1, s, hydroxyl group), 1.70 (3, d, J = 1.4 Hz) and 1.74 (3, d, J = 1.4 Hz, H at C_1 and methyl group at C_2), 5.18 (1, septet, J = 1.4 Hz, H at C_3).

Anal. Calcd for $C_{10}H_{20}O$ (156.27): C, 76.86; H, 12.90. Found: C, 76.96; H, 12.90.

2,4,4,5-Tetramethylhex-2-en-5-yl Benzoate. Following the previously described procedure, 274 mg (1.76 mmol) of 2,4,4,5-tetramethylhex-2-en-5-ol was converted to the corresponding potassium alkoxide and then to the benzoate ester with 248 mg (1.76 mmol) of benzoyl chloride: nmr (CCl_4) 1.28 (6, s, methyl groups at C_4), 1.62 (6, s, methyl group at C_5 and H at C_6), 1.73 (3, d, J = 1.7 Hz) and 1.78 (3, d, J = 1.7 Hz) (methyl group at C_2 and H at C_1), 5.38 (1, septet, H at C_3, J = 1.7 Hz), 7.4 (5, m, aromatic H).

α,α-Dimethyl-d_6-2,2,3,3-tetramethyl-1-hydroxymethylcyclopropane. A Schlenk apparatus was dried at 175° overnight and allowed to cool while being purged with dry nitrogen. Lithium metal was pounded into thin sheets with a hammer and 0.2 g (29 mmol) was cut into small pieces with scissors directly into a preweighed beaker of dry toluene. The weighed bits of metal were dried and placed in a Schlenk tube, which contained 10 ml of anhydrous ether. To the rapidly stirred mixture was slowly added 2.00 g (13 mmol) of methyl-d_6 iodide. The addition was accompanied by heat evolution. The mixture was heated at reflux for 7 hr, allowed to cool, and filtered into a 100-ml round-bottomed flask. Following the normal procedure, 494 mg (3.12 mmol) of ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate was added by a syringe. Work-up and distillation gave 355 mg (76%) of a fragrant, colorless oil: ir (CCl_4) 3620, 3500, 3020, 2980, 2930, 2915, 2800, 2860, 2220, 1460, 1375, 1195, 1110, 1045 cm^{-1}; nmr (CCl_4) 0.07 (1, s, H at C_1), 0.81 (1, s, hydroxyl group), 1.02, and 1.18 ppm (12, s, methyl groups at C_2 and C_3).

Anal. Calcd for $C_{10}H_{14}D_6O$: C, 74.00; H(D), 16.14. Found: C, 73.95; H(D), 15.73.

α,α-Dimethyl-d_6-2,2,3,3-tetramethyl-1-hydroxymethylcyclopropane Benzoate. Following the procedure described for the protio derivatives, 204 mg (1.26 mmol) of α,α-dimethyl-d_6-2,2,3,3-tetramethyl-1-hydroxymethylcyclopropane was converted to the corresponding potassium salt and then to the benzoate with 177 mg (1.26 mmol) of benzoyl chloride: nmr (CCl_4) 0.48 (1, s, H at C_1), 1.00 and 1.23 (12, s, methyl groups at C_2 and C_3), 7.2–7.8 ppm (5, aromatic H).

Preparative Solvolysis of 2-(2′,2′,3′,3′-Tetramethyl-1′-cyclopropyl)propan-2-yl Benzoate. A mixture of 0.8 g (3 mmol) of 2-(2′,2′,3′,3′-Tetramethyl-1′-cyclopropyl)propan-2-yl benzoate and 1 g of 2,6-lutidine in 50 ml of methanol was allowed to stir at 25° for 20 hr. The mixture was poured into 100 ml of water, and the resulting suspension was extracted with five 15-ml portions of pentane. The combined pentane extracts were washed with three 15-ml portions of water and dried over magnesium sulfate. Solvent was removed at reduced pressure to yield *ca.* 0.7 g of an oil. The mixture was separated by glpc at 100°. The first eluted product was 2,3,3,5-tetramethylhexa-1,4-diene, followed by two fragrant oils: α,α,2,2,3,3-hexamethyl-1-methoxymethylcyclopropane, ir (CCl_4) 3020, 2970, 2940, 2920, 2860, 2820, 1465, 1374, 1357, 1250, 1205, and 1075 cm^{-1}; nmr (CCl_4) 0.08 (1, m, H at C_1), 1.00 (6, s, methyls on cyclopropane), 1.11 (12 s, methyls on cyclopropane), and 3.08 ppm (3, s, methoxy group); 2-methoxy-2,3,3,5-tetramethylhex-4-ene, ir (CCl_4) 2970, 2930, 2820, 1655, 1640, 1370, 1360, 1140, and 1070 cm^{-1}; nmr (CCl_4) 0.82 (6, s, methyls at C_2 or C_3), 1.02 (6, s, methyls at C_2 or C_3), 1.55 (3, d, H at C_6 or methyl at C_5, $J \cong$ 1.5 Hz), 1.59 (3, d, H at C_6 or methyl at C_5, $J \cong$ 1.5 Hz), 2.95 (3, s, methoxy group), 5.17 (septet, 1, H at C_4).

Preparative Solvolysis of 2-(2′,2′,3′,3′-Tetramethyl-1′-cyclopropyl)propan-2-yl Benzoate-d_6. Following the procedure outlined for the nondeuterated benzoate, 220 mg of 2-(2′,2′,3,′3′-Tetramethyl-1′-cyclopropyl)propan-2-yl benzoate-d_6 and 0.2 g of 2,6-lutidine were allowed to stand in 50 ml of methanol at 25° for 24 hr. Work-up gave similar product ratios found for the nondeuterated benzoate. The products were separated by glpc; α,α-dimethyl-d_6-2,2,3,3-tetramethyl-1-methoxymethylcyclopropane was a fragrant, colorless oil: ir (CCl_4) 3010, 2970, 2930, 2860, 2810, 2220, 1460, 1375, 1200, and 1075 cm^{-1}; nmr (CCl_4) 0.08 (1, s, H at C_1), 1.00 (6, s, methyls at C_2 and C_3), 1.11 (6, s, methyls at C_2 and C_3), 3.08 (3, s, methoxy group); the homoallylic ether was also a colorless oil, ir (CCl_4) 3020, 2960, 2930, 2810, 2200, 2170, 2110, 2090, 1640, 1460, 1365, 1180, 1135, and 1065 cm^{-1}; nmr (CCl_4) 0.82 and 1.02 (12, s, methyl groups), 2.95 (3, s, methoxy group), and 5.17 ppm (1, s, allylic H). The nmr spectrum showed less than 1% protium in the region around 1.5–1.6 ppm.

Solvolysis of the deuterated benzoate in 80% aqueous acetone gave both cyclopropylcarbinyl and homoallylic alcohols without D scrambling. The homoallylic alcohol was a colorless oil: ir (CCl_4) 3620, 3570, 3490, 2940, 2910, 2870, 2240, 2220, 2180, 2120, 2100, 2060, 1640, 1460, 1365, 1145, and 1130 cm^{-1}; nmr (CCl_4) 1.11 (12, s, methyl groups), 1.21 (1, broad s, hydroxyl group), and 5.19 ppm (1, s, olefinic H).

Anal. Calcd for $C_{10}H_{14}D_6O$ (162.31): C, 74.00; H(D), 16.14. Found: C, 73.92; H(D), 15.96.

Preparative Solvolysis of 2,4,4,5-Tetramethylhex-2-en-5-yl Benzoate. A sealed ampoule containing a solution of 86 mg of 2,4,4,5-tetramethylhex-2-en-5-yl benzoate and 100 mg of 2,6-lutidine in 15 ml of anhydrous methanol was heated at 100° for 24 hr (~7.5 half-lives). Work-up of the mixture as previously described followed by glpc analysis revealed the presence of 2,3,3,5-tetramethylhexa-1,4-diene (45%), α,α,2,2,3,3-hexamethyl-1-methoxymethylcyclopropane (3%), and 2-methoxy-2,3,3,5-tetramethylhex-4-ene (52%). All of the solvolysis products gave ir spectra superimposable with those of authentic samples.

Analytical Product Solvolyses. Solutions 0.01 M in benzoate and 0.02 M in 2,6-lutidine were heated at the appropriate temperature. The solutions were worked up as described for preparative solvolyses except that the combined pentane extracts were analyzed

directly by glpc. Tridecane was used as an internal standard in all runs. To separate mixtures containing 5 μl of 2,6-lutidine, 2 mg of benzoic acid and 1 μl of tridecane in 2 ml of anhydrous methanol were added 2,3,3,5-tetramethylhexa-1,4-diene, α,α,2,2,3,3-hexamethyl-1-methoxymethylcyclopropane, and 2-methoxy-2,3,3,5-tetramethylhex-4-ene. Only α,α,2,2,3,3-hexamethyl-1-methoxymethylcyclopropane was unstable to the reaction conditions, giving 2,3,3,5-tetramethylhexa-1,4-diene (13%) and 2-methoxy-2,3,3,5-tetramethylhex-4-ene (87%).

1-*tert*-Butyl-1,3,3-trimethylallyl Cation. Approximately 10 mg of α,α,2,2,3,3-hexamethyl-1-hydroxymethylcyclopropane or 2,4,4,5-tetramethylhex-2-en-5-ol was dissolved in *ca.* 100 μl of methylene chloride. The solution was slowly pipeted onto *ca.* 300 μl of 1:1 (by volume) fluorosulfuric acid–sulfuryl chlorofluoride or 1:3 (by volume) of antimony pentafluoride–sulfuryl chlorofluoride in an nmr tube at −100°. After both layers were equilibrated at −100°, the contents of the nmr tube were rapidly mixed. The solution was stored in liquid nitrogen prior to recording spectra. The ion gave a colorless solution: nmr 1.46 (9, s, tertiary butyl group at C_1), 2.98 (3, s, methyl at C_1), 3.02 (6, s, methyls at C_3), and 7.93 ppm (H at C_2). Between 10 and 100°, the signals at 1.46 and 2.98 ppm broadened and merged into a single peak at 1.84 ppm.

1-*tert*-Butyl-3,3-dimethyl-d_6-1-methylallyl Cation. Using the same general procedure described for the protio derivative, α,α-dimethyl-d_6-2,2,3,3-tetramethyl-1-hydroxymethylcyclopropane gave the allylic cation with methyl-d_3 exclusively in the 3 position (<1% protium): nmr 1.46 (9, s, tertiary butyl group at C_1), 2.98 (3, s, methyl group at C_1), and 7.93 ppm (H at C_2). At 16°, a signal appeared at 3.02 ppm, with a first-order rate constant of 3.1×10^{-3} sec^{-1}.

Quenching of 1-*tert*-Butyl-1,3,3-trimethylallyl Cation. A solution of *ca.* 50 mg of 1-*tert*-butyl-1,3,3-trimethylallylic cation in 1:1 fluorosulfuric acid–sulfuryl chlorofluoride was poured into 25 ml of a rapidly stirred solution of 1 *N* sodium hydroxide solution at *ca.* 0°. The milky aqueous mixture was extracted with three 5-ml portions of pentane, and the combined pentane extracts were dried over magnesium sulfate. Solvent was carefully removed at reduced pressure, and glpc analysis of the residue showed two products in approximately equal amounts. The structure of the first eluted product was assigned as 2-*tert*-butyl-4-methylpenta-1,3-diene: ir (CCl_4) 3080, 2960, 2920, 1615, 1475, 1355, and 898 cm^{-1}; nmr (CCl_4) 1.06 (9, s, tertiary butyl group at C_2), 1.70 (3, d, allylic methyl, J = 1.5 Hz), 1.74 (3, d, allylic methyl, J = 1.5 Hz), 4.68 (1, broad t, cis H at C_1), 5.78 (1, octet, H at C_3).

Anal. Calcd for $C_{10}H_{18}$ (138.25): C, 86.88; H, 13.12. Found: C, 86.72; H, 13.24.

The second eluted product was assigned as 2-*tert*-butyl-4-methylpenta-2,4-diene: ir (CCl_4) 3080, 2960, 2900, 2860, 1630, 1460, and 890 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}$ (138.25): C, 86.88; H, 13.12. Found: C, 86.71; H, 13.09.

Protonation of 2,2,3,3-Tetramethylcyclopropanecarboxylic Acid. A solution of 1:1 (mol) HSO_3F–SbF_5 in SO_2 was cooled in an nmr tube to −80°. A solution of 36 mg of 2,2,3,3-tetramethylcyclopropanecarboxylic acid in 200 μl of of methylene chloride was slowly pipeted onto the cold superacid mixture. After both layers had equilibrated, the contents of the nmr tube were rapidly mixed. The resulting colorless solution had an nmr spectrum characteristic of protonated 2,2,3,3-tetramethylcyclopropanecarboxylic acid: nmr 1.41 (12, s, methyl groups at C_2 and C_3), 1.53 (1, s, H at C_1), and 10.99 ppm (1, s, H on hydroxyl group). The remaining hydroxyl proton was obscured by the solvent peak.

(a) 2,2,3,3-Tetramethylcyclopropaneacylium Ion. When the solution of protonated 2,2,3,3-tetramethylcyclopropanecarboxylic acid was warmed to −10°, the protonated acid cleanly eliminated water with a first-order rate constant, $k = 1.77 \times 10^{-3}$ sec^{-1}, to give the corresponding acylium ion, nmr 1.68 (6, s, methyl groups), 1.75 (6, s, methyl groups), and 2.60 ppm (1, s, H at C_1).

(b) 3,4,4-Trimethylpent-2-enacylium Ion. Warming the solution of 2,2,3,3-tetramethylcyclopropaneacylium ion to 20° gave a clean isomerization, first-order rate constant, $k = 1.47 \times 10^{-3}$ sec^{-1}, to 3,4,4-trimethylpent-2-enacylium ion: nmr 1.40 (9, s, tertiary group), 2.84 (3, s, methyl group at C_3), and 6.57 ppm (H at C_2).

(c) Quenching of 3,4,4-Trimethylpent-2-enacylium Ion. The above solution was poured into a rapidly stirred suspension of methanol–potassium bicarbonate at −78°. After 2 min, the mixture was poured into 100 ml of water, and the resulting basic solution (to pH paper) was extracted with ether. The combined ether layers were washed with water and dried over anhydrous magnesium sulfate. Solvent was removed at reduced pressure to give 29 mg (73% based on 36 mg of acid) of a fragrant colorless oil which was a 78:22 mixture, by glpc. The major product, methyl *trans*-3,4,4-trimethylpent-2-enoate, was isolated by glpc: nmr 1.11 (9, s, tertiary butyl group), 2.12 (3, d, methyl group at C_3, $J \sim 1.5$ Hz), 3.61 (3, s, methoxy methyl), and 5.66 ppm (1, q, H at C_2). The nmr spectrum was identical with that previously reported.[20]

The *minor component* was methyl *cis*-3,4,4-trimethylpent-2-enoate: nmr (CCl_4) 1.19 (9, s, tertiary butyl group), 1.84 (3, d, methyl group at C_3, $J \sim 1.5$ Hz), 3.61 (3, s, methoxy methyl), and 5.54 ppm (1, q, H at C_2).

Anal. Calcd for $C_9H_{16}O_2$ (156.23): C, 69.20; H, 10.32. Found: C, 69.41; H, 10.40.

Dimethylcyclopropylcarbonium Ion. (a) Following the general procedure used for 1-*tert*-butyl-1,3,3-trimethylallylic cation, 25 mg of α,α-dimethylcyclopropylcarbinol was extracted into HSO_3F–SO_2ClF at −100°. The nmr spectrum of dimethylcyclopropylcarbonium ion was identical with that previously reported.[6b] At −73° the cyclopropylcarbinyl action cleanly isomerized to *trans*-1,1,3-trimethylallyl cation, $k = 9.24 \times 10^{-4}$ sec^{-1}: nmr 2.89 (3, broad d, methyl group at C_3), 3.14 (6, broad s, methyl groups at C_1), 7.76 (1, d, H at C_2, $J_{2,3}$ = 14 Hz), 9.49 (1, d of q, H at C_3, $J_{3\text{-}CH_3}$ = 7 Hz).

(b) Using the above procedure with SbF_5–SO_2ClF an nmr spectrum of dimethylcyclopropanecarbonium ions was obtained. At −20° the cation was rapidly destroyed. The major decomposition product was polymeric, but a small amount of 1,1,3-trimethylallyl cation was observed.