into 20.0 ml of 0.021 *N* *n*-butylamine in dioxane. The mixtures were protected from moisture and allowed to stand overnight. The solutions were then titrated with 0.01 *N* HCl to the methyl red end point. A similar procedure was utlized for analysis of potassium perchlorate catalyzed isomerizations.

Acknowledgment. We with to thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

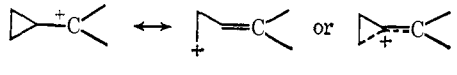
Carbonium Ion–Silane Hydride Transfer Reactions. III. Cyclopropylmethyl Cations

Francis A. Carey and Henry S. Tremper

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. *Received December 13, 1968*

Abstract: In methylene chloride–trifluoroacetic acid, cyclopropylcarbinols (**1a–e**) underwent rapid ring-opening reactions leading to 4-substituted 3-butenyl-1-trifluoroacetate esters (**2a–e**). With 1,1-dicyclopropylbenzyl alcohol (**1b**) and tricyclopropylcarbinol (**1c**), multiple ring opening occurred leading to bis- and tristrifluoroacetates **4** and **5**, respectively. With di- and triorganosilanes present in the reaction mixture, ring opening was suppressed and hydride transfer from ≡SiH to the carbonium ion took place, in several cases to the exclusion of ester formation. Hydride transfer produced cyclopropylmethanes (**3a–e**) exclusively and in no case was hydride transferred to a ring-opened homoallyl cation. This fact indicates that delocalization of the positive charge by the cyclopropyl ring takes place by some mechanism which does not make the ring carbons very electrophilic. The more highly substituted cyclopropylmethyl cations exhibit a greater tendency to ring open than the less substituted ones probably because of nonbonded repulsions in the ion. The stereochemical features of ring opening are discussed in terms of preferred conformations in the carbonium ion.

The reaction of silanes with carbonium ions produces alkanes by hydride transfer from silicon to carbon.[1,2] The primary products at silicon when trifluoroacetic acid is present are trifluoroacetoxysilanes[2] but these often undergo further reaction during work-up to afford silanols and disiloxanes. This transfer occurs readily under mild conditions and has been applied to carbonium ion studies as a nonnucleophilic irreversible trap for species such as the classical 2-phenylnorbornyl cation.[3] We were interested in observing if cyclopropylmethyl cations[4] could be trapped by silanes since the usual resonance description of these ions shows delocalization of positive charge into the three-membered ring and according to this description the possibility exists of hydride transfer to give cyclopropylmethanes and/or butenes.

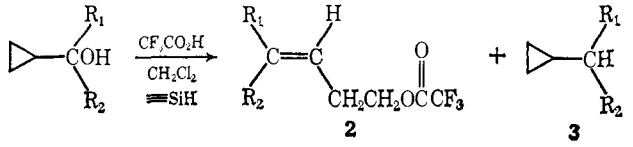


It seems reasonable that if hydride transfer from ≡SiH did occur that selection for attack at the ring methylene carbon or the cyclopropylcarbinyl carbon would bear some relationship to the electron deficiency at these positions and by examining several cyclopropylmethyl cations we could gain some insight into their structure.

(1) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, 90, 2578 (1968), and references cited there.
(2) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, 23, 2235 (1967).
(3) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, 34, 4 (1969).
(4) For reviews see: (a) M. Hanack and H.-J. Schneider, *Angew. Chem. Int. Ed. Engl.*, 6, 666 (1967); (b) S. Sarel, J. Yovell, and M. Sarel-Imber, *ibid.*, 7, 577 (1968); (c) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 129 (1964).

Results

The first carbonium ions examined were those which we thought would be the most stable and, therefore, the most likely to abstract hydride at rates competitive with ring opening. Cyclopropyldiphenylcarbinol (**1a**) when treated with trifluoroacetic acid in deuteriochloroform in an nmr tube underwent a very rapid reaction, complete in less than 1 min, to form 4,4-diphenyl-3-butenyl trifluoroacetate (**2a**) as the only detectable product. The structure was assigned on the basis of the characteristic nmr spectra of these types of esters.[5] For **2a–e** the signal for the vinyl proton appears in the region δ 4.8–6.8 coupled with the allylic methylene protons with a coupling constant of about 7 Hz. The signals for the protons in the $-CH_2OCOCF_3$ portion appear as a triplet in the region δ 4.2–4.5 and the allylic CH_2 signals as a symmetrical quartet at δ 2.3–2.8.



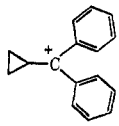
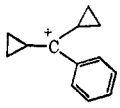
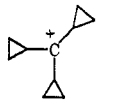
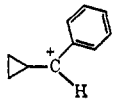
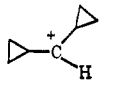
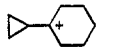
2 **3**

1a, $R_1 = R_2$ = Ph
b, R_1 = Ph, R_2 = *c*-C_3H_5
c, $R_1 = R_2$ = *c*-C_3H_5
d, R_1 = Ph, R_2 = H
e, R_1 = *c*-C_3H_5, R_2 = H
f, $R_1, R_2 = (CH_2)_5$

When the trifluoroacetolysis was carried out on a preparative scale **2a** was isolated in 70% yield after distillation. Ring opening was suppressed, however,

(5) For spectra of related compounds see: (a) H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, 86, 1957 (1964); (b) K. L. Servis and J. D. Roberts, *ibid.*, 87, 1331 (1965).

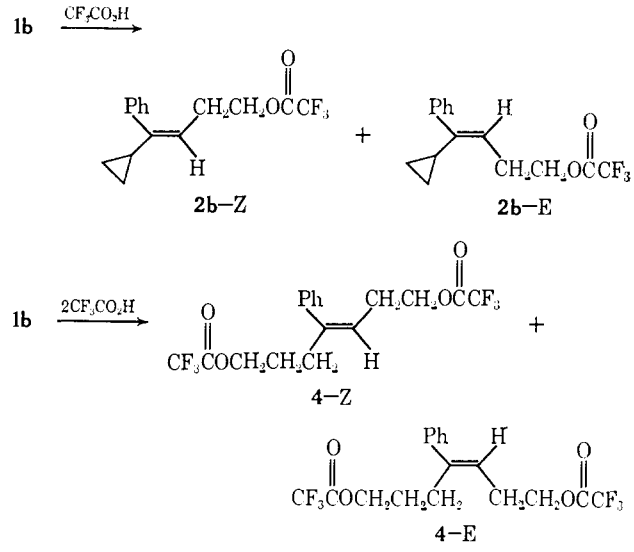
Table I

Ion	Temp, °C	Silane	2 ring opening, %	3 hydride transfer, %
	25	Triethyl	58	42
	−15	Triethyl	19	81
	25	Triphenyl	84	16
	−15	Triphenyl	59	41
	25	Triethyl	46[a]	54
	−15	Triethyl	15[a]	85
	25	Triphenyl	83[a]	17
	−15	Triphenyl	63[a]	37
	25	Triethyl	11[b]	89
	−15	Triethyl	1[b]	99
	25	Triphenyl	12[b]	88
	−15	Triphenyl	8[b]	92
	25	Triethyl	8	92
	−15	Triethyl	Trace	>99
	25	Triphenyl	27	73
	−15	Triphenyl	9	91
	25	Diethyl[c]	13	87
	−15	Diethyl[c]	0	100
	25	Triphenyl	18	82
	−15	Triphenyl	7	93
	25	Triethyl	Trace	>99
	25	Triphenyl	25	74
	−15	Triphenyl	10	90

[a] Mixture of **2b**-Z and **2b**-E. [b] Ring-opened product was not **2c** but was **7**. [c] Triethylsilane had the same retention time as dicyclopropylmethane so could not be used.

when the reacton was carried out in the presence of silanes (Table I). Both triethylsilane and triphenylsilane trapped the carbonium ion to give cyclopropyldiphenylmethane (**3a**) along with **2a**, triethylsilane being more efficient than triphenylsilane[6] and the proportion of **3a** increasing as the temperature was decreased from 25 to −15°. **2a** and **3a** were the only products which could be detected by glpc (other than silicon-containing products). There was no indication whatsoever of any 1,1-diphenylbutene present in the reaction mixture. It could be shown that **3a** was not formed by cyclization of **2a** by noting that the proportion of **3a**:**2a** was invariant with time and that 4,4-diphenyl-3-buten-1-ol gave no **3a** when subjected to the same reaction conditions.

1,1-Dicyclopropylbenzyl alcohol (**1b**) reacted similarly to **1a** with silanes in respect to the relative amounts of hydride transfer and ring-opened ester formation. Here again, the product from hydride transfer was **3b**, there being no evidence for 1-phenyl-1-cyclopropylbutene. The reaction is somewhat more complicated than **1a** in that the ring-opened trifluoroacetate fraction is a mixture of 4-phenyl-4-cyclopropyl-3-butenyl trifluoroacetate-Z (**2b**-Z) and 4-phenyl-4-cyclopropyl-3-butenyl trifluoroacetate-E (**2b**-E).[7] Moreover **2b**-Z and **2b**–E are unstable in the reaction medium and after protonation the second cyclopropyl ring also opens to



give a mixture of the bistrifluoroacetates **4**-Z and **4**-E.

A study of the trifluoroacetolysis of **1b** without silanes using preparative glpc to separate and purify the products showed the ratio of **2b**-Z to **2b**-E was 63:37. The structures were assigned on the basis of the nmr spectra of the purified products assuming the phenyl ring to be best accommodated in a conformation in which it is coplanar with the double bond. The phenyl ring should be more important conformationally than the cyclopropyl since recent work by Heathcock and Poulter indicates that there is no particular conformational preference for the cyclopropyl ring in vinylcyclopropanes.[8] From examination of models it can be seen that the cyclopropyl ring in **2b**-E is rather crowded and that this crowding can be minimized by allowing the cyclopropyl ring to assume a conformation in which the cyclopropyl methine hydrogen is perpendicular to the plane of the double bond. The nmr result of such a conformation is that long-range coupling of the vinyl proton and cyclopropyl methine proton should be observable since this geometry corresponds to a maximum for allylic coupling.[9] Long-range coupling of the vinyl hydrogen was clearly present in the minor product. There was no long-range coupling detectable in the nmr spectrum of the major product consistent with structure **2b**-Z where models show the cyclopropyl ring is probably in the "bisected" conformation with the methine proton and vinyl proton coplanar corresponding to a minimum in allylic coupling.

The bistrifluoroacetates **4**-Z and **4**-E were the only products formed from the reaction of **1b** with excess trifluoroacetic acid for longer times. The two isomers were formed in the ratio 85:15 but it was not unambiguously established which of the isomers was the major product.

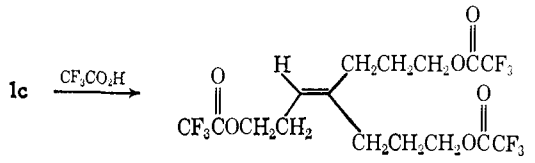
Multiple ring opening was likewise observed in the trifluoroacetolysis of tricyclopropylcarbinol (**1c**). Immediately after mixing CF_3CO_2H and **1c** in $CDCl_3$ in an nmr tube a mixture of products was observed. After 4 hr the tristrifluoroacetate **5** was the only product.

(6) This order of reactivity is consistent with previous observations[1,2] and unpublished rate studies of Mrs. C. W. Hsu.

(7) The descriptors Z and E to denote configuration about the double bond have been suggested by J. E. Blackwood, C. L. Gladys, D. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

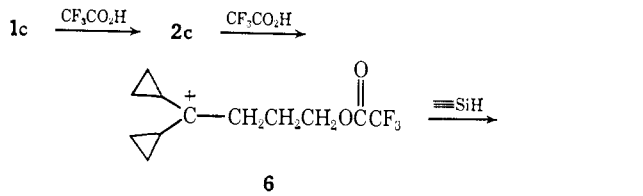
(8) C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968).

(9) N. S. Bhacca and D. H. Williams, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 108–110.

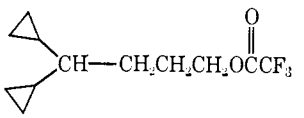


5

The tricyclopropylmethyl cation is effectively trapped by ≡SiH giving high conversion to tricyclopropylmethane (Table I). It is also interesting here that ring opening is so inhibited that only one ring opens. The reaction proceeds no further because protonation of **2c** gives cation **6** which is also efficiently trapped as evidenced by the fact that the minor product of the reaction is 4,4-dicyclopropylbutyl trifluoroacetate (**7**) and not **2c**.



6

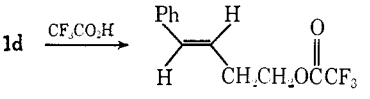


7

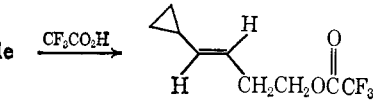
To verify this sequence **2c** was prepared by treatment of **1c** with trifluoroacetic anhydride in pyridine[10] and shown to be converted to **7** in 95% yield with triethylsilane–trifluoroacetic acid–methylene chloride.

An interesting fact became evident as we examined other cyclopropylmethyl cations, namely that our original premise that phenyl substituents at the carbonium ion site should stabilize the cyclopropylmethyl cation against ring opening was incorrect. The reverse was true. The simpler carbonium ions were less prone to ring open than were the ions derived from **1a** and **1b**. The conversions of **1d**, **1e**, and **1f** with triethylsilane in methylene chloride–trifluoroacetic acid were quite clean at low temperature and gave only small amounts of **2d**, **2e**, and **2f**. Here again, hydride transfer gave only cyclopropylmethanes.

Ring opening of **1d**, **1e**, and **1f** did occur readily when silanes were not present to give the corresponding 3-butenyl trifluoroacetates. From **1d** and **1e** these esters were shown to be the *trans* isomers by first-order analysis of their nmr spectra which showed a coupling constant of about 16 Hz for the vinyl protons.



2d



2e

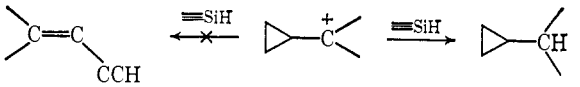
(10) Hart and Law[5a] have reported several spontaneous rearrangements of tricyclopropylmethyl esters to 4,4-dicyclopropyl-3-butenyl esters.

While the work described here was nearing completion, we were interested to see that simpler cyclopropylcarbinyl systems may also be converted to cyclopropylmethanes by hydride transfer. Kursanov[11] has briefly reported that vinylcyclopropane and 2-cyclopropylpropene are "ionically hydrogenated" to ethylcyclopropane and isopropylcyclopropane with triethylsilane and trifluoroacetic acid.

Discussion

The value of using ≡SiH hydride transfer in studying carbonium ion reactions is that effects of concerted nucleophilic displacements are minimized. Current thought is that intermolecular hydride transfers require true carbonium ion intermediates and that species such as protonated alcohols are not sufficiently electrophilic to abstract hydride from ≡CH.[12] Similar requirements seem to apply to ≡SiH → ≡C⁺ hydride transfers.[1] In using chemical reactions to deduce structures of intermediates such as cyclopropylmethyl cations the possibilities of nucleophilic displacements must be considered. Johnson[13] has recently explained the stereoselectivity in converting cyclopropylcarbinols to homoallyl bromides with HBr (Julia's olefin synthesis)[14] in terms of attack by bromide on the ring methylene carbon of protonated cyclopropylcarbinol. The cyclizations of homoallylic halides and arenesulfonates to cyclopropylmethyl products under solvolytic conditions reported by Hanack[4a,15] may be the result of nucleophilic attack on the ion pair at a region away from maximum encumbrance.[16]

The cyclopropylcarbinols described here all abstracted hydride from silanes to give cyclopropylmethanes.



In no case was there evidence for formation of ring-opened hydrocarbons. If the capacity to abstract hydride is related to the electron deficiency, the conclusion is that the ring methylene groups do not become very electrophilic whatever the mechanism of stabilization. It is pertinent in this regard that substitution of a methyl group for hydrogen at the carbinyl position in cyclopropylcarbinyl 3,5-dinitrobenzoate increases the rate of hydrolysis by a factor of 1000 while substitution of methyl for hydrogen in the ring increases the rate only 5- to 11-fold.[17] Here also, most of the electron demand is felt at the carbinyl position.

The fact that only 3-butenyl trifluoroacetates and no cyclopropylcarbinyl trifluoroacetates are obtained is probably a result of thermodynamic control in ester formation.

(11) Z. N. Parnes, G. A. Khotimskaya, M. Y. Lukina, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **178**, 680 (1968).

(12) N. C. Deno, H. Peterson, and G. Saines, *Chem. Rev.*, **60**, 7 (1960).

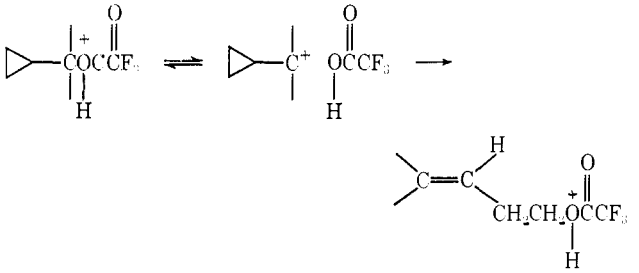
(13) S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, **90**, 2882 (1968).

(14) M. Julia, S. Julia, and S.-Y. Tchen, *Bull. Soc. Chim. Fr.*, 1849 (1961).

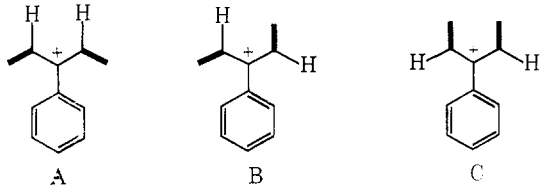
(15) M. Hanack, S. Kang, J. Haffner, and K. Gorler, *Ann.*, **690**, 98 (1965).

(16) Professor P. S. Skell has discussed the importance of local shielding by the leaving group and solvent clusters in influencing product distribution in carbonium ions: "Conference on Carbonium Ions," Cleveland, Ohio, Oct 25, 1968.

(17) P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

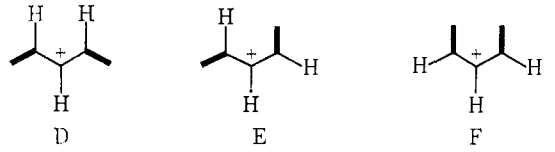


If the ratio of ring opening to hydride transfer (Table I) is examined it is apparent that the ions with multiple stabilizing groups are more prone to ring open than the simpler ions. In the absence of detailed investigation into this point we would like to propose as a tentative explanation that this increased tendency toward ring opening arises from *steric* destabilization of the carbonium ion. For the ion from **1b** three bisected[18] conformations are possible.



A B C

Models show unfavorable steric interactions in each with the result that the ion tends to form 3-butenyl trifluoroacetates to relieve these repulsions. If the phenyl group is replaced by hydrogen as in the dicyclopropylmethyl cation, three bisected structures are again possible. One of these (D) is much lower in energy than the other two and should be formed preferentially[19] during the ionization process and be more stable with respect to ring opening than A, B, and C.

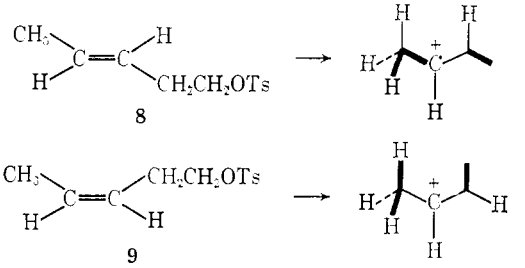


D E F

If, as the data currently available imply,[18] the barrier to interconversion of the conformers is high, a reasonable conclusion is that the stereochemistry of the double bond in the ring-opened product is controlled by and reflects the distribution of conformers of the carbonium ion. Thus, stereospecific ring opening of D would lead to a *trans*-double bond while F would lead to a *cis*-double bond. For conformer E a *cis*- or *trans*-double bond is possible depending on which ring opens. Analogous considerations apply to the carbonium ion from **1d**, where again only the *trans* olefin was observed.

With A, B, and C it is difficult to choose which is most stable if the p orbitals of the phenyl ring are to overlap with the p orbital of the cationic carbon. Twisting the phenyl ring out of the plane should not be resisted excessively on electronic grounds owing to the great stabilizing power of the cyclopropyl rings and should diminish (but not eliminate) the unfavorable steric repulsions. Therefore, A (which leads to **2b**-Z) should be favored over B (which leads to **2b**-Z + **2b**-E) with C (leading to **2b**-E) being the least stable conformer.[20]

The experimental observations regarding ring opening reported here while in accord with stereospecific ring opening of nonequilibrating conformers are not conclusive since the steric factors which influence conformer stability in the carbonium ions also influence isomer stability in the olefins. A corollary which may be tested experimentally is that the microscopic reverse, cyclization of homoallylic carbonium ions to cyclopropylmethyl cations should be sensitive to the geometry of the double bond. *trans*-Tosylate **8** should cyclize faster than *cis*-tosylate **9** if the ring closure reaction is stereospecific. This is in fact, the order observed, the relative rates being 7.6 for formolysis at 50°.[5b]



8 9

Experimental Section

Nmr spectra were recorded on a Varian A-60 and Hitachi Perkin-Elmer R-20 instruments in $CDCl_3$ with tetramethylsilane as an internal standard. Infrared spectra were measured on a Perkin-Elmer 337 grating spectrophotometer. The gas chromatograph used was a Varian Aerograph 90-P thermal conductivity instrument. Areas were determined by planimeter integration. Microanalyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Mulheim, West Germany.

Triethylsilane, triphenylsilane, and diethylsilane were obtained from the Pierce Chemical Co., Rockford, Ill. and the triphenylsilane recrystallized from hexane if its melting point indicated it was impure. Methylene chloride was stored over molecular sieves.

α,α-Diphenylcyclopropylcarbinol (**1a**), α,α-dicyclopropylbenzyl alcohol (**1b**), cyclopropylphenylcarbinol (**1d**), and dicyclopropylcarbinol (**1e**) were purchased from Aldrich. Tricyclopropylcarbinol (**1c**) was prepared by the method of Pittman and Olah.[18] Authentic samples of dicyclopropylmethane and phenylcyclopropylmethane for comparison purposes were purchased from Aldrich.

The analytical data reported in Table I were obtained by allowing solutions containing 1 mmol of **1a–f**, 2 mmol of trifluoroacetic acid, and 1.2 mmol of the silane in 4.0 ml of methylene chloride to stand at the indicated temperatures for 0.5 hr, adding excess solid potassium carbonate and analyzing by glpc. The glpc conditions and retention times are summarized in Table II. Preparation and separation of authentic samples and structure determination for reaction products are described in the remainder of this section.

α,α-Diphenylcyclopropylcarbinol (1a). Reaction with Trifluoroacetic Acid. A solution of 4.94 g (22.0 mmol) of α,α-diphenylcyclopropylcarbinol and 5.02 g (44.0 mmol) of trifluoroacetic acid in 88 ml of methylene chloride was allowed to stand at 25° for 2 hr, neutralized with solid sodium carbonate, filtered, and evaporated. The resulting yellow oil was distilled to give 4.94 g (70%) of 4,4-diphenyl-3-butenyl trifluoroacetate (**2a**) (bp 136–139° (0.7 torr)) which exhibited a strong ester carbonyl band in the ir spectrum at 1780 cm^{-1}: nmr spectrum $=CCH_2$ (δ 2.61, quartet, splitting 7.0 Hz), $-CH_2O$ (δ 4.39, triplet, splitting 6.8 Hz), $=CH$ (δ 6.05, triplet, splitting 7.1 Hz), $(C_6H_5)_2-$ (δ 7.22, multiplet).

Anal. Calcd for $C_{18}H_{15}F_3O_2$: C, 67.50; H, 4.72. Found: C, 67.68; H, 4.77.

Hydride Transfer. Trifluoroacetic acid (5.02 g, 44.0 mmol) was added to a stirred solution of 4.94 g (22.0 mmol) of **1a** and 3.6 g (26.4 mmol) of triethylsilane in 80 ml of methylene chloride. After

(18) This is the preferred geometry for stable cyclopropylmethyl cations. See C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, 87, 5123 (1965).

(19) The nmr data of Pittman and Olah[11] indicates D is the only conformer present in FSO_3H.

(20) For a somewhat similar analysis see ref 4b.

Table II. Gas Chromatography of Products[a]

Compd	Column temp, °C	Retention time, min
2a	200	13.7
3a	200	8.7
2b-Z	195	3.3
2b-E	195	4.0
3b	195	2.3
4-Z, 4-E	195	7.0, 8.7
3c	180	1.6
7	180	2.8
2d	150	7.8
3d	150	2.8
2e	125	10.0
3e	125	3.4

[a] All analyses were carried out on a 5 ft 20% SE-30 on Chromosorb P column using helium as the carrier gas at a pressure of 50 psi.

3 hr at 25° the solution was neutralized (Na_2CO_3), filtered, and evaporated. The residue was taken up in 60 ml of methanol containing 10 g of KOH and allowed to stand overnight in order to saponify the trifluoroacetate ester and make separation easier. This solution was poured into ice water and extracted with ether, and the ether extracts were dried ($MgSO_4$) and evaporated to leave 4.0 g of light yellow oil which was distilled at 6 torr. The fraction boiling at 154–156° was collected and identified as α,α-diphenylcyclopropylmethane (**3a**) by its ir spectrum which showed no functional groups and its nmr spectrum: *c*-C_3H_5 (δ 0.18–0.85, multiplet), >C*H* (δ 3.19, doublet, J = 9.2 Hz), C_6H_5- (δ 7.21, singlet). The methine proton on the cyclopropyl ring appeared as a broad multiplet from δ 1.0 to 1.5.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.87.

When 224 mg (1.0 mmol) of **1a** was allowed to react with 228 mg (2.0 mmol) of trifluoroacetic acid in 4 ml of methylene chloride for 1 hr at 25° and then 139 mg (1.2 mmol) of triethylsilane added, the sole product as determined by gas chromatography was the ring-opened ester **2a**.

α,α-Dicyclopropylbenzyl Alcohol (1b). Reaction with Trifluoroacetic Acid. After *40 hr* a solution of 1.88 g (10 mmol) of **1b** in 20 ml of methylene chloride containing 3 ml of trifluoroacetic acid was poured into saturated sodium bicarbonate solution and the organic phase dried ($MgSO_4$) and evaporated. The resulting crude syrup (3.27 g, 83%) was purified by evaporative distillation at 0.2 torr to give 2.73 g (69%) of analytically pure bistrifluoroacetates shown by gas chromatography to be a mixture of **4-Z** and **4-E** in the ratio (9:1): nmr spectrum C_6H_5- (δ 7.30, singlet); =C*H* (δ 5.68, triplet, splitting ~7 Hz), CH_2O (two overlapping triplet centered at δ 4.43 and 4.29 with splittings of *ca.* 7 Hz), $=CCH_2$- (overlapping signals appearing as a multiplet centered at δ 2.7), $-CH_2CH_2CH_2$ (multiplet centered at δ 1.8).

Anal. Calcd for $C_{17}H_{16}F_4O_6$: C, 51.26; H, 4.05. Found: C, 51.34; H, 4.11.

After 20 min a solution of 3.76 g (20 mmol) of **1b** and 3 ml of CF_3CO_2H in 20 ml of methylene chloride was worked up in the same manner and analyzed by glpc. The bistrifluoroacetates were present in minor amounts with the major products being **2b-Z** and **2b-E** in the ratio 63:37, respectively. This crude mixture weighed 5.37 g. Analytical samples of **2b-Z** and **2b-E** were isolated by preparative gas chromatography.

The product eluted first was assigned the structure **2b-Z** by comparing its nmr spectrum with that of the product having the longer retention time (see Results): nmr spectrum C_6H_5 (δ 7–8, multiplet), =C*H* (δ 5.42, triplet, J = 7 Hz), $-CH_2O$ (δ 4.25, triplet J = 7 Hz), $=CCH_2$ (δ 2.30, quartet, splitting of 7 Hz), cyclopropyl methine *H* (δ 2.5, multiplet), cyclopropyl ring *H* (δ 0.2–0.9, multiplet).

Anal. Calcd for $C_{15}H_{15}F_3O_2$: C, 63.38; H, 5.32. Found: C, 62.95, H, 4.93.

The ester eluted second from the column was assigned structure **2b-E** on the basis of its nmr spectrum which showed long-range coupling of the vinyl hydrogen (see Results): nmr spectrum C_6H_5- (δ 7.25, singlet), =C*H* (δ 5.58, triplet, J = 7.2 Hz further split by long-range coupling J = 1.6 Hz), CH_2O (δ 4.41, triplet, J = 7 Hz), $C{=}CCH_2$- (δ 2.80, quartet, splitting of 7 Hz), cyclopropyl methine *H* (δ 1.4–1.9, multiplet), cyclopropyl methylene *H* (δ 0.15–1, multiplet).

Anal. Calcd for $C_{15}H_{15}F_3O_2$: C, 63.38, H, 5.32. Found: C, 63.51; H, 5.51.

Hydride Transfer. Trifluoroacetic acid (2.55 g, 22.0 mmol) was added to a solution containing 2.07 g (11.0 mmol) of **1b** and 1.54 g of triethylsilane (13.2 mmol) in 44 ml of methylene chloride. After 40 min the solution was neutralized with anhydrous sodium carbonate and shown by gas chromatography to contain three components. The trifluoroacetate esters **2b-Z** and **2b-E** comprised 32 and 23%, respectively, of the reaction mixture while the remainder (45%) was shown to be dicyclopropylphenylmethane (**3b**). **3b** was isolated by preparative gas chromatography and its structure confirmed by the following data: nmr spectrum C_6H_5- (δ 7.21, doublet), the remaining protons gave rise to a broad multiplet from δ 0.1 to 1.84; infrared spectrum 3080, 3000, 2880 cm^{-1} (strong, CH stretch); 1017 cm^{-1} (cyclopropyl bending) and 700 cm^{-1} (monosubstituted phenyl).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.37; H, 9.46.

Tricyclopropylcarbinol (1c). Reaction with Trifluoroacetic Acid. A solution of 2.0 g of tricyclopropylcarbinol (13.2 mmol) in 50 ml of methylene chloride containing 9 g (79.2 mmol) of trifluoroacetic acid was allowed to stand 37 hr, neutralized (Na_2CO_3), and evaporated to leave 5.7 g (91%) of crude product. Distillation gave 3.15 g of pure **5** (bp 171–172° (4.6 torr)) corresponding to opening of all three cyclopropyl rings: nmr spectrum =C*H* (δ 5.25, triplet, splitting of 7 Hz), CH_2O (δ 4.34, triplet, splitting 7 Hz, all three trifluoroacetoxy methylenes had the same chemical shift), $=CCH_2$-CH_2O (δ 2.48, quartet, splitting 7 Hz), the remaining CH_2 groups showed a multiplet from δ 1.7 to 2.4—there were no signals at high field indicative of cyclopropane ring protons: infrared spectrum ester carbonyl at 1780 cm^{-1}, COC at 1250 and 1130 cm^{-1}.

Anal. Calcd for $C_{16}H_{17}F_9O_6$: C, 40.34; H, 3.60. Found: C, 40.66; H, 3.59.

Hydride Transfer. To 4.0 g (21.5 mmol) of tricyclopropylcarbinol and 3.3 g (25.0 mmol) of triethylsilane in 80 ml of methylene chloride was added 4.8 g (42.0 mmol) of trifluoroacetic acid and the reaction quenched with solid sodium carbonate after 30 min. After distilling the methylene chloride through a column, the residue was distilled on an 8-in. spinning-band column. The fraction boiling at 64–65° (20 torr) was *ca.* 73% pure by glpc and the main product was isolated by preparative gas chromatography: nmr spectrum—the only peaks present appeared as a complex multiplet from δ 1.0 to −0.2. This spectrum as well as the ir was identical with that reported[21] by Hart and Law for tricyclopropylmethane (**3c**).

4,4-Dicyclopropyl-3-butenyl Trifluoroacetate. A solution of **1c** (3.09 g, 16.5 mmol), 9.28 g of trifluoroacetic anhydride (44.0 mmol), and 3.6 ml of pyridine (44.0 mmol) in 50 ml of methylene chloride was stirred at 0° for 2 hr, acidified with 2 *N* HCl, and washed with water. After drying (Na_2CO_3) and evaporation of the methylene chloride the crude product (4.14 g, 100%) was distilled at 82–83° (2 torr) to give 1.77 g (43%) of **2c**; $n^{24}D$ 1.4310; nmr spectrum =C*H* (δ 5.09, triplet, J = 7 Hz), $-CH_2O$ (δ 4.40, triplet, J = 7 Hz), $=CCH_2$ (δ 2.64, quartet, splitting of 7 Hz), cyclopropylmethine *H* (δ 1.5–1.9, multiplet), cyclopropyl CH_2 (δ 0.2–1.1, multiplet). This compound did not keep well on storage and the analysis, while not satisfactory, is close to the calculated value.

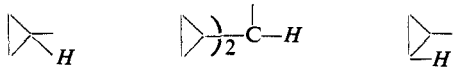
Anal. Calcd for $C_{12}H_{15}F_3O_2$: C, 58.06; H, 6.09. Found: C, 57.45; H, 6.13.

Treatment of **1c** with trifluoroacetic acid in methylene chloride for 30 min and analysis by glpc resulted in the formation of **2c** and a higher boiling one, probably the bistrifluoroacetate, in about equal amounts. **2c** was not present in the hydride transfer product from **1c** but was itself converted by protonation and hydride transfer to 4,4-dicyclopropylbutyl trifluoroacetate (**7**).

4,4-Dicyclopropyl-1-butyl Trifluoroacetate (7). To 1.77 g (7.1 mmol) of **2c** and 1.36 g (8.5 mmol) of triethylsilane in 28 ml of methylene chloride was added 1.99 g (14.2 mmol) of trifluoroacetic acid. After 14 hr anhydrous sodium carbonate was added and the solvent removed to leave 1.68 g of **7** (95%) as a colorless liquid homogeneous to glpc. Evaporative distillation afforded the analytical sample (trifluoroacetate carbonyl at 1780 cm^{-1}): nmr spectrum $-CH_2O$ (δ 4.38, triplet, J = 7 Hz), $-CH_2CH_2CH_2O$- and A (δ 1.3–2.2, multiplet), B and C (δ −0.2 to 1.0, multiplet). There were no signals in the vinyl region.

Anal. Calcd for $C_{12}H_{17}F_3O_2$: C, 57.59; H, 6.85. Found: C, 57.46; H, 6.89.

(21) P. Law, Ph.D. Thesis, Michigan State University, 1962. We thank Professor Hart for copies of these spectra.



A B C

Cyclopropylphenylcarbinol (1d). Reaction with Trifluoroacetic Acid. To 1 g (6.75 mmol) of cyclopropylphenylcarbinol in 10 ml of methylene chloride was added 2 ml of trifluoroacetic acid. After 4 hr the solution was shaken with 30 ml of saturated sodium bicarbonate solution, dried over magnesium sulfate, and evaporated to leave 1.43 g (88%) of *trans*-4-phenyl-3-butenyl trifluoroacetate (**2d**) as a yellow syrup which gave a single peak on glpc. The analytical sample was purified by evaporative distillation at 100° (0.2 torr): nmr spectrum C_6H_5- (δ 7.40, singlet), HC=CH (δ 5.85-6.75, eight-line spectrum in which the coupling constant between the two vinyl protons is 15.8 Hz and the higher field doublet is further split into triplets by coupling with the C=CCH_2 protons, J = 6.2 Hz), CH_2O (δ 4.45, triplet, J = 6.9 Hz), C=CCH_2- (δ 2.60, quartet, splitting ~7 Hz).

Anal. Calcd for $C_{12}H_{11}F_3O_2$: C, 59.02; H, 4.54. Found: C, 58.84; H, 5.19.

Hydride Transfer. Trifluoroacetic acid (2 ml) was added to 1.48 g (10 mmol) of **1d** and 2.60 g (10 mmol) of triphenylsilane in 40 ml of methylene chloride at −15°. After 0.5 hr solid K_2CO_3 was added, the solution filtered, and the solvent evaporated through a 10-cm Vigreux column. The residue was chromatographed on 20 g of Woelm silica gel and eluted with pentane. After distillation of the pentane through the Vigreux column 633 mg (48%) of phenylcyclopropylmethane was obtained which had an nmr spectrum identical with authentic material.

Dicyclopropylcarbinol (1e). Reaction with Trifluoroacetic Acid. A solution of 4.88 g (44.0 mmol) of dicyclopropylcarbinol and 10.0 g (88.0 mmol) of trifluoroacetic acid in 70 ml of methylene chloride was refluxed for 2 hr then neutralized (Na_2CO_3). The solution was filtered, the solvent removed, and the residue distilled to give 3.07 g (33%) of *trans*-4-cyclopropyl-3-butenyl trifluoroacetate (**2e**) (bp 74–76° (6 torr)). The infrared spectrum showed a carbonyl band at 1780 cm^{-1} and C=C at 1660 cm^{-1}. The vinyl region of the nmr spectrum was quite complex but corresponded to a first approximation to the expected pattern for **2e**. The vinyl protons form an AB system with a coupling constant of 16 Hz. The vinyl proton β to the cyclopropyl ring is split further into a doublet of triplets (J = 6 Hz) by the =CCH_2 protons and the vinyl proton on the same carbon atom as the cyclopropyl ring is split by the cyclopropyl methine proton to give a doublet of doublets (J = 7 Hz). The expected first-order spectrum consists of ten lines for the vinyl protons while the observed spectrum shows nine distinct signals with one being much stronger than expected and, therefore, is concluded to result from overlap of two peaks. These peaks appear from δ 5.7 to 4.8: -CH_2O (δ 4.34, triplet, J = 7 Hz), =CCH_2 (δ 2.39, quartet, J = 7 Hz), cyclopropylmethine H (δ 1.2–1.6, multiplet), cyclopropylmethylene H (δ 0.18–1.0, multiplet).

Anal. Calcd for $C_9H_{11}F_3O_2$: C, 51.92; H, 5.33. Found: C, 51.72; H, 5.41.

1-Cyclopropylcyclohexanol. Lithium sand (2.1 g, 0.3 g-atom) was stirred in 200 ml of dry ether while 13.8 g (0.14 mol) of cyclopropyl bromide was added while cooling an ice bath. The solution was stirred 1 hr then 11.7 g (0.12 mol) of cyclohexanone in 100 ml of dry ether was added. After stirring for 3 hr at 0° and 28 hr at 25°, after hydrolysis, drying, and evaporation, the residue was distilled (8 torr) through a 8-in. silver-jacketed column. Fraction **1** (1.25 g, bp 64–70°) was 40% **1f**:60% cyclohexanone by glpc. Fraction 2 (3.9 g, bp 71–75°) was 67% **1f**:33% cyclohexanone. Fraction 3 (6.2 g, bp 78–81°) was 97% pure **1f** and was used in the reactions described. The analytical sample was obtained by preparative glpc.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50; Found: C, 76.77; H, 10.75.

Reaction of 1f with Trifluoroacetic Acid. Trifluoroacetic acid (2.28 g, 20 mmol) was added to a solution of 1.4 g (10 mmol) of **1f** in 40 ml of methylene chloride and the solution neutralized with potassium carbonate after 0.5 hr. Evaporation of the solvent left 1.24 g of crude product (52%). The analytical and nmr samples were purified by glpc: nmr spectrum =CH (δ 5.05, triplet, J = 7.5 Hz), -CH_2O- (δ 4.25, triplet, J = 7 Hz), =CCH_2- (δ 2.4, quartet, J = 7 Hz), ring =CCH_2- (2.1, multiplet), ring $CH_2CH_2CH_2$- (δ 1.45, broad singlet).

Anal. Calcd for $C_{11}H_{15}F_3O_2$: C, 55.92; H, 6.40. Found: C, 55.90; H, 6.47.

Hydride Transfer. To 1.4 g (10 mmol) of **1f** and 3.12 g (12 mmol) of triphenylsilane in 40 ml of methylene chloride at −10° was added 2.28 g (20 mmol) of trifluoroacetic acid. The reaction mixture was worked up in the usual fashion after 0.5 hr and the residue chromatographed on 10 g of alumina. Elution with 70 ml of pentane and removal of the pentane afforded **3f** (1.30 g, 100%) which was homogeneous to glpc and was further purified by distillation through a short-path column to give 0.95 g (76%) of pure material (bp 59–60° (15 torr), $n^{23}D$ 1.4540) (lit.[22] bp 157.6° (760 torr), $n^{20}D$ 1.4538): nmr spectrum: multiplets for cyclohexyl ring protons from δ 1 to 2 and cyclopropyl ring protons from δ 0.5 to −0.05.

Anal. Calcd for C_9H_{16}: C, 87.01; H, 12.99. Found: C, 86.69; H, 12.62.

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(22) P. J. C. Fierens and J. Nasielski, *Bull. Soc. Chim. Belges*, **71**, 187 (1962).