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SOLVOLYTIC BEHAVIOR OF SILICON-SUBSTITUTED CYCLOPROPYLCARBINYL TRIFLUOROACETATES[1]

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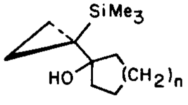
Summary: Through solvolysis in 2,2,2-trifluoroethanol, 1-trimethylsilylcyclopropylcarbinyl trifluoroacetate and its *cis*- and *trans*-2-substituted isomers are shown to be 25-45 times more reactive toward ionization than the parent unsubstituted system.

The cyclopropylcarbinyl-cyclobutyl-homoallyl interchange has fostered many kinetic studies,[2] NMR investigations,[3] and theoretical calculations.[4] Although enhanced solvolytic rates have led to proposals that a common, highly stabilized intermediate is produced, no concensus has been reached as to its true nature. A composite of "extreme" contributing resonance structures may be involved.[5]

Customarily, a β-silicon atom, if properly aligned stereoelectronically, so strongly accelerates the departure of a leaving group that elimination results.[6] Exceptions to this general rule have recently surfaced in trimethylsilyl substituted cyclopropane systems where elimination would have generated a methylenecyclopropane product and introduced significant additional strain.[7,8] The smooth, acid-catalyzed dehydration of 1 without rearrangement,[7] the boron trifluoride etherate-promoted isomerization of 2 to 2-((1-trimethylsilylcyclopropyl)-cycloalkanones,[7] and the transformation of 3 into 1-(trimethylsilyl)cyclopropyl alkenes upon solvolysis in refluxing *tert*-butyl alcohol[8] are exemplary.



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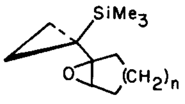

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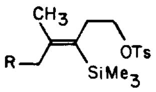

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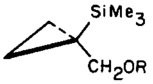
Because the particular kinetic sensitivities of the trimethylsilyl group in these "abnormal" settings were unknown, we have chosen to examine the kinetic behavior of trifluoroacetates 4b-6b. Involvement of the silicon atom via inductive or comparable through-bond influences,[9] or by vertical stabilization[10] where possible was believed probable, whereas the formation of bicyclic siliconium ions by neighboring group participation was not (excessive ring strain). The manner in which these modes of stabilization would partition relative to those normally available to a developing cyclopropylcarbinyl cation was unclear.

Alcohol 4a was available from an earlier study.[11] Two approaches to 5a and 6a were examined. In the first, trimethylvinylsilane was treated with dibromocarbene generated from bromoform under phase transfer conditions (20%)[12] or preferably from phenyl(tribromomethyl)-

mercury in refluxing benzene (50%).[13] Following monodebromination with methylmagnesium bromide in tetrahydrofuran,[14] the combined action of cold (-78°C) *tert*-butyllithium and formaldehyde gave the epimeric alcohols (29%). MPLC separation on silica gel gave pure **5a** and **6a** which were identified by the splitting patterns of their $-C\underline{H}_2OH$ absorptions (<u>AB</u>X) at 300 MHz (Figure 1). A more efficient and stereochemically unequivocal route to these products entailed Simmons-Smith cyclopropanation ($EtZnI$, CH_2I_2) of the pure <u>Z</u>-and <u>E</u>-isomers of 1-(trimethylsilyl)propen-3-ol[15] (65%). The trifluoroacetates[16] were purified by VPC before use.



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a, R = H ; **b**, R = $COCF_3$; **c**, R = CH_2CF_3

In order to minimize the effect of external nucleophiles,[17] the solvolysis rates were determined in 2,2,2-trifluoroethanol (ampoule technique) involving titration of the liberated acid with sodium methoxide (mixed bromothymol blue-bromocresol purple indicator, Table I). The use of theoretical infinity titers was made necessary because of the nonideality of the experimental infinity values (80% for **4b** and **5b**; 70% for **6b**). Good first-order kinetics were observed throughout. Nonetheless, several conductometric kinetic measurements[18] were carried out in 97% trifluoroethanol to verify the titrimetric results.[19]

At 50.3°C, **4b** was cleanly converted ($CaCO_3$ as buffer) to a mixture of **4c** (20%), **7a** (20%),[20] and **7b** (60%). The unreactivity of **7a** to the reaction conditions (10 half-lives) revealed it to be singularly responsible for the lowered acid production in this example. Where **5b** and **6b** are concerned, extensive degradation to lower molecular weight substances occurred. Characterization of these materials has been hampered by their coelution with solvent during VPC and/or fragmentation under GC-MS conditions (no M^+ ions observed). On a more positive note, the solvolysis mixture from **5b** (79.9°C, $CaCO_3$, 11 h) delivered a less volatile fraction (25%) consisting of **5c** (70%), a 1,3-disubstituted cyclobutane presumed to be the trans isomer **8** (20%),[21a] and an unidentified ester (< 10%). For **6b** (79.7°C, $CaCO_3$, 5 h), the major less volatile product **9**[21b] is clearly isomeric with **8**.

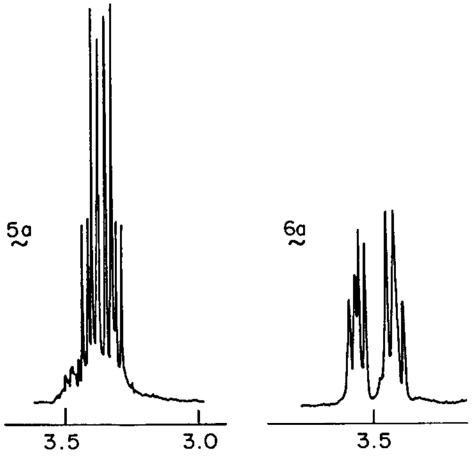


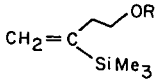
Figure 1. Partial 300 MHz ^1H NMR spectra of **5a** (left) and **6a** (right) ($CDCl_3$ solution).

Significantly, the rate enhancement produced by positioning a Me_3Si group at C_1 and C_2 of cyclopropylcarbinyl trifluoroacetate (**10**) are appreciable (25 to 45-fold), though not excessively large as in cyclohexyl

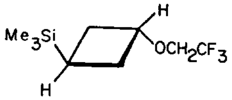
Table I. First-Order Rate Data for Solvolysis of **4b**-**6b** in 2,2,2-Trifluoroethanol

Compd	Temp, °C	$k \times 10^5$, $\sec^{-1}$ [a]	$\Delta H^{\ddagger}$(25°C), kcal/mol	$\Delta S^{\ddagger}$(25°C), eu	k_{rel}
4b	50.30	0.869	21.0	-17.0	27
	65.15	3.89			
	79.70	14.2			
5b	50.30	0.828[b]	20.6	-18.1	25
	65.15	4.04			
	79.70	12.9			
6b	50.30	1.10[b]	23.1	-10.0	45
	65.15	5.90			
	79.70	23.6			
10	79.70	0.524[b]	----	----	1

[a] Average of two determinations. [b] The theoretical infinity titers were used. The rate constants using experimental infinity titers are: **5b**, 1.21, 5.19, 19.6; **6b**, 2.30, 11.9, 45.6.



7a, R = $COCF_3$
b, R = CH_2CF_3



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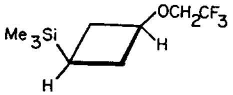

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systems.[9] The earlier Schleyer-Van Dine study of methyl substituent effects (5 to 11-fold acceleration) on cyclopropylcarbinyl solvolysis rates[22] allows us to deduce that additional acceleration is attainable when a trimethylsilyl group is present. The faster rate for **6b** is probably due to ground state strain. The entirely comparable kinetic behavior of **4b** and **5b** reveals that direct neighboring group participation does not operate in the first instance. All in all, through bond effects appear to be at the root of the accelerative influences which are low because of charge dispersal.[23]

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(19) Our observations that the conductometric rate constants averaged 1.4 times faster than those derived titrimetrically likely derive from the presence of 3% water.

(20) Independently prepared from 1-(trimethylsilyl)vinyl bromide by sequential reaction with magnesium, ethylene oxide, and trifluoroacetic anhydride in pyridine.

(21) (a) ^{1}H NMR (CDCl$_3$) δ 4.02 (quint, *J* = 7.5 Hz, 1 H), 3.71 (q, *J* = 9 Hz, 2 H), 2.3-2.1 (m, 4 H), 1.45 (m, 1 H), -0.10 (s, 9 H); ^{13}C NMR (CDCl$_3$) ppm 74.78, 65.56, 31.38, 11.66, -3.60 (CF$_3$ not observed). (b) ^{1}H NMR (CDCl$_3$) δ 4.09 (quint, *J* = 7.5 Hz, 1 H), 3.71 (q, *J* = 9 Hz, 2 H), 2.21 (m, 2 H), 1.77 (m, 2 H), 1.09 (m, 1 H), -0.3 (s, 9 H).

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