Table I. F^{19} and H^1 Nmr Shifts of Pentafluorophenylcarbonium Ions (in ppm from CCl_3F and TMS)

	Methyl alcohol, halide				Carbonium ion			
	δ_{CH}[b]	ϕ_{ortho}[a]	ϕ_{meta}[a]	ϕ_{para}[a]	δ_{CH}	ϕ_{ortho}	ϕ_{meta}	ϕ_{para}
Tris(pentafluorophenyl)-methyl alcohol		+140.98	+161.54	+152.22		+126.25	+154.29	+112.12[c]
Bis(pentafluorophenyl)-methyl alcohol	−3.67	+144.17	+162.28	+153.69	~[−9.30]	+111.61	+153.86	+100.36[c]
Pentafluorophenyl methyl fluoride α-F: ϕ = +211.74 J_{HF} = 47.8 Hz	−5.47	+143.57	+162.53	+152.27	−9.60	+103.18	+151.53	+ 74.89[d]

[a] In $CDCl_3$ at 25° from internal CCl_3F. [b] In SO_2 at −20° from TMS capillary. [c] In FSO_3H–SbF_5–SO_2 at 60° from CCl_3F in a separate tube (F^{19}) or TMS capillary (H^1). [d] In SbF_5–SO_2 at −60° from CCl_3F in a separate tube (F^{19}) or TMS capillary (H^1).

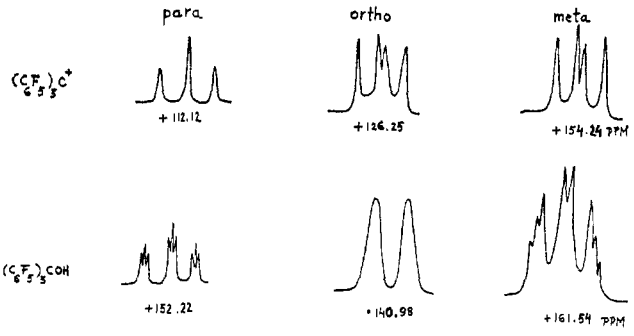
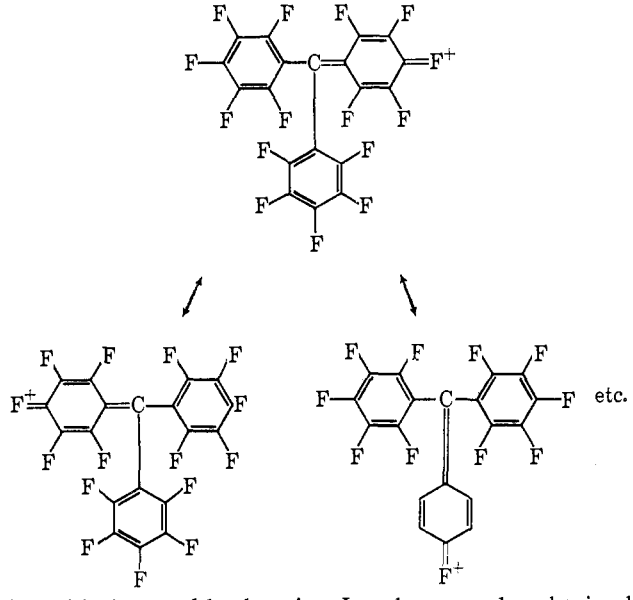
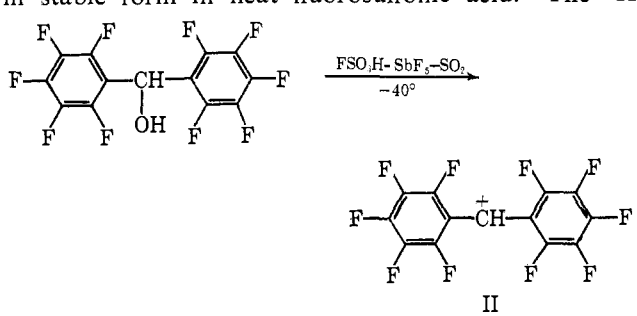


Figure 1.

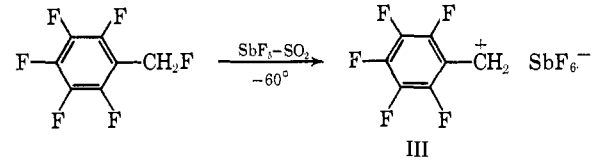
be generated from bis(pentafluorophenyl)carbinol[6] in FSO_3H–SbF_5–SO_2 solution at −60°. Ion II is considerably less stable than ion I and cannot be obtained in stable form in neat fluorosulfonic acid. The ^1H and ^{19}F nmr data of ion II together with those of the starting alcohol are summarized in Table I. The deshielding pattern of the ring fluorine atoms follows that of ion I. The aliphatic methine proton in ion II is partially masked by the solvent acid.



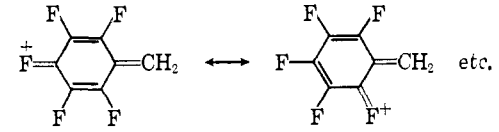


II

Pentafluorophenylcarbonium ion (III) was obtained from pentafluorobenzyl fluoride (prepared from pentafluorobenzyl bromide[6] and HgF_2) in SbF_5–SO_2 solution at −60°. The methylene protons in ion III are at −9.60 ppm. The deshielding effect of the ring fluorine is very substantial in the *para* and *ortho* positions, which can be well explained assuming strong contributions from the quinoidal forms.



III



The *m*-fluorine peaks in II and III have almost identical appearances to the *m*-fluorines of I (Figure 1). The *o*- and *p*-fluorine resonances in II and III are considerable broadened, indicating long-range coupling to the α-hydrogen(s). This broadening is more noticeable for the *p*-fluorines (substantiating a stronger contribution from the *p*-quinoidal resonance forms) and, as expected, is greater for III than for II.

All nmr spectra were obtained on a Varian Model A56-60A spectrometer, equipped with a variable-temperature probe and operated at 56.4 and 60 MHz.

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(6) Obtained from Imperial Smelting Ltd., Bristol, England.

(7) National Science Foundation predoctoral research investigator.

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Cyclopropanones. V. Inhibition of Polymerization and Addition of Acids[1]

Sir:

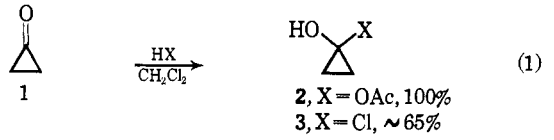
A simple, high-yield preparation of cyclopropanone (**1**) has recently been reported.[1] However **1** was found to polymerize rapidly at room temperature, and only

(1) See N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966), for paper IV.

study of its reactions which occurred smoothly at low temperatures appeared feasible. We have now found that addition of molar quantities of acetic anhydride or acetyl chloride to methylene chloride solutions of **1** retards polymerization substantially, so that **1** possesses a half-life of the order of days at room temperature, in the presence of these polymerization inhibitors.[2]

2,2-Dimethylcyclopropanone is reported to yield a mixture of α-chloro ketones upon treatment with dry hydrogen chloride.[1,3] We wish to report now the results of addition of hydrogen chloride and acetic acid to **1**.

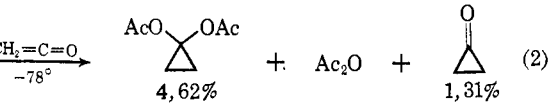
Addition of an excess of acetic acid or hydrogen chloride to methylene chloride solutions of **1** (at 25° in the presence of inhibitors or at −78° in the absence of inhibitors) results in high yields of 1-acetoxy-1-hydroxycyclopropanone (**2**) and 1-chloro-1-hydroxycyclopropane (**3**), respectively.[4] Both compounds decompose slowly at room temperature.



(1)

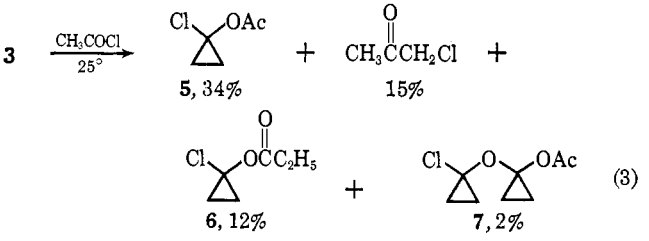
The nmr spectrum of **2** shows an A_2B_2 pattern centered at τ 8.9, and the nmr spectrum **3** shows a singlet at τ 8.7. The reaction of **1** and acetic acid is reversible even at −78°. For example, addition of excess ketene to a CH_2Cl_2 solution of **2** results in formation of 1,1-diacetoxycyclopropane (**4**), acetic anhydride, *and cyclopropanone.*

Compound **4** shows nmr absorption at τ 7.87 (singlet, 6 H) and 8.76 (singlet, 4 H); infrared absorption at 1755, 1210, 1150, and 1000 cm^{-1}.



(2)

Addition of excess acetyl chloride to CH_2Cl_2 solutions of **3** results in partial acylation to yield 1-chloro-1-acetoxycyclopropane (**5**), chloroacetone, 1-chloro-1-propionyloxycyclopropane (**6**), and **7**.



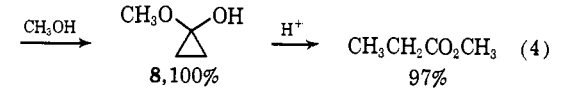
(3)

Compound **5** shows nmr absorption[5] at τ 8.7 (singlet, 4 H) and 7.9 (singlet, 3 H). Its mass spectrum shows (*inter alia*) peaks at *m/e* 136, 134 (M^+, weak), 99 (M^+ − Cl), 56 (M^+ − CH_3CO_2Cl), 43 (CH_3CO^+); infrared absorption at 3015, 1775, 1210, and 1030 cm^{-1}.

Compound **6** shows nmr absorption at τ 8.76 (triplet, J = 7 cps, 3 H), 8.60 (multiplet, 4 H), and 7.45 (quartet, J = 7 cps, 2 H). Its mass spectrum shows (*inter alia*) peaks at *m/e* 150, 148 (M^+) 77, 75 (M^+ − $C_2H_5CO_2$), 57 ($C_2H_5CO^+$), 56 (M^+ − $C_2H_5CO_2Cl$); infrared absorption at 1770 cm^{-1}.

Compound **7** shows nmr absorption at τ 8.5–9 (multiplet, 8 H) and 7.9 (singlet, 3 H).

Further evidence for the structures of **2** and **3** is derived from their reaction with methanol to yield the methyl hemiketal of cyclopropanone, **8**, which in turn is smoothly converted to methyl propionate in the presence of acid.

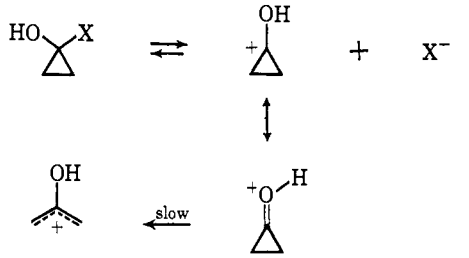


(4)

The occurrence of a double bond exocyclic to a three-membered ring is expected to confer high reactivity to a molecule because of the strong driving force from sp^2 toward sp^3 hybridization (I strain).[6]

The low rate of solvolytic displacements of cyclopropyl tosylates indicates that the cyclopropyl cation requires high activation for formation. When it does form, rearrangement to the more stable allyl cation usually follows rapidly.[7-9]

Our results imply that the activation energy for formation of the 1-hydroxycyclopropyl cation from **2** or **3** is indeed very low. This result is somewhat surprising in view of the small rate enhancements often observed when carbonium ion stabilizing substituents are substituted at C-1 in the cyclopropyl cation.[10,11]



It is of further interest that the presumed intermediate cation does not rearrange rapidly to an allylic cation.[10]

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(2) The role of these "inhibitors" is not completely clear at this time. Presumably, these compounds serve as scavangers for traces of moisture or bases which could initiate the polymerization.

(3) The products in this case were isolated after a work-up procedure. An attempt to observe precursors to these α-chloro ketones is being made.

(4) (a) Although hemiacylals are known, we are unaware of any reports of the preparation of an α-chlorohydrin. For a review see C. D. Hurd, *J. Chem. Educ.*, **43**, 527 (1966). (b) Compounds **2** and **3** were not isolated, but were characterized by their nmr spectra in CH_2Cl_2 solution and by their reactions with ketene and methanol. Compounds **4** through **8** were isolated and purified by preparative vpc and characterized by spectral data.

(5) Methylene chloride solution, TMS external standard.

(6) Evidence for an equilibrium between cyclopropanones and their hemiketals is available: H. H. Wasserman and D. C. Clagett, *J. Am. Chem. Soc.*, **88**, 5368 (1966); N. J. Turro, W. B. Hammond, P. A. Leermakers, and H. T. Thomas, *Chem. Ind.* (London), 990 (1965).

(7) J. D. Roberts and V. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).

(8) J. D. Roberts and V. Chambers, *ibid.*, **73**, 5034 (1951).

(9) R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 256–259.

(10) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wridemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965).

(11) P. von R. Schleyer, G. W. Van Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(12) Fellow of the Alfred P. Sloan Foundation.

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