Stable Carbonium Ions. XXIV.[1] Trifluoromethylcarbonium Ions, Protonated Trifluoromethyl Alcohols, and Protonated Fluoro Ketones

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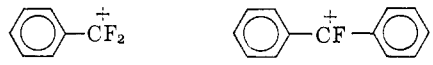
Abstract: Using the previously developed methods for carbonium ion formation, the trifluoromethyldiphenyl- (III), trifluoromethylcyclopropylphenyl- (IV), and trifluoromethylmethylphenylcarbonium (V) ions were obtained from the corresponding alcohols in FSO_3–SbF_5–SO_2 solution at low temperature. Bis(trifluoromethyl)methanols are only protonated and do not form bis(trifluoromethyl)carbonium ions. A series of protonated fluoro ketones, useful as models of fluorinated carbonium ions, were also obtained and investigated.

The observation of the first stable fluorocarbonium ions, the phenyl-(I) and diphenylfluorocarbonium (II) ions, was recently reported.[2] It thus is obvious that fluorine directly attached to the electropositive sp^2-hybridized carbon atom of the carbonium ions exerts a substantial stabilizing effect, as the unbound fluorine



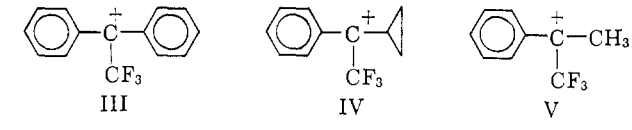
I II

electron pairs conjugate into the vacant p orbital. This is shown by the large downfield shifts of the F^{19} nmr of the ions relative to their precursor compounds.

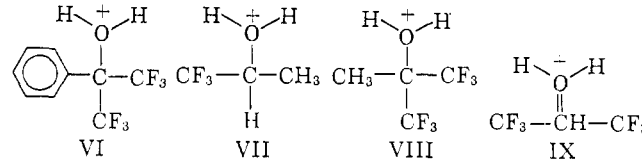
Whereas fluorine substitution directly on the carbonium ion carbon atom is highly stabilizing, fluorine substitution adjacent or further removed, because of the high electronegativity of fluorine, would be expected to destabilize carbonium ions. In order to test the effect of fluorine substitution on carbonium ion stability, it seemed of interest to investigate trifluoromethylcarbonium ions and the behavior of their alcoholic precursors in strongly acidic solvent systems. Since protonated ketones can serve as models for carbonium ions, the investigations were also extended to the protonation of fluoro ketones.

Results and Discussion

Using the method developed previously[3] for generating stable carbonium ions from their corresponding alcohols in FSO_3H–SbF_5–SO_2 at low temperature, we have now observed the trifluoromethyldiphenyl- (III) trifluoromethylcyclopropylphenyl- (IV), and trifluoromethylmethylphenylcarbonium (V) ions. Though trifluoromethyl groups destabilize carbonium ions, there is sufficient conjugative stabilization in ions III–V to permit their observation. However, if a second CF_3 group is added (as in VI) or conjugative stabilization is absent (as in VII–IX) only protonated alcohols and not carbonium ions are formed. The nmr positions of the protons in a wide variety of carbonium ions are now well known.[4] The H^1 band position and the change in chemical shift from the alcohol to the ion in ions III–V are very close to the values observed for



III IV V



VI VII VIII IX

the known alkylcarbonium ions where the CF_3 group is replaced by a CH_3.[4,5] Furthermore, the $\Delta\phi$ shift of the CF_3 group from the alcohol to the ion is larger for the carbonium ions (III–V) than for either protonated fluoro ketones (see subsequent discussion) or the protonated alcohols VI–IX. The F^{19} and H^1 nmr chemical shifts of all investigated ions and their precursor alcohols are summarized in Table I.

Among ions III–V, III with delocalization of charge into two phenyl rings shows, as expected, the smallest $\Delta\phi$ for the CF_3 group (−7.6 ppm) compared to −24.8 ppm in ion V where only one phenyl ring delocalizes the charge. $\Delta\phi$ going from the alcohols to the corresponding protonated alcohols in VI–IX is between −1.6 and −2.8 ppm. The protonated alcohols also exhibit smaller proton shifts than the corresponding carbonium ions.

As fluorines are progressively added α to a hydroxyl group, the acidity of the alcohol increases rapidly. 1,1,1-Trifluoro-2-propanol is 10^4 times as acidic as 2-propanol, while 1,1,1,3,3,3-hexafluoro-2-propanol is 10^6 times more acidic. Perfluorinated primary alcohols of the type $CF_nF_{2n}CH_2OH$ are 10^6 times as acidic as their parent alcohols.[7] Thus in the series VI to IX, C–OH ionization to carbonium ions does not take place even in FSO_3H–SbF_5–SO_2 but the alcohols are quantitatively protonated.

Protonated fluoro ketones can serve as models for fluorocarbonium ions. Concentrated H_2SO_4 is known

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(2) G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 362, (1966).

(3) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997, (1965).

(4) For a review, see N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(5) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998, (1965).

(6) F. Swarts, *Bull. Soc. Chim. Belges*, **38**, 99 (1929).

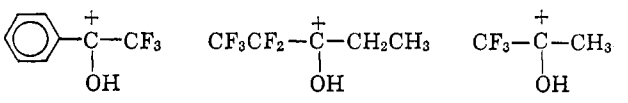
(7) A. L. Henne and W. C. Francis, *J. Am. Chem. Soc.*, **75**, 991, (1953).

Table I. F^{19} and H^1 Nmr Shifts (ppm) of Trifluoromethyl Alcohols (in SO_2) and Their Corresponding Trifluoromethylcarbonium Ions (in SO_2-SbF_5-FSO_2H) or Protonated Alcohols (in SO_2-SbF_5-FSO_3H) (from External CCl_3F and TMS, Respectively)

Alcohol, and carbonium ion or protonated alcohol	CF_3		CH_3		Cyclopropyl H	>CH—OH	OH	Phenyl H main peak	
	ϕ	$\Delta\phi$	δ	$\Delta\delta$				δ	$\Delta\delta$
III-OH	74.1						−3.4	−7.09	
		−7.6							−0.92
III	66.5							−8.01	
IV-OH	78.4				α −1.30		−2.59	−7.18	
		−9.1			β +0.2 to −0.35				−0.67
IV	69.3				−2.0 to −3.0[a]			−7.85	
V-OH	81.1		−1.31				−3.01	−7.12	
		−24.8		−1.99					−1.18
V	56.3		−3.30					−8.30	
VI(−H)	75.2						−4.16	−7.27	
		−1.6							−0.36
VI	73.6							−7.63	
VII(−H)	82.4[b]		−0.71[d]			−3.54[f]	−2.51		
		−2.0		−0.76					
VII	80.4[c]		−1.47[e]			−5.09[a]			
VIII(−H)	84.2[g]		−0.90[h]				−3.05		
		−2.3		−0.90					
VIII	81.9[a]		−1.80[a]						
IX(−H)	75.1[i]					−4.27[j]	−4.06		
		−2.8							
IX	72.3[i]					−5.05[j]			

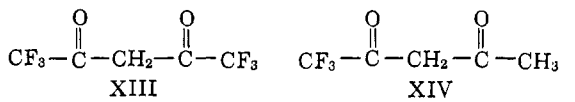
[a] Broadened. [b] Doublet, $J_{H\text{-}F}$ = 7.5 cps. [c] Doublet, $J_{H\text{-}F}$ = 5.7 cps. [d] Doublet, $J_{H\text{-}H}$ = 6.5 cps. [e] Doublet, $J_{H\text{-}H}$ = 7 cps. [f] Multiplet. [g] Quartet, $J_{H\text{-}F}$ = 1 cps. [h] Multiplet (heptet?), $J_{H\text{-}F}$ = 1 cps. [i] Doublet, $J_{H\text{-}F}$ = = 6 cps. [j] Heptet, $J_{H\text{-}F}$ = 6 cps.

to quantitatively protonate aliphatic ketones,[8] but fluorines α to the carbonyl group progressively lower the basicity of the carbonyl oxygen requiring a stronger acidity for protonation. We have found that SbF_5-FSO_3H in SO_2 solution at −60° will quantitatively protonate ketones with up to three α-fluorine atoms. 1,1,1-Trifluoroacetophenone, pentafluoroethyl ethyl ketone, and 1,1,1-trifluoroacetone were fully protonated (X–XII) as shown by the downfield fluorine and hydrogen shifts in the nmr spectra of acid solutions of the ketone (relative to SO_2 solutions of the same ketones). The downfield shifts of the α and β hydro-

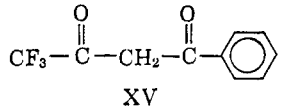


X XI XII

gens agreed well with known shifts of protonated aliphatic ketones. The fluoro β-diketones (XIII, XIV,

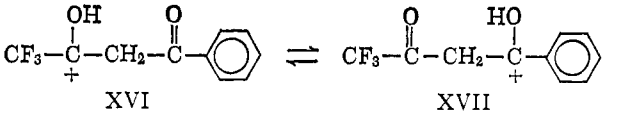


XIII XIV



XV

XV) were readily protonated, even hexafluoroacetylacetone (XIII), as shown by the shift of both the CH_2 (−0.71 ppm) and CF_3 (−3.39 ppm) group going from the unprotonated to protonated form. The equivalency of the CF_3 groups (assuming only monoprotonation as the observed deshielding effects are not compatible with diprotonation) indicates either rapid equilibration of the proton with solvent or rapid proton equilibration between the two carbonyl groups. The large shift $\Delta\phi$ of the CF_3 group in benzoyltrifluoroacetone indicates that protonation at the carbonyl group adjacent to the CF_3 group (XVI) makes a significant contribution along with the form with the proton on the carbonyl adjacent to the phenyl group (XVII).



XVI XVII

1,1,3,3-Tetrafluoroacetone (XVIII) and hexafluoroacetone (XIX), with four and six α-fluorine atoms, respectively, could not be protonated even in the extremely acidic solvents used.

The chemical shifts of the investigated fluoro ketones and the protonated fluoro ketones are summarized in Table II. The magnitude of the downfield shift for the α fluorines (usually $\Delta\phi$ = ~3.5 ppm) is larger than that of protonated aliphatic fluoro alcohols and smaller than that of a CF_3 group α to the positively charged carbon atom at a carbonium ion[2] indicating both forms XX and XXI make significant contributions to the true structure.

XX XXI

Experimental Section

1,1,1-Trifluoro-2-propanol, α,α,α-trifluoroacetophenone, pentafluoroethyl ethyl ketone, 1,1,1-trifluoroacetone, hexafluoroacetone, hexafluoroacetylacetone, and trifluoroacetylacetone were obtained

(8) H. J. Campbell and J. T. Edwards, *Can. J. Chem.*, **38**, 2109, (1960).

Table II. F^{19} and H^1 Nmr Shifts (ppm) of Fluoro Ketones (in SO_2) and Protonated Fluoro Ketones (in SO_2–SbF_5–FSO_3H) at −60° (from external CCl_3F and TMS, Respectively)

Ketone, and protonated ketone[i]		α F	Δφ	β F	Δφ	α H	Δδ	β H	Δδ	Phenyl H (main peak)	Δδ
X(−H)	SO_2	71.0								−6.90 to −7.66	
			−7.6								−0.8
X	Acid	63.4								−7.83 to −8.97	
XI(−H)	SO_2	124.5[c]		83.4[d]		−2.47[e]		−0.59[f]			
			−3.5		−2.0		−1.33		−0.61		
XI	Acid	121.0[g]		81.4[h]		−3.80[i]		−1.20[i]			
XII(−H)	SO_2	80.1[a]				−1.92[a]					
			−3.5				−1.42				
XII	Acid	76.6[b]				−3.34[b]					
XIII	SO_2	77.3				−6.25					
			−3.4				−0.71				
XIII(+H)	Acid	73.9				−6.96					
XIV	SO_2	85.6				−5.75 CH_2		−1.79 CH_3			
			−1.4				−1.14		−1.11		
XIV(+H)	Acid	84.2				−6.89		−2.90			
XV	SO_2	76.5				−6.40				−7.25 to −7.71	
			−3.4				−0.65				−0.4
XV(+H)	Acid	73.1				−7.05				−7.36 to −8.40	
CF_2H—C(=O)—CF_2H	SO_2	133.3[k]				−6.14[k]					
			−0.1								
XVIII	Acid	133.2				−6.30[k]	−0.16				
CF_3—C(=O)—CF_3	SO_2	84.0									
			+0.1								
XIX	Acid	84.1									

[a] J_{HF} = 1.1 cps quartet. [b] J_{HF} = 1.3 cps quartet. [c] Quartet, J_{FF} = 1 cps. [d] Triplet, J_{FF} = 1 cps. [e] Quartet, J_{HH} = 7 cps. [f] Triplet, J_{HH} = 7 cps. [g] Quartet, J_{FF} = 2.5 cps. [h] Triplet, J_{FF} = 2.5 cps. [i] Quartet, J_{HH} = cps. [j] Triplet, J_{HH} = 6 cps. [k] J_{F-H} = 54.5; J_{FCCCH} = 5 cps. [l] In all cases, the top line of each group refers to the ketone and the second and third lines refer to the protonated ketone.

from Peninsular Chemresearch, Inc. Phenylbis(trifluoromethyl)-methanol, 1,1,1-trifluoro-2-trifluoromethyl-2-propanol, trifluoroacetylacetophenone, and 1,1,1,2,2,2,-hexafluoro-2-propanol were obtained from the Pierce Chemical Co.

Diphenyltrifluoromethylmethanol. Trifluoroacetophenone (29 g, 0.123 mole) in 100 ml of diethyl ether was added dropwise to a solution of phenyllithium (12.4 g, 0.145 mole) in hexane (Foote Mineral Co.). An immediate exothermic reaction was noted and it continued throughout the addition. The reaction mixture was refluxed for 2 hr after the addition was completed and then was hydrolyzed. The organic layer was separated, water-washed three times, and dried over anhydrous $MgSO_4$. Diphenyltrifluoromethylmethanol was isolated by aspiration of the solution and was recrystallized twice from petroleum ether (bp 60–70°)–ether (4:1) solution. White crystals melted at 73.5 to 74.5° and gave both F^{19} and H^1 nmr spectra consistent with structure as shown in Table I. The infrared spectrum contained no carbonyl absorption and was also consistent with structure.

Phenylcyclopropyltrifluoromethylmethanol. Cyclopropyl bromide (7 g, 0.06 mole) in ether was added to an ether suspension of 0.5 g (0.07 ml) of lithium sand at 0° with rapid stirring under a nitrogen atmosphere. Cyclopropyllithium is formed as indicated by the disappearance of the lithium over a 2-hr period. An ether solution of 8.4 g (2.05 moles) of trifluoromethylacetophenone was then added dropwise to the cyclopropyllithium solution, still at 0°, followed by 2 hr of stirring at room temperature for the reaction to go to completion. The reaction mixture was then hydrolyzed, the organic layer was separated, washed, and dried with Na_2SO_4, and the alcohol was obtained by vacuum distillation at 72–75° (5 mm). The structure was confirmed both by the F^{19} and H^1 nmr (Table I) and by infrared which showed no trace of trifluoromethylacetophenone.

Phenylmethyltrifluoromethylmethanol. α,α,α-Trifluoroacetophenone (20 g, 0.123 mole) was added dropwise to 0.2 mole of methyllithium (Foote Mineral Co.) in diethyl ether. A vigorous exothermic reaction was noted throughout the addition. The reaction mixture was hydrolyzed after 2 hr. The organic layer was separated, washed, and dried, and on vacuum distillation 20 g of the alcohol was obtained, bp 80–81° (13 mm) (88% yield). The structure was confirmed by F^{19} and H^1 nmr (Table I) and by infrared which showed no carbonyl absorption.

Nmr Spectra. The nmr spectra were obtained on Varian Associates Model A-60, A-56-60, and HA-60 spectrometers, equipped with variable-temperature probes. The techniques of preparing the solutions of the carbonium ions have been discussed in detail previously.[3,5] The fluoro compounds need no special conditions except in the case of the phenylcyclopropyltrifluoromethylmethanol. This compound was dissolved in SO_2 at −50° and this solution was added dropwise to a rapidly stirring FSO_3H–SbF_5–SO_2 solution at −80°. The nmr spectrum of this solution was obtained at −75 to −70°. Warming to −50° causes the spectrum to vanish, presumably by opening of the cyclopropyl ring and subsequent polymerization. All other compounds in this study could simply be dissolved in SO_2 and added to FSO_3H–SbF_5 or FSO_3H–SbF_5–SO_2 over a wide range of temperature. The prime function of SO_2 is to dissolve the compound so it can be easily dispersed into the acid media and to lower the viscosity of the solutions. Thus solutions once made up could be warmed slowly and SO_2 distilled off. The ions were stable in SbF_5–FSO_3H solution even at room temperature. All spectra reported were taken at −60°.

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