drybox). An equimolar amount of aziridine was dissolved in 2 ml of *n*-pentane and the cold solution added with vigorous agitation to the SO_2 solution of the oxocarbonium ion salt. The solutions of the N-acylaziridinium ions were used directly in the nmr spectroscopic studies. The **N-acylpyridinium ions** were prepared similarly to the N-acylaziridinium ions.

Protonation of N-Aziridin-1-ols. N-Aziridine-1-ethanol and N-aziridine-1-propanol were prepared by the method described by Rabourn and Howard,[45] condensing acetaldehyde (propionylaldehyde) and aziridine at 0 to −5°. Protonation was carried out in CF_3COOH–SO_2 solution at −40 to −60°.

Nmr Spectra. Varian Associates A-56/60A spectrometer with a variable-temperature probe was used for all spectra. Coupling constants are believed accurate to ±0.1 Hz. Samples of isolated aziridinium ions in SO_2 at −60° or solutions of protonated N-alkylaziridinium ions made up as described in acid–SO_2 solutions at −60° were used for all the nmr studies. Small solvent effects on the chemical shift were observed ($\Delta\delta$ 0.2 ppm) when acid concentrations or gegenions were changed.

Acknowledgment. Support of this work by a grant of the National Institutes of Health is gratefully acknowledged (GM 14082-03). The Dow Chemical Company and Dr. George Ham are thanked for samples of aziridines.

Stable Carbonium Ions. LXXXI.[1]

Alkyl(aryl)halocarbonium Ions and Haloarylcarbonium Ions[2]

George A. Olah and Melvin B. Comisarow[3]

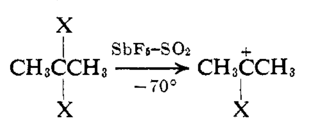
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 30, 1968*

Abstract: Sixteen stable alkyl(aryl)halocarbonium ions and haloarylcarbonium ions containing conjugatable halogen have been prepared and examined using ^1H and ^{19}F nmr spectroscopy. The charge distributions in these ions are discussed.

In previous publications[4] from these laboratories it has been shown that a wide variety of heteroatom-substituted carbonium ions can easily be formed. As expected, these ions exhibit an enhanced stability relative to the corresponding ions with hydrocarbon fragments in place of the heteroatom. This work describes related work with halogen as the heteroatom. Part of this work has been reported in preliminary communications.[5]

Results

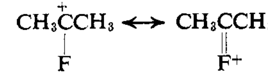
Dimethylhalocarbonium Ions. When 2,2-dihalopropane (**1**) is treated with SbF_5 in SO_2 at −70°, the corresponding dimethylhalocarbonium ion **2** is formed.



$$CH_3\overset{X}{\underset{X}{C}}CH_3 \xrightarrow[-70°]{SbF_5-SO_2} CH_3\overset{+}{\underset{X}{C}}CH_3$$

1-F, X = F　　**2**-F, X = F
1-Cl, X = Cl　　**2**-Cl, X = Cl
1-Br, X = Br　　**2**-Br, X = Br

The pmr spectra of **1-F** and **2-F** (Figure 1) shows that the methyl groups in the ion are considerably deshielded from those of the precursor **1-F**, indicating carbonium ion formation. The methyl absorption of **1-F** is split into a triplet by the two equivalent fluorine nuclei (J_{HF} = 17.6 Hz), while the pmr spectra of the ion **2-F**, is a doublet (J_{HF} = 25.4 Hz), showing coupling to only one fluorine nucleus. The fluorine nmr spectra of **1-F** and **2-F** (Figure 1) is completely consistent with the conclusions reached from the proton spectra and illustrates the importance of charge delocalization onto fluorine. The ^{19}F resonance of the ion **2-F** is at ϕ −181.91, 267 ppm deshielded from the resonance of **1-F**.



$$CH_3\overset{+}{\underset{F}{C}}CH_3 \longleftrightarrow CH_3\underset{F^+}{\overset{}{C}}CH_3$$

The proton resonance of **2**-Cl (singlet δ 4.06) is deshielded from that of its precursor **1**-Cl. The same is true for the spectra of **1**-Br and **2**-Br.

Both **2**-F and **2**-Cl are stable to −30° for at least 30 min. In contrast, ion **2**-Br is only stable below −70°; above this temperature **2**-Br is converted to ion **2**-F. Whether this is due to the ion's low C–Br bond strength (as compared to that of C–F and C–Cl) or if the ion is inherently unstable because of a lesser amount of charge delocalization onto bromine is unknown. The nmr spectra of the dimethylhalocarbonium ions and their precursors are tabulated in Table I.

Table I. Chemical Shifts of Dimethylhalocarbonium Ions

Precursors $(CH_3)_2$–CX_2, **1**			Ion CH_3–CX–CH_3, **2**	
X	CH_3	^{19}F	CH_3	^{19}F
F	1.30[a]	ϕ +84.93[a]	3.83[b]	ϕ −181.91[b]
Cl	1.89		4.06	
Br	2.38		3.82	

[a] J_{CH_3-F} = 17.6 Hz. [b] J_{CH_3-F} = 25.4 Hz.

Phenylmethylhalocarbonium Ions. When α,α-dihaloethylbenzene (**3**) is treated with SbF_5 in SO_2 at −70°,

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[1] Part LXXX: G. A. Olah and P. J. Szilagyi, *J. Amer. Chem. Soc.*, **91**, 2949 (1969).

[2] Taken in part from the Ph.D. Thesis, M. B. Comisarow, Case Western Reserve University, Cleveland, Ohio, 1968.

[3] Texaco Research Fellow, 1967–1968.

[4] (a) G. A. Olah and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 1721 (1967); (b) G. A. Olah and A. M. White, *ibid.*, **84**, 3591 (1967); (c) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967).

[5] (a) G. A. Olah, C. A. Cupas, and M. B. Comisarow, *ibid.*, **88**, 362 (1966); (b) G. A. Olah, R. D. Chambers, and M. B. Comisarow, *ibid.*, **89**, 1268 (1967); (c) G. A. Olah and M. B. Comisarow, *ibid.*, **89**, 1027 (1967).

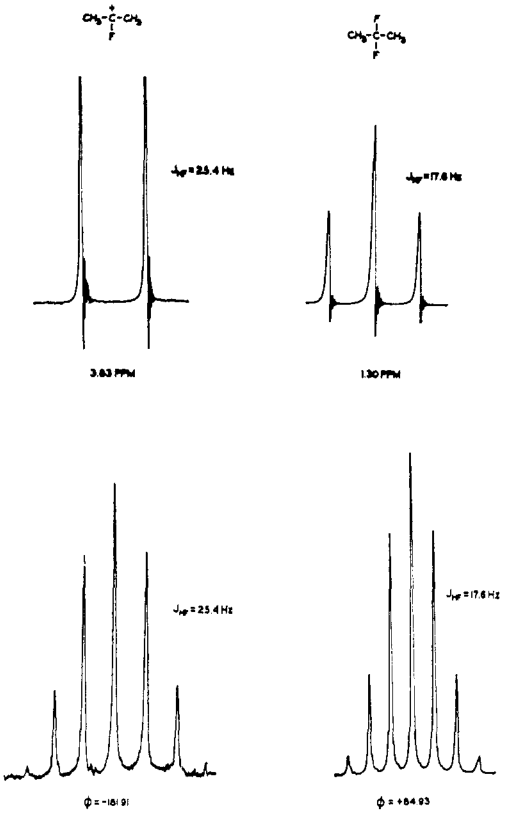


Figure 1. ^{1}H and ^{19}F nmr spectra of 2,2-difluoropropane (**1-F**) and the dimethylfluorocarbonium ion (**2-F**).

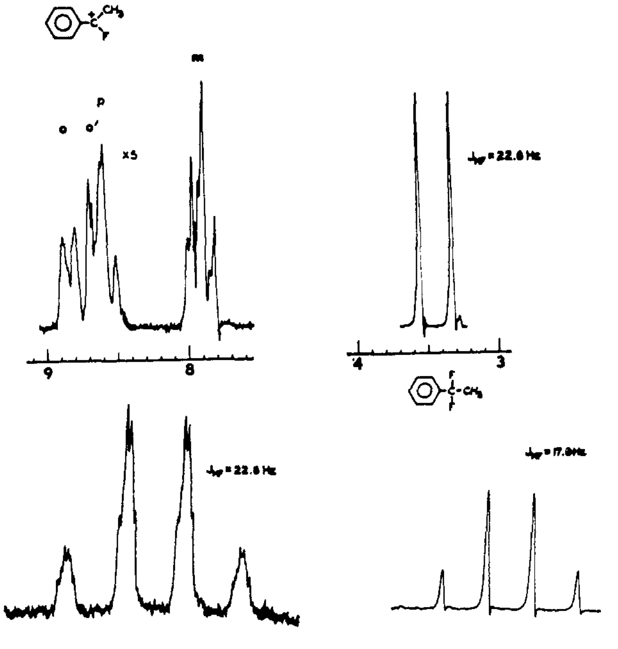


Figure 2. ^{1}H and ^{19}F nmr spectra of α,α-difluoroethylbenzene (**3-F**) and the phenylmethylfluorocarbonium ion (**4-F**).

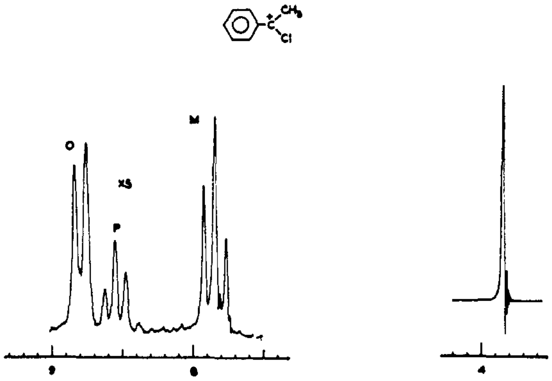


Figure 3. Pmr spectrum of the phenylmethylchlorocarbonium ion (**4-Cl**).

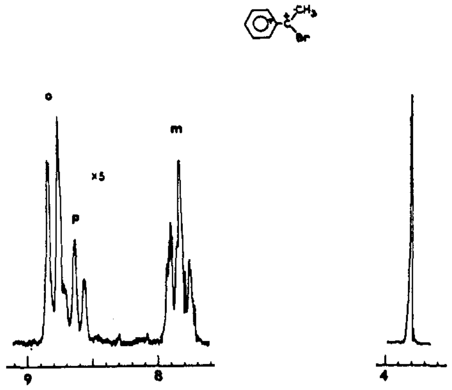
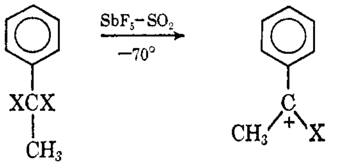


Figure 4. Pmr spectrum of the phenylmethylbromocarbonium ion (**4-Br**).

the phenylmethylhalocarbonium ion (**4**) is formed. The nmr spectra of the ions **4** are shown in Figures 2, 3, and 4.

The pmr spectrum of ion **4-F** (Figure 2) shows the expected deshielded doublet for the methyl group and a deshielded aromatic ring. The two chemical shifts of the *ortho* protons are considerably different indicating that rotation around the C_{arom}–C_α bond is restricted. This is a general characteristic of benzylic cations with two different α substituents.[6,7] The ^{19}F nmr spectra of **3-F** and **4-F** (Figure 2) shows the greatly deshielded fluorine resonance in the ion, and in addition a larger coupling to the ring protons in the ion **4-F** than in the precursor **3-F**. This coupling is approximately 1 Hz assuming equal couplings to the two *ortho* and one *para* proton. The pmr spectrum of **4-Cl** (Figure 3) shows the expected deshielded methyl and aromatic absorptions. The chemical shifts of the two *ortho* protons are virtually identical indicating that the sum totals of the shielding effects (bond anisotropy and steric) of the chlorine and methyl groups upon the ring protons are approximately equal. The pmr spectra of **4-Br** is shown in Figure 4 and is similar to that of **4-Cl**. Surprisingly, although the *ortho* proton have virtually identical chemical shifts, the *meta* shifts appear to be slightly different.



3-F, X = F　　**4-F**, X = F
3-Cl, X = Cl　　**4-Cl**, X = Cl
3-Br, X = Br　　**4-Br**, X = Br

(6) G. A. Olah, M. B. Comisarow, and C. J. Kim, *ibid.*, **91**, 1458 (1969).

(7) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 5254 (1967).

Table II. Chemical Shifts of Phenylmethylhalocarbonium Ions

	Precursor 3					Ion 4					
X	*o*	*m*	*p*	CH_3	F	*o*	*o'*	*m*	*p*	CH_3	F
F	7.19	7.19	7.19	1.62[a]	+88.69[a]	8.83	8.67	7.90	8.58	3.46[b]	−51.48[b]
Cl	8.50	≈8.16	≈8.16	2.30		8.81	8.90	7.87	8.57	3.72	
Br	7.47	≈7.02	≈7.02	2.71		8.80	8.80	7.83	8.64	3.82	

[a] J_{CH_2-F} = 17.8 Hz. [b] J_{CH_3-F} = 22.8 Hz.

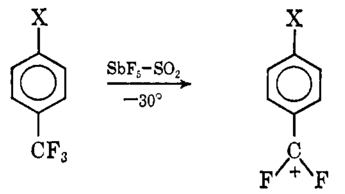
Table III. Chemical Shifts of Aryldihalocarbonium Ions

	Precursor				Ion			
Ion	*o*	*m*	*p*	CF_3	*o*	*m*	*p*	CF_2^+
6-H	~7.31	~7.15	~7.15	63.63	8.88[i]	8.04	8.84[j]	−11.99[i]
6-F	7.36[a,d]	6.87[c,l]	+108.52[b−d]	62.92[a,b]	9.00[e,f]	8.96[g]	ϕ +40.41[f−h]	−6.77[e,h]
6-Cl	7.26[k]	7.15[k]		63.49	8.80[i]	8.06		−8.61[i]
6-Br	7.23[k]	7.31[k]		63.54	8.64[i]	8.23		−8.78[i]
7	~7.70	7.22	7.25		9.00	8.04	8.82	

[a] $J_{CF_3-o\text{-}H}$ = 0.5 Hz. [b] J_{F-F} = 1.8 Hz. [c] $J_{F-m\text{-}H}$ = 8.5 Hz. [d] $J_{F-o\text{-}H}$ = 4.8 Hz. [e] $J_{CF_2-o\text{-}H}$ = 1.1 Hz. [f] $J_{F-o\text{-}H}$ = 4.6 Hz. [g] $J_{F-m\text{-}H}$ = 8.4 Hz. [h] J_{CF_2-F} = 19.8 Hz. [i] $J_{o\text{-}H-F}$ = 1.0 Hz. [j] $J_{p\text{-}H-F}$ = 1.0 Hz. [k] Assignments based on analogies with corresponding halobenzenes, H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961). [l] Coupling constants extracted from decoupling experiments.

All of the phenylmethylhalocarbonium ions (**4**) are stable to −30°. The nmr spectra of the phenylmethylhalocarbonium ions together with those of their precursors are tabulated in Table II.

Phenyldihalocarbonium Ions. Reaction of SbF_5 in SO_2 at −30° with *p*-X-benzotrifluoride (**5**) yields the *p*-X-phenyldifluorocarbonium ion (**6**). Ion **6**-H can also be formed at −60° by ionization of benzodifluoride chloride.

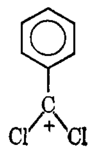


5-H, X = H
5-F, X = F
5-Cl, X = Cl
5-Br, X = Br

6-H, X = H
6-F, X = F
6-Cl, X = Cl
6-Br, X = Br

The benzotrifluorides are somewhat inert at −70° and warming to higher temperatures is necessary for complete ionization. Once formed, all the ions **6** are stable throughout the temperature range −30 to −75°. The resonances of the CF_2^+ groups of all of the ions **6** are deshielded about 70 ppm from the resonance of the precursor benzotrifluorides **5**, and show fine structure which is absent in the spectra of precursors. This fine structure is due to coupling to the aromatic protons. In **6**-H this coupling (1.0 Hz) is approximately equal to the *para* and *ortho* protons resulting in the quartet[8] structure of the resonance of this ion. The structure of the CF_2^+ resonance for both **6**-Cl and **6**-Br is a triplet due to coupling (~1.0 Hz) to the two *ortho* protons. The long-range F–F coupling (19.8 Hz) in ion **6**-F is much greater than that in the precursor **5**-F (1.8 Hz). The nmr spectra of the aryldifluorocarbonium ions are shown in Figures 5 to 7 and tabulated in Table III.

The phenyldichlorocarbonium ion (**7**) is formed when benzotrichloride is ionized with SbF_5–SO_2 at −60°. The pmr spectrum of this ion is given in Figure 8 and tabulated in Table III.



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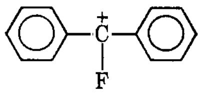
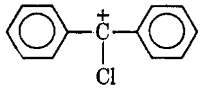
Diphenylhalocarbonium Ions. Ionization of diphenyldifluoromethane with SbF_5–SO_2 at −70°, yields the diphenylfluorocarbonium ion (**8**-F). The phenyl



8–F

resonance of ion **8**-F (Figure 9) is typical of phenylcarbonium ions and the fluorine resonance (ϕ −11.26) is to low field of that in the precursor (ϕ +89.61). The fluorine resonance is broadened relative to that in the precursor indicating a nonresolvable coupling (~0.5 Hz) to the ring (presumably *ortho* and *para*) hydrogens.

Ionization of diphenyldichloromethane yields the diphenylchlorocarbonium ion (**8**-Cl). The *ortho*



8–Cl

resonance (8.17) of this ion is to high field of the *para* resonance (8.27). This *ortho–para* order is reversed from that in the ion 8-F. Farnum[9] showed that in a series of α-substituted diphenylcarbonium ions, the *ortho* resonance moves upfield with increasing size of the α substituent. This was attributed by him to an increasing angle of twist and thus a decreasing deshielding phenyl anisotropy. The chemical shifts of the diphenylhalocarbonium ions (**8**) will be discussed further subsequently and are also summarized in Table VI.

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(8) The relaxation time of the C^+–F_2 fluorine nuclei is rather long and very slow sweep time (0.1 Hz/sec) must be used to obtain undistorted spectra.

(9) D. G. Farnum, *J. Amer. Chem. Soc.*, **89**, 2970 (1967).

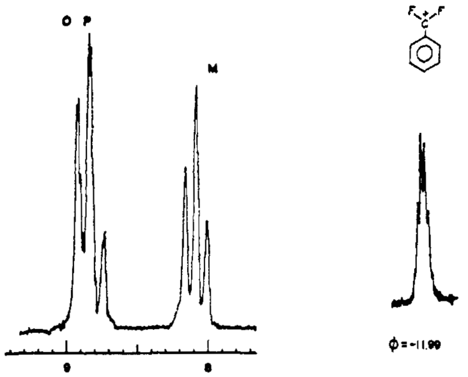


Figure 5. ^1H and ^{19}F nmr spectra of the phenyldifluorocarbonium ion (6-H).

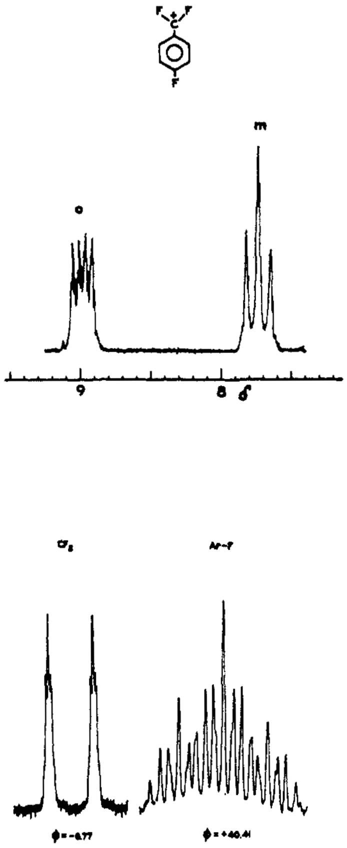


Figure 6. ^1H and ^{19}F nmr spectra of the *p*-fluorophenyldifluorocarbonium ion (6-F).

Pentafluorophenylcarbonium Ions. Tris(pentafluorophenyl)carbinol (**9**) can be ionized with fluorosulfuric acid in SO_2 at −60° to yield the tris(pentafluorophenyl)carbonium ion (**10**). The ^{19}F spectra of **9** and **10** are shown in Figure 10. All of the fluorine nuclei in **10** are well deshielded from the corresponding nuclei in **9** (*ortho* −14.73 ppm, *meta* −6.21 ppm, *para* −40 ppm) with the deshielding being greatest for the *p*-F atoms. The ion **10** may also be obtained from **9** by reaction with FSO_3H-SbF_5 but with this reagent, the *p*-F atoms are obscured by the Sb–F resonance.

Ionization of bis(pentafluorophenyl)carbinol (**11**), with FSO_3H-SbF_5 yields the bis(pentafluorophenyl)carbonium ion (**12**). Ion **12** is less stable than ion **10** and cannot be obtained as a stable species in neat fluorosulfuric acid.

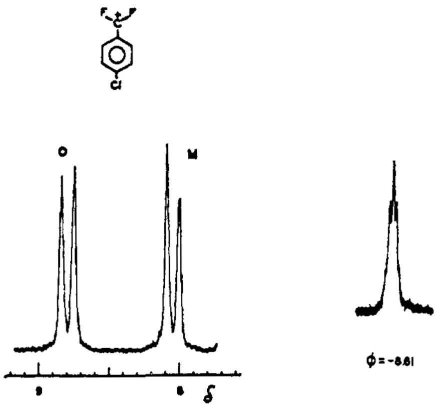


Figure 7. ^1H and ^{19}F nmr spectra of the *p*-chlorophenyldifluorocarbonium ion (6-Cl).

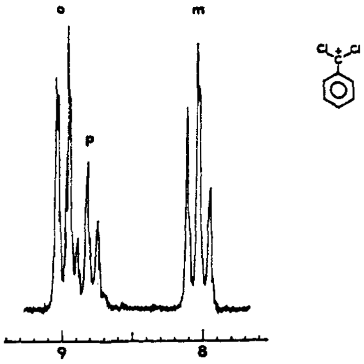


Figure 8. Pmr spectrum of the phenyldichlorocarbonium ion (7).

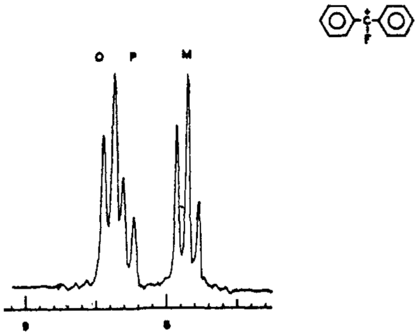
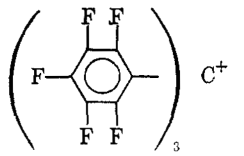


Figure 9. Pmr spectrum of the diphenylfluorocarbonium ion (8-F).

The pentafluorophenylcarbonium ion (**14**) was obtained by ionization of pentafluorobenzyl fluoride (**13**) with SbF_5 in SO_2 at −60°. The ion **14** cannot be



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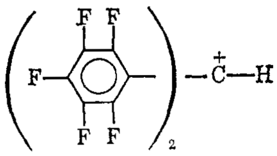
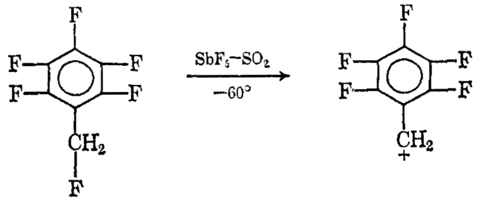


12



13 **14**

Table IV. ^{19}F and ^{1}H Nmr Shifts of Pentafluorophenylcarbonium Ions[a]

	Methyl alcohol, halide				Carbonium ion			
	δ_{CH}[c]	ϕ_{ortho}[b]	ϕ_{meta}[b]	ϕ_{para}	δ_{CH}	ϕ_{ortho}	ϕ_{meta}	ϕ_{para}
Tris(pentafluorophenyl)-methyl alcohol (**9**)		+140.98	+161.54	+152.22		+126.25	+154.29	+112.12[d] (**10**)
Bis(pentafluorophenyl)-methyl alcohol (**11**)	−3.67	+144.17	+162.28	+153.69	−10.10	+111.61	+153.86	+100.36[d] (**12**)
Pentafluorophenyl methyl fluoride (**13**) 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[e] (**14**)

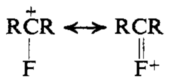
[a] In parts per million (ppm) from CCl_3F and TMS. [b] In $CDCl_3$ at 25° from internal CCl_3F. [c] In SO_2 at −20° from TMS capillary. [d] In FSO_3H-SbF_5-SO_2 at 60° from CCl_3F in a separate tube (^{19}F) or TMS capillary (^{1}H). [e] In SbF_5-SO_2 at −60° from CCl_3F in a separate tube (^{19}F)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

obtained by ionization of pentafluorobenzyl bromide with SbF_5 in SO_2 at −30° or by reaction of pentafluorobenzyl alcohol with FSO_3H-SbF_5 (neat or in SO_2).

The *m*-F peaks in **12** and **14** have almost identical appearances with the *meta* fluorines of **10** (Figure 10). The *o*- and *p*-F resonances in **12** and **14** are considerably broadened, indicating long-range coupling to the α-hydrogen(s). This broadening is more noticeable for the *p*-F nuclei. The nmr chemical shifts of the pentafluorophenylcarbonium ions are tabulated in Table IV.

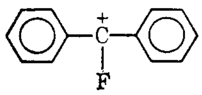
Discussion

In all of the fluorinated carbonium ions discussed in this paper, the fluorine nuclei are considerably deshielded relative to their covalent precursors indicating considerable charge delocalization onto fluorine. Within a homologous series such as **8-F**,



$$R\overset{+}{C}R \longleftrightarrow RCR$$

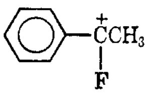
4-F, and **2-F** the fluorine resonance moves progressively to lower field as the delocalizing ability of the remaining ligands on the central carbon atom decreases.



8-F

ϕ −11.26

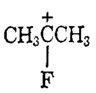
Δ −100.87



4-F

ϕ −51.48

Δ −140.17



$CH_3\overset{+}{C}CH_3$

2-F

ϕ −181.91

Δ −266.84

In the above series, Δ is the difference between the fluorine shifts of the ion and its precursor.

A second general feature of the spectra of fluorinated carbonium ions is that the coupling of the fluorine nuclei to other nuclei in the molecule is greater in the carbonium ion than in the covalent precursor. Similar increased couplings (both 3 bond and long-range) have been observed in many other stable carbonium ions,[10] and have been taken to be an indication of sp^2 hybridization at the central positively charged carbon atom.

The magnitudes of the H–F couplings in the fluorocarbonium ions appear to qualitatively correlate with the expected positive charge density on fluorine. For instance consider the pairs **2-F**, **4-F** and **4-F**, **8-F**. Since the expected fluorine atom charge densities are in the order **2-F** > **4-F** > **8-F**, it is evident that both

2-F	**4-F**	**8-F**	**6-H**
$CH_3\text{–}\overset{+}{C}F\text{–}CH_3$	$C_6H_5\text{–}\overset{+}{C}F\text{–}CH_3$	$C_6H_5\text{–}\overset{+}{C}F\text{–}C_6H_5$	$C_6H_5\text{–}CF_2^+$
$J_{CH_3-F} = 25.4$ Hz	$J_{CH_3-F} = 22.8$ Hz $J_{F-o,p} = 1$ Hz	$J_{F-o,p} = 0.5$ Hz	$J_{F-o,p} = 1$ Hz

methyl–fluorine couplings and *ortho*- (*para*-) fluorine couplings increase as the fluorine atom charge density increases.

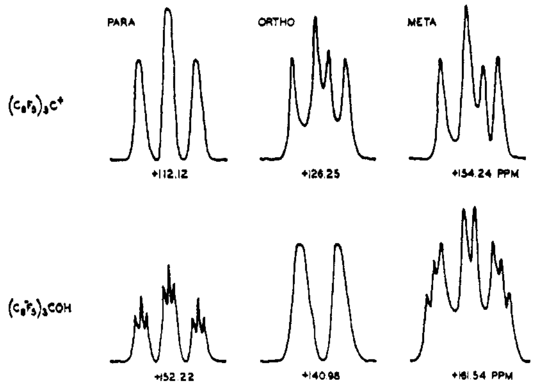


Figure 10. ^{19}F nmr spectra of the tris(pentafluorophenyl)carbonium ion (**10**), and tris(pentafluorophenyl)carbinol (**9**).

If ion **6-H** can be included in the above correlation then by comparing the fluorine-*ortho* (*para*) hydrogen couplings in **6-H**, **8-F**, and **4-F** it can be deduced that the order of charge delocalizing ability is phenyl > methyl ≈ fluorine for these groups.

The chemical shift data (Table III) for the *p*-X-phenyldifluorocarbonium ions (**6**) strongly suggests that the order of dispersal of positive charge onto the *para* substituents is F > Cl > Br > H. The fact that the precursor benzotrifluorides **5** are shielded in the reverse order compared to the ions **6**, suggests that in the ions this charge dispersal outweighs the effect of the electronegativity of the *para* substituent which presumably is responsible *via* bond polarization for the variation in the benzotrifluoride shifts. The above results suggest that *para* halogen should be a stabilizing substituent for phenylcarbonium ions. Some literature pK_R^+ data which are relevant to the above discussion is given in Table V.

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(10) For a review, see G. A. Olah, J. M. Bollinger, and A. M. White, "Progress in NMR Spectroscopy," Vol. V, Pergamon Press, New York, N. Y., 1969, in preparation.

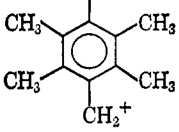
Table V. pK_R^+ Values for Some Phenylcarbonium Ions

Carbonium ion	pK_R^+
$(m\text{-}FC_6H_4)_3C^+$ (**16**)	−10.71[11]
$(p\text{-}FC_6H_4)_3C^+$ (**17**)	−6.05,[11] −5.96[12]
$(C_6F_5)_3C^+$ (**10**)	−17.5[12]
$(C_6H_5)_3C^+$ (**15**)	−6.44[13]
$(p\text{-}ClC_6H_4)_3C^+$ (**18**)	−7.44[a]

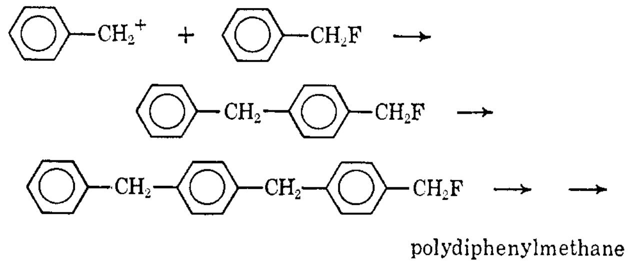
[a] N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3052 (1955).

Schuster[11] and Filler[12] and their coworkers found that the pK_R^+ value of the triphenylcarbonium ion (−6.44)[13] increased slightly upon *p*-F substitution to −6 for the tris(*p*-fluorophenyl)carbonium ion. This indicates that the *p*-F substitution stabilizes the resulting carbonium ion. These workers also found that *m*-F substitution was destabilizing; the pK_R^+ value of tris(*m*-fluorophenyl)carbonium ion (**10**) being −10.71. Since the inductive destabilizing effect of *o*-F substitution may be expected to be greater than that for *m*-F substitution, and the resonance-stabilizing effect similar to that for *p*-F substitution with the former (inductive) effect predominating it is not surprising that the tris(pentafluorophenyl)carbonium ion (**10**) has a lower pK_R^+ value (−17.5[12]) than does the triphenylcarbonium ion (**15**). An additional factor affecting the relative stability of **10** and **15** is that the twist angle in **10** may be larger than in **15** because of the greater size of *o*-F relative to *ortho* hydrogen. The fact that the tris(*p*-chlorophenyl)carbonium ion (**18**) is less stable relative to its precursor carbinol than is the triphenylcarbonium ion is interesting when compared with the chemical shift data for **6**-Cl and **6**-H. Apparently the inductive effect of *para* chlorine destabilizes the carbonium ion **18**, to a greater extent than it deshields the fluorine chemical shift of the ion **6**-Cl, and/or the mesomeric effect of chlorine stabilizes the carbonium ion **18** to a lesser extent than it shields the fluorine chemical shift of the ion **6**-Cl; all relative to the stability of the ion **15** and fluorine chemical shift of ion **6**-H.

In the Results section it was stated that pentafluorobenzyl bromide could not be ionized at −60° to the corresponding carbonium ion **14**, but that pentafluorobenzyl fluoride did ionize under these conditions. Under similar conditions benzyl bromide *does* ionize. These observations suggest that the pentafluorobenzyl cation (**14**) is less stable than the benzyl cation (**19**). In a recent study of benzyl cations from these laboratories[14] it was noted that although the benzyl cation (**19**) could not be obtained as a stable long-lived species substituted benzyl cations such as **20** were quite stable. Since benzyl halides reacted quite rapidly with SbF_5 at low temperatures it was suggested that the "instability" of the benzyl cation was due to the facile polycondensation side reaction.



20



The data suggested that the stability of ion **20** compared with **19** was due to a steric blocking of the polycondensation pathway and/or was due to the fact that the substituents were electron releasing and thus stabilizing. The facts given above suggest that since ion **14** is less stable than **19**, the blocking mechanism must be responsible for the nontransient nature of the pentafluorobenzyl cation **14**.

In a recent paper Farnum[9] discussed the factors affecting the pmr shifts in a series of phenylcarbonium ions and deduced that the *p*-H shift was a reasonably accurate measure of charge density on the phenyl ring. In Table VI are given the pmr shifts of a series of phenylcarbonium ions. Some chemical shifts appear to be at variance with Farnum's conclusion and suggest that caution be exercised in using his qualitative charge density–chemical shift relationship. First-order techniques were used to analyze all the spectra except that of **15**. The shifts for **15** were deduced by determining the *para* shift in **15** and assuming the same *ortho–para* and *meta–para* shift differences as found by Farnum.[9]

Table VI. Pmr Chemical Shifts[a] of Some Phenylcarbonium Ions

Carbonium ion	*ortho*	*meta*	*para*
Phenyl[b,d] Dimethyl (**21**)	8.73	7.82	8.42
Phenyl[c] Difluoro (**6**-H)	8.88	8.04	8.84
Phenyl[c] Dichloro (**7**)	9.00	8.04	8.82
Benzhydryl[c] (**22**)	8.36	7.83	8.27
Diphenyl[c] (**8**-F) Fluoro	8.41	7.86	8.34
Diphenyl[c] Chloro (**8**-Cl)	8.17	7.78	8.27
Triphenyl methyl[d] (**15**)	7.56	7.74	8.12

[a] Ions were formed by ionizing the appropriate chloride or fluoride with SbF_5. Shifts are as the hexfluoroantimonate or pentafluorochloroantimonates in SO_2 at −60° from external (capillary) TMS and were determined at 100 MHz. [b] Reference 6. [c] This work. [d] Reference 9.

The *p*-H shift of the benzhydryl cation **22** is to high field of the *p*-H shift of the diphenylfluorocarbonium ion (**8**-F). Since the deshielded fluorine resonance (ϕ −11.26) in **8**-F strongly suggests charge dispersal onto fluorine, charge dispersal onto phenyl should be less than in ion **22**. The relative *para* shifts in the ions **6**-H and **21** may also be at variance with Farnum's conclusions. The same is true for the *para* shifts in **22** and **8**-Cl.

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(11) I. I. Schuster, A. K. Colter, and R. J. Kurlane, *J. Amer. Chem. Soc.*, **90**, 4679 (1968).

(12) R. Filler, *et al.*, *ibid.*, **89**, 1026 (1967).

(13) E. M. Arnett and R. D. Bushick, *ibid.*, **86**, 1564 (1964).

(14) J. M. Bollinger, M. B. Comisarow, C. A. Cupas, and G. A. Olah, *ibid.*, **89**, 5687 (1967).

Experimental Section

Nmr single resonance spectra were obtained on Varian HA 100 (^{1}H) and A56-50 (^{19}F) spectrometers. ^{1}H(^{19}F), ^{19}F(^{1}H), and ^{19}F(^{19}F) double-resonance experiments were performed on a Varian HA-60 instrument operating at 56.4 and 60.0 MHz. Octafluorocyclobutane, CCl_3F, CF_2ClCF_2Cl, and $C_6H_5CF_3$ were used as lock signals for the ^{19}F experiments. The necessary irradiating field for the heteronuclear decoupling experiments was provided by a NMR Specialties Model SD-60B heteronuclear spin decoupler. All of the benzotrifluorides **5** were obtained from Columbia Organic Chemicals.

α,α-Difluorotoluene was prepared from benzaldehyde and SF_4.[15]

α,α,α-Difluorochlorotoluene. In a three-necked, 250-ml flask equipped with a thermometer, gas inlet tube, and reflux condensor was placed 30 ml of α,α-difluorotoluene and 50 mg of azobisisobutyronitrile. The flask was then heated to 70° while chlorine gas was bubbled through the reaction mixture. The reaction was followed by ^{19}F nmr and by testing the effluent gas for HCl and was found to be over in about 90 min. The product was then distilled: bp 140°, 61° (50 mm); nmr (CCl_3) multiplet δ 7.5, ^{19}F ϕ 49.36.

2,3,4,5,6-Pentafluorobenzyl Fluoride. The apparatus consisted of a 250-ml, three-necked flask equipped with an addition funnel, a motor-driven stirrer, and an exit tube leading to a Dry Ice trap connected to a vacuum pump. The apparatus was flushed with dry nitrogen and then 48 g (0.2 mol) of finely powdered HgF_2 was placed in the flask and 10 g (0.04 mol) pentafluorobenzyl bromide (Penninsular Chem Research) was placed in the funnel. After evacuation of the flask the bromide was then added dropwise to the rapidly stirred mercuric fluoride over a period of 15 min. The product which collected in the Dry Ice trap was then filtered from a few grams of NaF, yield 1.8 g (45%). The nmr spectrum is given in Table IV.

Decafluorobenzhydrol was obtained from Imperial Smelters Ltd.

Tris(pentafluorophenyl)carbinol was a gift from Professor R. Filler.[12]

α,α-Difluoroethylbenzene was prepared from HF and phenylacetylene according to Matsuda, *et al.*[16] A procedural change suggested in ref 27 of this paper was followed and resulted in a yield of 24% rather than the 18% reported.

α,α-Dichloroethylbenzene. A solution of 50 g of phenylacetylene in 100 ml of methylene chloride was cooled to −40° and saturated with anhydrous HCl for 4 hr. After removal of the solvent and excess HCl on a rotary evaporator, the product was vacuum distilled. After collection of a small portion of α-chlorostyrene the product was collected and then redistilled: bp 71° (4 mm), 50° (1 mm); nmr (CCl_4) multiplet 7.68 (2), multiplet 7.28 (3), 2.50 (3), yield 75%. The **α-chlorostyrene** fraction was redistilled: bp 98° (46 mm); nmr (CCl_4) multiplet 7.55 (2), multiplet 7.25 (3), doublet 5.67 (1), doublet 5.44 (1), yield 10%. The title compound should be stored at 0°.

α,α-Dibromoethylbenzene was prepared from anhydrous HBr and phenylacetylene using a procedure analogous to the one used for preparing α,α-dichloroethylbenzene, yields: α,α-dibromoethylbenzene, bp 76° (0.15 mm); nmr (CCl_4) multiplet 7.70 (2), multiplet 7.25 (3), 3.94 (3), 25%; **α-bromostyrene**, bp 61° (0.5 mm); nmr (CCl_4) multiplet 7.52 (2), multiplet 7.25 (3), doublet 6.03 (1), doublet 5.71 (1), 60%. The title compound should be stored at 0°.

2,2-Dihalopropanes. The fluorine compound was prepared according to the literature[15] from acetone and SF_4. The chlorine compound was obtained from J. T. Baker and the bromine compound from K and K Laboratories.

Dihalodiphenylmethanes. The fluorine compound was prepared from SF_4 and benzophenone.[15] The chlorine compound was obtained from Frinton Laboratories and distilled before use.

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The Nature of the Carbonium Ion. I. The π-Route Norbornyl Cation from a Thiocyanate–Isothiocyanate Isomerization

Langley A. Spurlock and Walter G. Cox

Contribution from the Department of Chemistry, Temple University
of the Commonwealth System of Higher Education,
Philadelphia, Pennsylvania 19122. *Received October 10, 1968*

Abstract: 2-(Δ^3-Cyclopentenyl)ethyl thiocyanate was isomerized to a mixture of *exo*-2-norbornyl thiocyanate, *exo*-2-norbornyl isothiocyanate, and 2-(Δ^3-cyclopentenyl)ethyl isothiocyanate in a variety of solvents. No *endo*-norbornyl products were detected. The rate of reaction and product composition were directly governed by the solvent employed. The necessity of the double bond for isomerization was established by the failure of the saturated 2-cyclopentylethyl thiocyanate to isomerize under these conditions. Rate measurements confirmed the isomerization as a first-order process and activation parameters were calculated. The catalytic effects of potassium perchlorate, potassium thiocyanate, and boron trifluoride were studied and the results were used in deducing the nature of the norbornyl cations which serve as intermediates for isomerization.

Prior investigations have given evidence that the thermal rearrangements of alkyl thiocyanates to their isomeric isothiocyanates can proceed by several mechanistic pathways. It can be seen that the choice of isomerization mode is dependent on the structure of the alkyl moiety, the nature of the solvent employed as an isomerizing medium, and on catalysts. In the cases of most allylic thiocyanates, rearrangement occurs by way of a six-membered cyclic transition state involving little to no charge separation.[1,2] These reactions are therefore relatively insensitive to solvent and catalyst effects.[3,4a] Nonallylic thiocyanates present a

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