Stable Carbocations. CLIII.[1] Fluorinated Phenylcarbenium Ions and Benzoyl Cations

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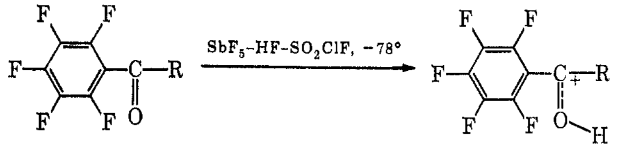
The preparation and nmr study of a series of fluorinated phenylcarbenium ions and benzoyl cations is described. Resonance stabilization (charge delocalization) of these ions is discussed on the basis of their fluorine nmr spectra.

Fluorinated phenylcarbenium ions were first prepared and studied by Olah and Comisarow.[2] Recently, Pozdnyakovich and Shteingarts reported the preparation and ^{19}F nmr of the $C_6F_5CF_2^+$ and $(C_6F_5)_2CF^+$ ions.[3] The unusual stability of these ions suggests that it is due to n–π conjugative stabilization *via* fluorine "back-donation."[4] In order to gain a better understanding of fluorinated carbocations and of the electronic structure of these ions, we have now undertaken the preparation and nmr study of a series of additional fluorinated phenylcarbenium ions and benzoyl cations.

Results and Discussion

Pentafluorophenylcarbenium Ions.—Protonation of pentafluorobenzaldehyde (**1a**) and -benzoic acid (**1b**) and



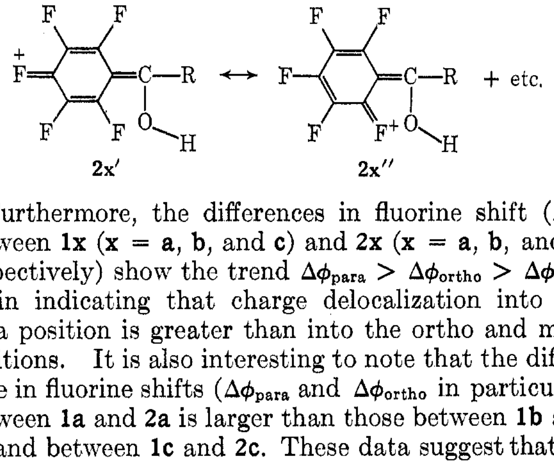
1a, R = H
b, R = OH
c, R = C_6F_5

2a, R = H
b, R = OH
c, R = C_6F_5

decafluorobenzophenone (**1c**) was achieved in SbF_5–HF–SO_2ClF solution at −78°. The nmr (^1H and ^{19}F) parameters of **1x** (**x** = **a**, **b**, and **c**) and their protonated derivatives **2x** (**x** = **a**, **b**, and **c**) are summarized in Table I. The nmr (^1H and ^{19}F) spectrum of ion **2a** is shown in Figure 1.

The ^{19}F nmr data of **1b** have been reported by Graham and Hogben.[5] The small differences in chemical shifts are primarily due to the use of an external capillary reference ($CFCl_3$) as well as the solvent (SO_2ClF) at low temperature (−30°) in the present work. The ^{19}F nmr spectra of the pentafluorophenyl group should be considered as an AA'KXX' type (as Graham and Hogben did in their study of a series of pentafluorophenyl derivatives[5]). It is, however, in the nmr spectra of the ions obtained at low temperature, difficult to obtain good enough resolution to allow detailed analysis. In case of ion **2c** the four meta fluorines of the two C_6F_5 groups display further only one multiplet at ϕ 155.6. Instead of a complete analysis, therefore, only a simple first-order interpretation of spectra was used. Fortunately, this does not affect our purpose to study the conjugative stabilization in these ions, which is primarily based on relative deshielding of fluorine shifts.

The ortho fluorine atoms of **1a**, **1b**, and **1c** are more deshielded than the corresponding para fluorine atom, presumably because the former experience a greater inductive withdrawing effect by the carbonyl group. On the other hand, the para fluorine atom of the protonated species **2x** is generally more deshielded than the ortho fluorine atoms. These data suggest that the degree of charge delocalization into the para position is greater than into the ortho positions. Consequently, resonance forms of para-quinoidal nature **2x′** are more important than ortho-quinoidal forms such as **2x″**.



2x′ 2x″

Furthermore, the differences in fluorine shift ($\Delta\phi$) between **1x** (**x** = **a**, **b**, and **c**) and **2x** (**x** = **a**, **b**, and **c**, respectively) show the trend $\Delta\phi_{para} > \Delta\phi_{ortho} > \Delta\phi_{meta}$ again indicating that charge delocalization into the para position is greater than into the ortho and meta positions. It is also interesting to note that the difference in fluorine shifts ($\Delta\phi_{para}$ and $\Delta\phi_{ortho}$ in particular) between **1a** and **2a** is larger than those between **1b** and **2b** and between **1c** and **2c**. These data suggest that, in the pentafluorophenylcarbenium ions **2x**, the order of stabilization by substituents is OH > C_6F_5 > H.

In accordance with the partial double bond character of $C_{Ar}{=\!=}C_\alpha HOH$,[6] two different ortho fluorine shifts were observed in ion **2a**. The difference in the meta fluorine shifts must be small, since only a single multiplet at ϕ 156.2 was observed. The pmr spectrum of ion **2a** shows two doublets at δ 10.3 (J_{HH} = 8 Hz) and 14.4 (J_{HH} = 8 Hz), indicating that the OH proton is syn to the aldehydic proton. In ion **2c**, two readily distinguishable para-F shifts were found. It reveals that there are two different C_6F_5 rings; one is anti and the other syn to the OH group. However, only two ortho and one meta fluorine multiplet absorptions were observed, presumably owing to the small differences in fluorine shifts between each pair of ortho fluorine atoms and also between the four meta fluorine atoms. For ion **2c**, only three fluorine absorptions at ϕ 129.1 (triplet, J_{FF} = 16 Hz, *o*-F), 156.5 (doublet of doublets, J_{FF} = 16 and 20 Hz, *m*-F), and 127.8 (quintet, J_{FF} = 20 Hz, para) were observed, because of the rapid pro-

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[1] Part CLII: G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 2212 (1973).

[2] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **89**, 1027 (1967); **91**, 2955 (1969).

[3] Yu. V. Pozdnyakovich and F. D. Shteingarts, *Zh. Org. Khim.*, **6** (8), 1753 (1970).

[4] G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 3551 (1972).

[5] (a) M. G. Hogben and W. A. G. Graham, *ibid.*, **91**, 283 (1969); (b) M. G. Hogben, K. S. Oliver, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **91**, 291 (1969).

[6] G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

TABLE I

NMR (^1H AND ^{19}F) PARAMETERS OF PENTAFLUOROPHENYLCARBENIUM IONS AND THEIR PRECURSORS[a]

				R		
C_6F_5R	ϕ, ortho	ϕ, meta	ϕ, para	δ, CH	δ, OH	ϕ, CF
CHO (**1a**)	146.5 (m)	163.2 (m)	146.5 (m)	10.2 (s)		
^+CHOH (**2a**)	115.2 (m) 125.0 (m)	156.2 (m)	111.2 (m)	10.3 (d) J_{HH} = 8 Hz	14.4 (d) J_{HH} = 8 Hz	
COOH (**1b**)	141.7	163.8 (m)	152.2 (m)		11.6 (s)	
$^+COOH_2$ (**2b**)	129.1 (t) J_{FF} = 16 Hz	156.5 (d d) J_{FF} = 16, 20 Hz	127.8 (q) J_{FF} = 20 Hz		12.8 (s br)	
COC_6F_5 (**1c**)	143.3 (m)	162.3 (m)	148.7 (t t) J_{FF} = 20, 6 Hz			
$^+COHC_6F_5$ (**2c**)	125.4 (m) 130.2 (m)	155.6 (m)	119.1 (m) 123.1 (m)		14.0 (s br)	
CHF_2 (**4a**)	145.3 (m)	163.1 (m)	151.6 (t) J_{FF} = 20 Hz	7.03 (t) J_{HF} = 53 Hz		115.2 (d t d) J_{FF} = 2, 16 Hz, J_{HF} = 52 Hz
^+CHF (**3a**)	97.2 (m) 71.8 (m)	151.4 (t) J_{FF} = 21 Hz	106.1 (m)	9.93 (d) J_{HF} = 59 Hz		−31.35 (m)
CF_2Cl (**4b**)	141.6 (m)	162.0 (m)	151.2 (t t) J_{FF} = 6, 20 Hz			47.5 (t) J_{FF} = 31 Hz
$^+CF_2$ (**3b**)	100.6 (m)	148.1 (m)	81.6 (m)			−32.6 (m)

[a] Proton and fluorine chemical shifts are referred to external capillary TMS and $CFCl_3$, respectively.

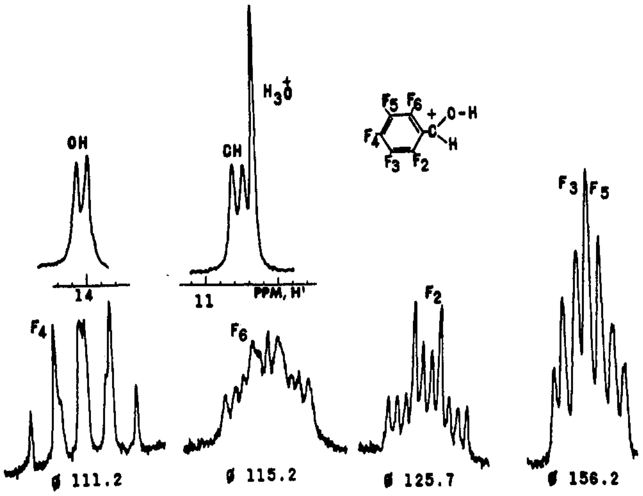


Figure 1.—^1H and ^{19}F nmr spectra of protonated pentafluorobenzaldehyde in SbF_5–HF–SO_2ClF solution at −78°.

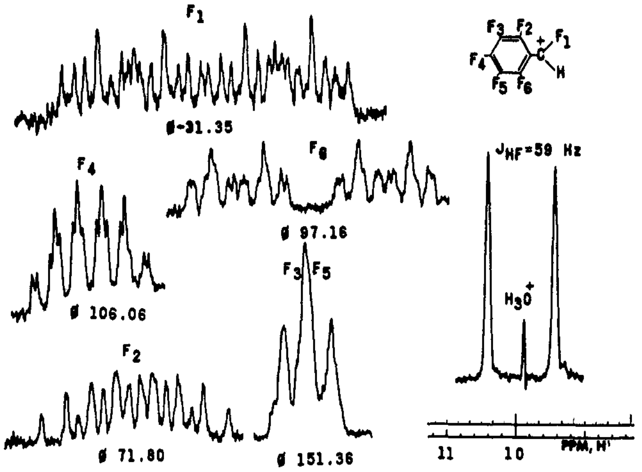
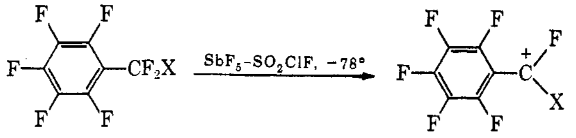


Figure 2.—Proton and fluorine nmr spectra of pentafluorophenylfluorocarbenium ion (**3a**).

ton exchange with the superacid. Indeed, the OH proton of **2b** shows a broadened absorption at δ 12.8 in the pmr spectrum. Similar results were observed when benzoic acid was protonated in HF–SbF_5–SO_2ClF solution at −78°.[7]

We also have prepared the pentafluorophenylfluorocarbenium ion ($C_6F_5C^+HF$, **3a**) and for comparison reinvestigated the perfluorobenzyl cation ($C_6F_5C^+F_2$, **3b**) by ionizing pentafluorobenzyl fluoride ($C_6F_5CHF_2$)



4a, X = H
b, X = Cl

3a, X = H
b, X = F

and heptafluorobenzyl chloride ($C_6F_5CF_2Cl$), respectively, in SbF_5–SO_2ClF solution. The nmr (^1H and ^{19}F) spectra of ions **3a** and **3b** are shown in Figures 2 and 3, respectively. The ^{19}F nmr spectrum of ion **3b** is similar to that reported by Pozdnyakovich and Shteingarts[3] (prepared from octafluorotoluene and SbF_5) but was obtained with much better resolution. The pmr spectrum of ion **3a** displays a doublet at δ 9.93 (J_{HF} = 59 Hz), indicating that ionization of $C_6F_5CHF_2$ has occurred.

The ^{19}F nmr spectrum of ion **3a** displays a very deshielded symmetrical multiplet centered at ϕ −31.35 which could be assigned to the benzylic fluorine (F_1). Fluorine F_1 must be strongly coupled to one of the ortho fluorines, since it is symmetrically split into two multiplets by 128 Hz. By comparison with the studied *o*-fluorophenyldifluorocarbenium ion,[8] fluorine F_2 of ion **3a** should be strongly coupled to F_1. Indeed, fluorine F_2 shows two sets of doublet of triplets at ϕ 97.16 (first-order analysis), again separated by 128 Hz. The other ortho fluorine (F_6) shows a multiplet at ϕ 71.80. It is also coupled to fluorine F_1, as well as

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(7) G. A. Olah and P. W. Westerman, unpublished results.

(8) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 2686 (1973).

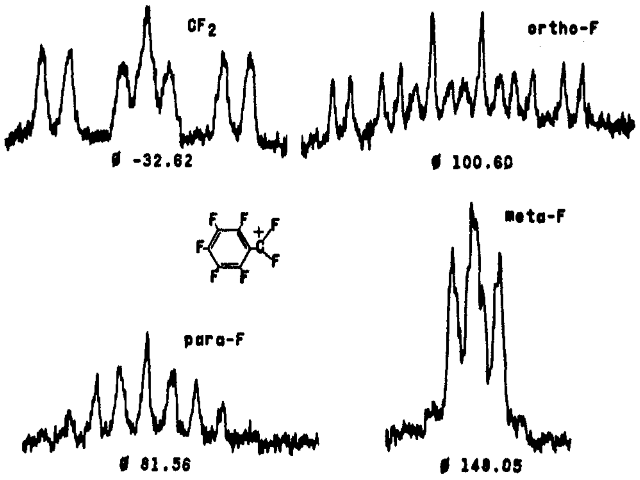
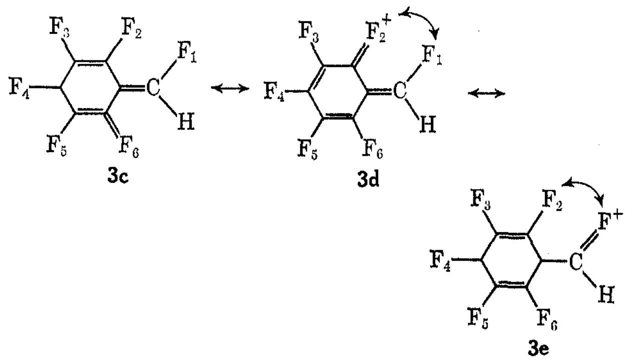


Figure 3.—Fluorine-19 nmr spectrum of perfluorobenzyl cation (**3b**).

the aromatic fluorine atoms (F_2, F_4, and F_5). One possible explanation why fluorine F_6 is being more deshielded than F_2 is that fluorine back-donation of F_6 (**3c**) is greater than that of F_2 (**3d**). This is because the latter is affected by the obvious charge–charge replusion (**3e**). The para fluorine of ion **3a** displays a sextet of multiplets at ϕ 106.06. The nonequivalent meta fluorines (F_3 and F_5) display a triplet of multiplets centered at ϕ 151.36.


3c
3d
3e

Ion **3a** is the first secondary arylfluorocarbenium ion ever prepared. Attempts to prepare the parent phenylfluorocarbenium ion, $C_6H_5C^+HF$, by ionizing C_6H_5-CHF_2 with SbF_5–SO_2ClF solution at −78° were unsuccessful. Only polymeric materials and tar were observed in the reaction.

Owing to the symmetry of ion **3b**, its ^{19}F nmr spectrum (Figure 3) is more simple than that of ion **3a**. The benzylic fluorines (CF_2^+) display two sets of doublet of doublets at −32.62, indicating the long-range fluorine–fluorine coupling with the ortho fluorine (J_{FF} = 82 and 66 Hz) and para fluorine (J_{FF} = 21 Hz). The para fluorine is coupled to all the six fluorine atom in ion **3b**, and thus displays a heptet at ϕ 81.56 (J_{FF} = 21 Hz). The ortho fluorines show a symmetrical multiplet centered at ϕ 100.06. They couple to all the fluorine atoms in ion **3b**, but the one that is para to each of them. The meta fluorenes are coupled to both ortho and para fluorines and thus show a shielded triplet at ϕ 148.05.

Fluorinated Benzoyl Cations.—Tomalia[9] reported the pmr studies of a series of substituted benzoyl cations, including the *o*-, *m*-, and *p*-fluorobenzoyl cations. The ^{19}F nmr spectra of these ions were not yet reported. In our continuing studies of fluorocarbenium ion we undertook a study of these fluorinated benzoyl cations, as well as that of the pentafluorobenzoyl cation. The isomeric fluorobenzoyl cations and the pentafluorobenzoyl cation were prepared by ionizing the corresponding benzoyl chlorides with SbF_5–SO_2ClF solution

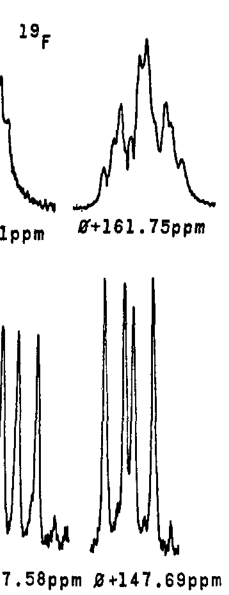
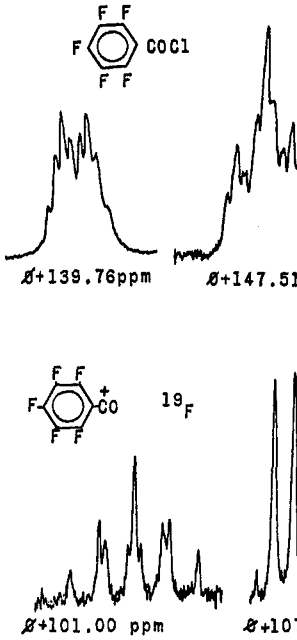
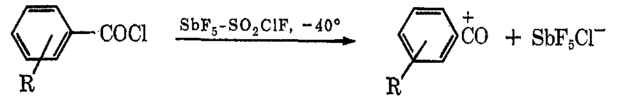



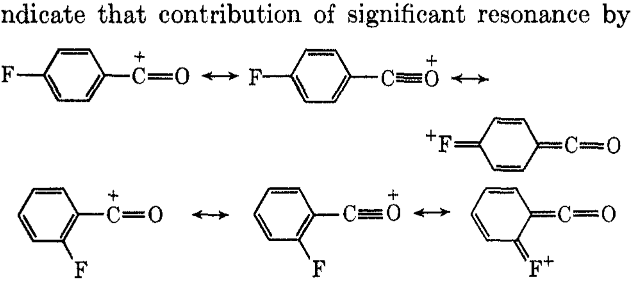
Figure 4.—^{19}F nmr spectrum of pentafluorobenzoyl chloride and pentafluorobenzyl cation.



R = *o*-F, *m*-F, *p*-F, and F_5 R = *o*-F, *m*-F, *p*-F, and F_5

at −40°. Nmr data of these ions and their precursors are summarized in Table II. The pmr data of isomeric fluorobenzoyl cations are identical with those reported by Tomalia.[9] The ^{19}F nmr data of pentafluorobenzoyl chloride has been reported by Graham and Hogben.[5] The slight differences in chemical shifts are presumably due to the use of external capillary $CFCl_3$ as reference, as well as the use of a different solvent (SO_2ClF) at lower temperature (−30°). The ^{19}F nmr spectra of the pentafluorobenzoyl cation and its precursor are shown in Figure 4.

The ^{19}F nmr chemical shifts of these ions are interesting. The chemical shift differences ($\Delta\phi$) between the ions and their precursors are significant in the case of the *o*- ($\Delta\phi$ = 28.7 ppm) and the *p*-fluorobenzoyl ($\Delta\phi$ = 35.2 ppm) cation, but are smaller in the case of the *m*-fluorobenzoyl cation ($\Delta\phi$ = 10.6 ppm). These data indicate that contribution of significant resonance by



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(9) D. A. Tomalia, *J. Org. Chem.*, **34**, 2583 (1969).

Table II

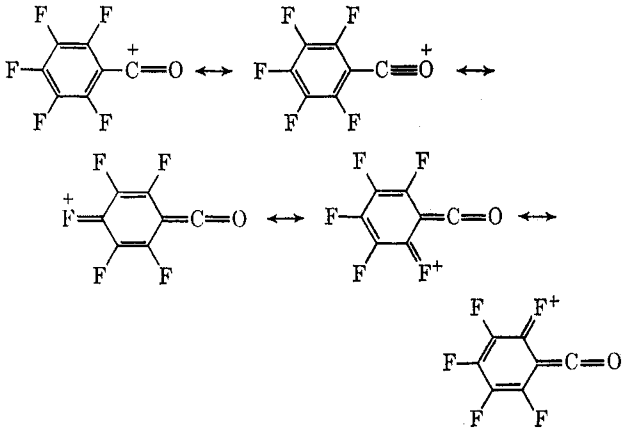
^{19}F and ^{1}H Nmr Chemical Shifts of Fluorobenzoyl Chlorides and Cations[b]

Registry no.	Chlorides and cations	Ortho		Meta		Para	
		δ, CH	φ, CF	δ, CH	φ, CF	δ, CH	φ, CF
393-52-2	*o*-Fluorobenzoyl chloride	+7.68 (m)	+111.31 (m)	+7.41[a] +7.30[a]		+8.20 (c, d) J_{HF} = 2 and 7 Hz	
39982-32-6	*o*-Fluorobenzoyl cation	+8.85[a]	+82.62 (m)	+8.15[a] +8.30[a]		+8.85[a]	
1711-07-5	*m*-Fluorobenzoyl chloride	+7.90[a] +7.50[a]		+7.40[a]	+112.19 (m)	+7.90[a]	
39981-34-5	*m*-Fluorobenzoyl cation	+8.70[a]		+8.70[a]	+101.59 (m)	+8.70[a]	
403-43-0	*p*-Fluorobenzoyl chloride	+8.25 (d d)		+7.26 (t)			+102.30 (m)
39981-36-7	*p*-Fluorobenzoyl cation	+9.22 J_{HF} = 4 and 8 Hz		+8.17 (t) J_{HF} = 9 Hz			+67.06 (m)
2251-50-5	Pentafluorobenzoyl chloride		+139.76 (m)		+161.75 (m)		+147.51 (t t) J_{FF} = 7 and 20 Hz
39981-37-8	Pentafluorobenzoyl cation		+107.58 (d d) J_{FF} = 26 and 14 Hz		+147.69 (d d) J_{FF} = 14 and 21 Hz		+101.00 (t t) J_{FF} = 21 and 26 Hz

[a] No attempt was made to determine the multiplicities since they are complicated patterns. [b] m, multiplet; d, doublet; and t, triplet.

fluorine back-donation occurs in the *o*- and *p*-fluorobenzoyl cations, but not in the case of *m*-fluorobenzoyl cation.

Similar results are obtained in the case of pentafluorobenzoyl cation.



The differences in fluorine shifts (Δφ) are 46.5 ppm in the case of ortho, 32.2 ppm in the case of para, and only 14.1 ppm in the case of meta positions. The unusual stability of this ion can again be accounted for by resonance contributions of the ortho and para fluorine atoms.

Fluorine is the most electronegative element and should inductively destabilize carbocations. However, its n–π conjugative stabilization *via* back-donation of the nonbonded electron pairs in carbocations can now be considered as one of the most important factors related to their stability. The degree of fluorine back-donation is related to the fluorine chemical shifts of the fluorinated carbocations. The proton and ^{13}C nmr study of phenylcarbenium ions indicates that substantial charge is delocalized into the ortho and para positions.[10] Consequently, fluorine at these positions (*i.e.*, in phenylcarbenium ions) is capable of stabilizing the ions *via* fluorine back-donation. The present data further substantiate this concept by the study of fluorine chemical shifts in the studied series of fluorinated phenylcarbenium ions, and benzoyl cations.

Experimental Section

Materials.—All of the fluorinated benzoyl chlorides were commercially available (K & K Laboratories). Pentafluorobenzaldehyde, pentafluorobenzoic acid, and decafluorobenzophenone were obtained from Aldrich Chemical Co. α,α-Difluorotoluene was prepared from benzaldehyde and sulfur tetrafluoride.[11]

Antimony pentafluoride (Allied Chemical) was triply distilled before use.

Preparation of Ions and Their Nmr Studies.—Solution of the ions in SbF_5–SO_2ClF or SbF_5–HF–SO_2ClF solution were prepared as described previously.[2] ^{1}H and ^{19}F nmr spectra were obtained on a Varian A-56-60A nmr spectrometer equipped with a variable-temperature probe. Proton and fluorine shifts are referred to external capillary TMS and $CFCl_3$, respectively.

The nmr spectra of the precursors were obtained as 15–20% (w/w) solution in SO_2ClF at −30°.

Registry No.—**1a,** 653-37-2; **1b,** 602-94-8; **1c,** 853-39-4; **2a,** 39981-38-9; **2b,** 40082-97-1; **2c,** 39981-39-0; **3a,** 39981-40-3; **3b,** 29680-43-1; **4a,** 22006-44-6; **4b,** 40081-60-5.

Acknowledgment.—Support of our work by grants of the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[10] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91,** 5801 (1969).

[11] W. R. Hasek, W. C. Smith, and V. A. Engelhartdt, *ibid.*, **82,** 543 (1960).