(350 mg) recrystallized from 95% ethanol (mp >350°): ir (KBr) 3247 (NH), 1665 (amide I), and 1600 cm^{-1} (amide II).

The hydrochloride (**3h**) was prepared by treating a solution of 100 mg of **3d** dissolved in 5 ml of anhydrous ether with dry hydrogen chloride gas. Recrystallized of the residue from evaporation gave 80 mg, mp 336–340° dec (methanol–ethanol).

Preparation of 4c by Nitration of 4a.—A finely powdered sample of **4a** (500 mg) in 50 ml of acetic anhydride at −5° was treated with 6 ml of fuming red nitric acid by dropwise addition. The mixture was stirred for 1 hr, then poured into ice water. The product was 240 mg (33%, ethanol), mp 225–228°. Two further recrystallizations raised the melting point to 230°.

Anal. Calcd for $C_{26}H_{38}B_2N_2O_4$: C, 63.44; H, 7.78; N, 11.38. Found: C, 63.16; H, 7.78; N, 11.49.

Spectral data for compound **4c** are found in Tables I, III, and IV.

Conversion of 4h to 4b.—**4h** (100 mg) in 4.5 ml of concentrated hydrochloric acid in an ice bath was treated with sodium nitrite (1.4 g) in small portions. A cold solution of 3 g of freshly prepared cuprous chloride[19] in 10 ml of 8 *N* hydrochloric acid was added and the mixture allowed to warm to room temperature. It was heated for 30 min on a steam bath, then diluted with cold water. The brown residue which remained was chromatographed on Florisil using ether to give 20 mg of a pale yellow semisolid which was identical with authentic **4b** (ir).

Registry No.—**2b**, 20116-72-7; **3a**, 1756-53-2; **3b**, 20122-54-7; **3c**, 20122-55-8; **3d**, 20122-56-9; **3e**, 3657-04-3; **3f**, 4040-72-6; **3g**, 20122-59-2; **3h**, 20122-60-5; **3i**, 3657-05-4; **4a**, 20122-62-7; **4b**, 20122-63-8; **4c**, 20122-64-9; **4d**, 20122-65-0; **4f**, 2179-88-6.

Acknowledgment.—The work described in this paper was supported financially by the National Institutes of Health (CA 6369). The authors wish to thank K. Servis (University of Southern California) for 32.1-MHz spectra and J. Crandall (Indiana University) for the use of laboratory facilities.

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Heteronuclear Stabilized Carbonium Ions. I. Nuclear Magnetic Resonance Examination of Aryl Oxocarbonium Ions

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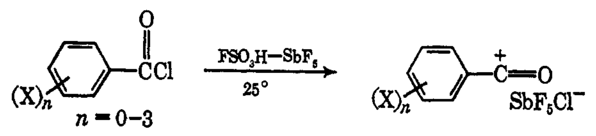
Aryl oxocarbonium ions were generated by the addition of benzoyl chlorides to FSO_3H–SbF_5 and were characterized by nmr spectroscopy at room temperature. In some instances ionizations were observed in neat FSO_3H. Chemical shift assignments were deduced from model compounds. For 28 cations the ranges of deshielding from the covalent precursors were as follows: $\Delta\delta_o$ 0.44–0.62 ppm, $\Delta\delta_m$ 0.44–0.57 ppm, and $\Delta\delta_p$ 0.93–1.09 ppm. Evidence is presented for alternating charge delocalization in the aromatic nucleus. Sulfonation products were observed when the cations possessed suitable electron-donating groups.

Oxocarbonium ions have been generated from acyl fluorides and SbF_5,[1–4] acyl chlorides and silver hexafluoroantimonate[1,2] or in some cases $SbCl_5$,[2,5] acyl sulfinylamines, or isocyanates and nitrosonium salts[6] as well as from the cleavage of esters[7] or carboxylic acids[8] in strong acid media. To date alkenyl,[8] alkylene,[9] cycloalkyl,[10] and alkyl[1–4] oxocarbonium ions have been directly observed and systematicly examined by nmr spectroscopy; however, such an examination of aryl oxocarbonium ions has not yet been reported.[11] As part of a related study of the behavior of methyl benzoates in strong acid media[12] it was necessary to characterize spectroscopically a number of aryl oxocarbonium ions. Characterization of these carbonium ions is reported herein.

Results and Discussion

Using a modified version of the procedures employed by Volz[5] and Olah[1–4] a number of *ortho*-, *meta*-, and *para*-substituted aryl oxocarbonium ions were prepared, by merely adding appropriate benzoyl chlorides to an excess of 1:1 *M* FSO_3H–SbF_5 solutions. The resulting homogeneous, although sometimes colored, solutions were for the most part stable enough to be examined by nmr spectroscopy at room temperature. Well-resolved spectra were generally obtained. In some cases, when steric and electronic effects were appropriate, the benzoyl chlorides could be ionized to their respective oxocarbonium ions in neat FSO_3H at room temperature.



The adequacy of the FSO_3H–SbF_5 method was demonstrated by converting acetyl chloride into its previously reported oxocarbonium. By this method a singlet was observed for this cation at −3.91 ppm and compares with a value of −3.93 ppm (20% oleum) reported by Deno and coworkers.[13] Additional efficacy was provided by observing chemical shift changes that occurred upon dissolving the benzoyl chlorides in neat

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[1] G. A. Olah, *Rev. Chim. Acad. Rep. Populaire Roumaine* (1962).

[2] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Amer. Chem. Soc.*, **84**, 2733 (1962).

[3] G. A. Olah, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **7**, 1139 (1962).

[4] G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, **85**, 1328 (1963).

[5] H. Volz and J. J. Volz de Leca, *Tetrahedron Lett.*, **38**, 3413 (1965).

[6] G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *J. Amer. Chem. Soc.*, **88**, 5328 (1966).

[7] G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

[8] G. A. Olah and A. M. White, *ibid.*, **89**, 405, 3591, 4752 (1967).

[9] G. A. Olah and M. B. Comisarrow, *ibid.*, **88**, 3313 (1966).

[10] G. A. Olah and M. B. Comisarrow, *ibid.*, **88**, 442 (1966).

[11] Cryoscopic measurements of a number of aryl oxocarbonium have been reported and are reviewed in "Carbonium Ions," D. Bethell and V. Gold, Ed., Academic Press, New York, N. Y., 1967, p 284.

[12] D. A. Tomalia, to be published.

[13] N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **86**, 4370 (1964).

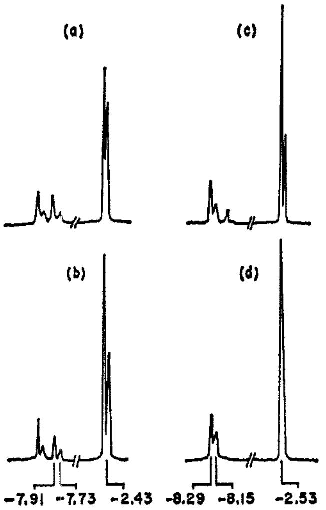
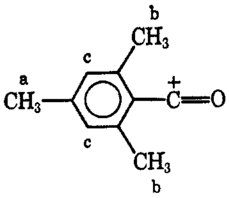


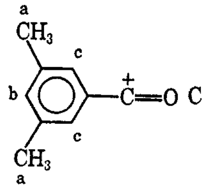
Figure 1.—Nmr spectra (δ) of 3,5-dimethylbenzoyl chloride: (a) in neat FSO$_3$H; (b, c) addition of less than a stoichiometric amount of SbF$_5$; (d) addition of a stoichiometric excess of SbF$_5$.

TABLE I



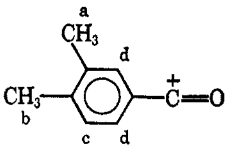
1

a 2.62 (s)
b 2.75 (s)
c 7.46 (s)
a:c:b 3:6:2



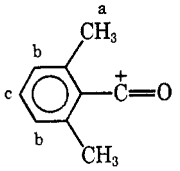
2

a 2.53 (s)
b 8.22 (s)
c 8.29 (s)
a:(b + c) 2:1



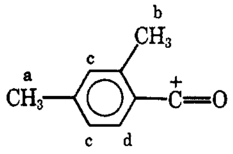
3

a 2.48 (s)
b 2.65 (s)
c 7.77 (d)
d 8.42 (d)
a:b:c:d 3:3:1:2



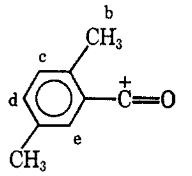
4

a 2.83 (s)
b 7.66 (d)
c 8.24 (t)
a:b:c 6:2:1



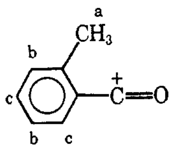
5

a 2.69 (s)
b 2.89 (s)
c 7.66 (d)
d 8.39 (d)
a:b:c:d 3:3:2:1



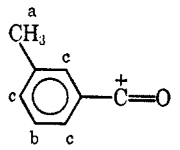
6

a 2.51 (s)
b 2.83 (s)
c 7.66 (d)
d ~8.21 (m)
e ~8.31 (s)
a:b:c (d + e) 3:3:1:2



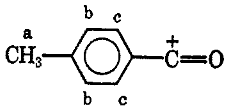
7

a 2.88 (s)
b 7.83 (m)
c 8.46 (m)
a:b:c 3:2:2



8

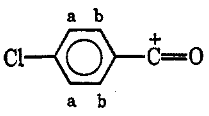
a 2.59 (s)
b 7.90 (t)
c 8.47 (t)
a:b:c 3:1:3



9

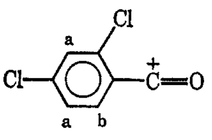
a 2.75 (s)
b 7.87 (d)
c 8.54 (d)
a:b:c 3:2:2

TABLE II



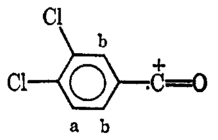
10

a 8.01 (d)
b 8.61 (d)
a:b 1:1



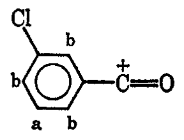
11

a 7.96 (m)
b 8.53 (d)
a:b 2:1



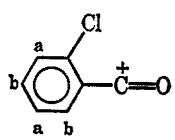
12

a 8.14 (d)
b 8.60 (m)
a:b 1:2



13

a 7.98 (t)
b 8.56 (m)
a:b 1:3



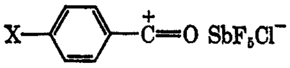
14

a 7.97 (t)
b 8.55 (m)
a:b 1:1

FSO$_3$H and then subsequently adding SbF$_5$. 2,4,6-Trimethyl and 2,6-dimethyl benzoyl chloride were completely ionized to their respective oxocarbonium ions in neat FSO$_3$H giving the chemical shift parameters for cations **1** and **4** shown in Table I. The addition of even a molar excess of SbF$_5$ did not cause any further deshielding. Furthermore the chemical shifts observed for cation **1** were essentially identical with those previously reported by Deno[13] and Volz.[5] When benzoyl chloride precursors to cations **2**, **3**, **5**, **6**, and **7** were added to neat FSO$_3$H, various degrees of ionization to the respective oxocarbonium ions were observed. Two discernible species could be observed by nmr in each of these cases. Figure 1 illustrates the spectrum (a) that was obtained for 3,5-dimethylbenzoyl chloride in neat FSO$_3$H, and those spectra (b and c) which were recorded for successive additions of SbF$_5$. Spectrum d shows the oxocarbonium ion, **2**, which was obtained by adding an excess (molar) of SbF$_5$. The downfield signals at −8.29, −8.15, and −2.53 ppm were assigned to the oxocarbonium ion and the upfield signals at −7.91, −7.73, and −2.43 ppm were assigned to protonated benzoyl chloride which is presumably undergoing proton exchange with the benzoyl chloride. This is supported by the fact that no highly deshielded $-C{=}O^{+}H$ signals were observed downfield except those for FSO$_3$H. Second, successive additions of an external chloride ion source (*e.g.*, LiCl) caused progressive upfield shifts in both the oxocarbonium ion and protonated acid chloride resonances accompanied by considerable signal broadening. As LiCl was added, the protonated acid chloride peaks increased commensurate amounts whereas the oxocarbonium ion signals decreased. By integrating either the aromatic or methyl protons of samples, which had been allowed to equilibrate for 1 hr, the per cent of ionization was determined for all of the cations listed in Table I. In the order listed (*i.e.*, cations **1–9**), the per cent of ionization was found to be as follows: 100, 48, 48, 100, 66, 64, 67, 0, and 0. Qualitatively the degree of ionization in this series appears to be more profoundly influenced by the amount of substitution in the *ortho* position rather than by favorable electronic effects that might arise from methyl substituents in the other positions. This is particularly apparent if one examines cations **7**, **8**, and **9**. It should be noted, however, that two methyl groups in either the *meta* or *meta* and *para*

TABLE III

NMR CHEMICAL SHIFTS OF *para*-SUBSTITUTED ACYLIUM IONS AT 25° IN FSO_3H-SbF_5 (1:1 MOLAR)

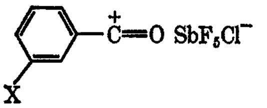


X	Registry no.	*ortho* protons	*meta* protons	X protons	$\Delta\delta_o$ [a]	$\Delta\delta_m$ [b]	$\Delta\delta_s$
$(CH_3)_3C$	20116-73-8	8.61 (d)	8.13 (d)	1.43 (s)	0.61	0.64	0.07
CH_3	20116-80-7	8.54 (d)	7.87 (d)	2.75 (s)	0.64	0.65	0.34
H	20116-74-9	~8.71 (m)	8.03 (t)		0.65	0.57	
F	20116-75-0	8.79 (m)	7.72 (t)		0.65	0.55	
Cl	20116-76-1	8.61 (d)	8.01 (d)		0.60	0.57	
Br	20116-77-2	8.49 (d)	8.21 (d)		0.52	0.58	
F_3C	20116-78-3	8.90 (d)	8.30 (d)		0.64	0.50	
NO_2	20116-79-4	9.06 (s)	9.06 (s)		0.67	0.67	

[a] $\Delta\delta_{o(av)}$ 0.62 ppm. [b] $\Delta\delta_{m(av)}$ 0.59 ppm.

TABLE IV

NMR CHEMICAL SHIFTS OF *meta*-SUBSTITUTED ACYLIUM IONS AT 25° IN FSO_3H-SbF_5 (1:1 MOLAR)

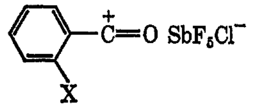


X	Registry no.	*ortho* protons	*meta* protons	*para* protons	X protons	$\Delta\delta_o$ [a]	$\Delta\delta_m$ [b]	$\Delta\delta_p$ [c]	$\Delta\delta_s$
CH_3	20147-91-5	8.47 (t)	7.80 (t)	8.47 (t)	2.59 (s)	0.63	0.54	1.11	0.16
H		~8.71 (m)	8.03 (t)	~8.50 (m)		~0.65	0.57	~0.88	
F	20116-81-8	8.29 (m)	8.29 (m)	8.29 (m)		~0.70	~0.70	~0.70	
Cl	20116-82-9	8.56 (m)	7.98 (t)	8.56 (m)		0.56	0.45	1.03	
Br	20116-83-0	8.68 (m)	7.91 (t)	8.68 (m)		0.72	0.51	0.72	
F_3C	20116-84-1	8.86 (t)	8.26 (t)	8.86 (t)		0.66	0.46	1.06	
NO_2	20116-85-2	2 H 9.57 (m) 6 H 9.15 (m)	8.33	9.15 (m)		2 H 0.60 6 H 0.61	0.50	0.61	

[a] $\Delta\delta_{o(av)}$ 0.62 ppm. [b] $\Delta\delta_{m(av)}$ 0.49 ppm. [c] $\Delta\delta_{p(av)}$ 0.93 ppm.

TABLE V

NMR CHEMICAL SHIFTS OF *ortho*-SUBSTITUTED ACYLIUM IONS AT 25° IN FSO_3H-SbF_5 (1:1 MOLAR)



X	Registry no.	*ortho* protons	*meta* protons	*para* protons	X protons	$\Delta\delta_o$ [a]	$\Delta\delta_m$ [b]	$\Delta\delta_p$ [c]	$\Delta\delta_s$
CH_3	20116-86-3	~8.56 (m)	7.83 (m)	~8.43 (m)	2.88 (s)	0.38	0.45	0.94	0.34
H		~8.71 (m)	8.03 (t)	~8.50 (m)		0.65	0.57	0.88	
F	20116-87-4	~8.70 (m)	7.79 (q)	~8.56 (m)		0.63	0.59	0.90	
Cl	20116-88-5	~8.55 (m)	7.97 (t)	~8.55 (m)		0.49	0.47	1.15	
Br	20116-89-6	~8.51 (m)	8.04 (m)	~8.51 (m)		0.47	0.48	0.95	

[a] $\Delta\delta_{o(av)}$ 0.44 ppm. [b] $\Delta\delta_{m(av)}$ 0.44 ppm. [c] $\Delta\delta_{p(av)}$ 1.02 ppm.

positions (*e.g.*, cations **2** or **3**) provide a sufficient driving force to produce ionization to the extent of 47–48%. Spontaneous ionization was not detected in neat FSO_3H for any of the more electron-deficient benzoyl chlorides including monosubstituted *o*-bromo-or *o*-chlorobenzoyl chloride. By adding less than stoichiometric amounts of SbF_5 to these more electron-deficient benzoyl chlorides one could observe mixtures of the oxocarbonium ions and protonated acid chlorides. For example, 4-trifluoromethylbenzoyl chloride exhibited two doublets centered at −8.46 and −8.00 ppm in neat FSO_3H. By adding less than a stoichiometric amount of SbF_5 one could generate the oxocarbonium ion as two downfield doublets centered at −8.93 and −8.36 ppm in addition to and at the expense of the upfield signals. Complete conversion to the carbonium ion was observed when an excess of SbF_5 was added.

In several instances the FSO_3H–SbF_5 solutions of the acid chlorides were examined by infrared spectroscopy and were found to contain characteristic oxocarbonium ion absorptions in the 2200–2300-cm^{-1} region.[4] Extensive etching of the cells (AgCl) precluded extensive characterization by this means.

Anomalous behavior was noted in the FSO_3H–SbF_5 medium for those acid chlorides containing substituents at each extreme of the Hammett σ range. These features will be commented on later.

Proton chemical shift assignments for the methyl- and chloro-substituted aryl oxocarbonium ions are summarized in Tables I and II. Assignments for mono-*para*-, *meta*-, and *ortho*-substituted cations are listed in Tables III, IV, and V, respectively.

These assignments were based on consideration of both the respective proton integrations as well as on the relative proton deshielding that was observed in suitably substituted model compounds. For example, 4-methylphenyl oxocarbonium ion, **9**, exhibited two symmetrical doublets in a ratio of 1:1 at −8.54 and

−7.87 ppm. The downfield signal was tentatively assigned to the *ortho* protons.[14] This assignment was corroborated by examination of those cations in Table I possessing *ortho* protons which could be unequivocally identified and distinguished from *meta* protons by integration. 3,4-Dimethylphenyl oxocarbonium ion, **3**, contains two *ortho* protons and one *meta* proton. This cation exhibited two unsymmetrical doublets at −8.42 and −7.77 ppm in a ratio of 2:1, respectively. Cation **2** which possesses only *ortho* and *para* protons exhibits singlets at −8.29 and −8.22 ppm in a ratio of 2:1 and were identified as *ortho* and *para* protons, respectively. From a series of these comparisons it becomes apparent that the chemical shift ranges for this group of cations are as follows: *meta,* −7.46 to −7.87; *para,* −8.22 to −8.47 and *ortho,* −8.29 to −8.54.

A series of chlorophenyl oxocarbonium ions (cations **10–14**) was examined in the same manner. As shown in Table II, chemical shift assignments could be made unambiguously by referring to the respective proton integrations.

Similar analyses of the other members of this carbonium ion system revealed the same general trend wherein the *ortho* protons are most deshielded followed by the *para* and then the *meta* hydrogens. The general range of chemical shifts for the respective protons in the 28 carbonium ions which were examined is as follows: *ortho* (−9.15 to −8.29 ppm, average −8.57 ppm); *para* (−8.86 to −9.22 ppm, average −8.53 ppm); *meta* (−8.26 to −7.46 ppm, average −7.92 ppm). These assignments paralleled those which were made in the cumyl cation[15] and 2-aryl-1,3-dioxolenium cation (cyclic dialkoxycarbonium ion)[16] systems.

In an effort to gain some insight as to the extent of charge delocalization to the various positions in the aromatic ring it was of interest to compare the chemical shift values of the carbonium ions with their respective benzoyl chloride precursors. The deshielding experienced in going from the covalent to the ionic species is indicated in Tables I–VII by $\Delta\delta_o$, $\Delta\delta_m$, $\Delta\delta_p$, and $\Delta\delta_s$ for the respective positions and substituents. One must exercise due caution in rationalizing relative deshielding entirely as a function of charge delocalization since other effects may contribute to the observed shielding. Many of these pitfalls are described by Fraenkel and Farnum,[16] particularly in the case of the triphenylcarbonium ion system. As cited by Farnum,[17] shielding due to the ring current effects of adjacent phenyl groups in these cations can profoundly affect relative deshielding of the respective aromatic positions. This is most pronounced for the *ortho* position. Upon appropriate treatment of the spectral data for these effects, Farnum did conclude that there is definitely charge alternation in these cations with the greatest amount of charge being delocalized to the *ortho* and *para* positions.

Table VI

Deshielding of Methyl-Substituted Acylium Ions Compared with Benzoyl Chloride Precursors (CCl_4)

Cation	$\Delta\delta_o$ [a]	$\Delta\delta_m$ [b]	$\Delta\delta_p$ [c]	$\Delta\delta_{o\text{-}CH_3}$ [d]	$\Delta\delta_{m\text{-}CH_3}$ [e]	$\Delta\delta_{p\text{-}CH_3}$ [f]
1		0.64		0.40		0.34
2	0.65		0.97		0.16	
3	0.70	0.60			0.19	0.36
4		0.53	1.11	0.43		
5	0.32	0.57		0.38		0.30
6	0.36	0.64	0.95	0.34	0.11	
7	0.28	0.45	1.08	0.34		
8	0.63	0.54	1.11		0.16	
9	0.64	0.65				0.34

[a] $\Delta\delta_{o(av)}$ 0.58 ppm. [b] $\Delta\delta_{m(av)}$ 0.57 ppm. [c] $\Delta_{p(av)}$ 1.07 ppm. [d] $\Delta\delta_{o\text{-}CH_3(av)}$ 0.39 ppm. [e] $\Delta\delta_{m\text{-}CH_3(av)}$ 0.17 ppm. [f] $\Delta\delta_{p\text{-}CH_3(av)}$ 0.35 ppm.

Table VII

Deshielding of Chloro-Substituted Acylium Ions Compared with Benzoyl Chloride Precursors (CCl_4)

Cation	$\Delta\delta_o$ [a]	$\Delta\delta_m$ [b]	$\Delta\delta_p$ [c]
1	0.60	0.57	
2	0.47	0.54	
3	0.59	0.55	
4	0.56	0.45	1.03
5	0.49	0.47	1.15

[a] $\Delta\delta_{o(av)}$ 0.54 ppm. [b] $\Delta\delta_{m(av)}$ 0.52 ppm. [c] $\Delta\delta_{p(av)}$ 1.09 ppm.

In an attempt to detect such a parallelism in the aryl oxocarbonium ion series, the monosubstituted cations were examined both as a function of their substituent position and as a function of the Hammett σ values of the substituent. By comparing the individual $\Delta\delta_o$, $\Delta\delta_m$, and $\Delta\delta_p$ values for 22 mono-*ortho*-, *meta*-, and *para*-substituted oxocarbonium ions (Tables III–V) one finds that, with but few exceptions, the deshielding values ($\Delta\delta$) decrease in the following order: $\Delta\delta_p > \Delta\delta_o > \Delta\delta_m$. This is most apparent by comparing average values which were determined for the respective positions as shown in Tables III and IV. The average $\Delta\delta$ values shown in Table V do not make this distinction between the *ortho* and *meta* positions as obvious. This may be due to the fact that resonance signals for the *ortho* and *para* protons were usually badly overlapped. This undoubtedly introduces some error in determining exact chemical shift values for these positions. However, large differences in the $\Delta\delta$ values for the *meta* and *para* positions are quite evident. These tables list the substituents in each case in order of their Hammett σ values (*i.e.*, from σ −0.27 to σ +0.78). Any deshielding effects as a function of the the substituents ability to accommodate charge (*i.e.*, as a function of the substituents Hammett σ value) should become apparent by vertically examining the δ and $\Delta\delta$ values in Tables III–V. Although the chemical shift values tend to move downfield as the σ value becomes more positive, no regular or quantitative trend is evident. Such a trend for the $\Delta\delta$ values is even less obvious.

As suggested by Fraenkel and coworkers,[18] π-electron densities in aromatic systems might be estimated from nmr data if other contributions to the chemical shifts such as special solvent effects, paramagnetic shifts, and substituent anisotropies were absent or could be determined independently. In an attempt to assess charge delocalization in a system where varying substituent an-

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[14] Olah has reported that the *ortho* protons in phenyl oxocarbonium hexafluoroantimonate are the most deshielded ring hydrogens in that cation. (See ref 1.)

[15] G. Fraenkel and D. G. Farnum in "Carbonium Ions," Vol. I, G. A. Olah and P. V. R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968, p 251.

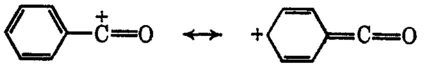
[16] D. A. Tomalia, unpublished results.

[17] D. G. Farnum, *J. Amer. Chem. Soc.*, **89**, 2970 (1967).

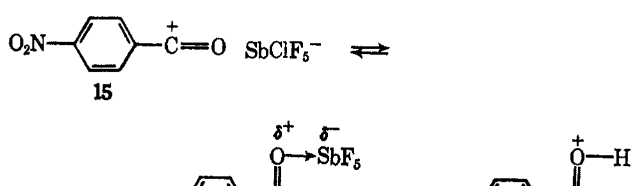
[18] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *ibid.*, **82**, 5846 (1960).

sotropy effects were minimized or at least constant we next compared deshielding values ($\Delta\delta$) for the methyl- and chloro-substituted aryl oxocarbonium ions described in Tables I and II. These data are presented in Tables VI and VII. In each system charge alternation is suggested as reflected by the relative $\Delta\delta$ values; however, dramatic differences between $\Delta\delta_o$ and $\Delta\delta_m$ are not apparent. This alternation effect is dramatically illustrated, however, by the $\Delta\delta$ values for the methyl substituents.

It should be noted that in all cases examined the *para* aromatic protons are consistently deshielded approximately twice as much as the *ortho* or *meta* protons [*i.e.*, $\Delta\delta_p \cong (2)(\Delta\delta_o)$ or $(2)(\Delta\delta_m)$]. This suggests that there may be considerable charge delocalization to the *para* position and reflects on the importance of the following resonance contribution.



As stated earlier, unusual behavior was noted for those acid chlorides which contained either strong electron-withdrawing substituents or strong electron-donating moieties. For example, 4-nitrobenzoyl chloride (σ +0.78) did not appear to be completely converted into its acylium ion at room temperature. An nmr spectrum of this reaction mixture consisted of a broad singlet at −9.06 ppm which partially overlaps with what appears to be a quartet centered at −8.84 ppm. The downfield signal was assigned to the carbonium ion, **15**. This assignment was based on the fact that this signal is 0.67 ppm downfield from 4-nitrobenzoyl chloride (CCl_4). This is consistent with the $\Delta\delta$ values of 0.64 and 0.50 ppm for the *ortho* and *meta* positions in the closely related 4-trifluoromethyl phenyl oxocarbonium ion (σ +0.55). The upfield signal was assigned to a donor-type complex, **16**, or perhaps the protonated acid chloride, **17**. Birchall and Gillespie have observed the closely related protonated 4-nitroacetophenone as a quartet centered at −8.87 ppm.[19] Judging from the broadness of the resonances a slow equilibrium may exist such as

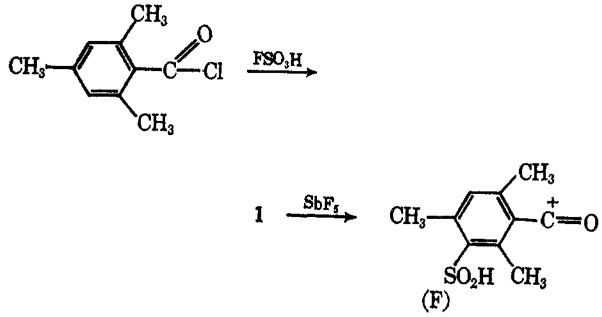


Broadness of the nmr resonance signals for 3-nitrobenzoyl chloride (σ +0.71) in FSO_3H–SbF_5 was also observed at room temperature. Although two discernible species could not be detected, an equilibrium as shown above may account for the poorer resolution.

In some instances observation of oxocarbonium ions was troubled by secondary reactions. This was particularly true of electron rich benzoyl chlorides which contained methoxy, cyclopropyl, or polymethyl groups.

Most notable was the complete decomposition of 4-cyclopropylbenzoyl chloride in FSO_3H–SbF_5 even at temperatures as low as −50°. Samples were prepared by dropping the acid chloride into a mixture consisting of equal volumes of FSO_3H–SbF_5 (1:1 *M*) and sulfur dioxide at ~−80°. Brilliant orange-red solutions were obtained which quickly degenerated into dark resinous syrups upon attempting to record spectra at −50°. Although this aspect was not investigated in detail, protonation of the cyclopropane ring is suspected as the source of this disturbance.[20-22]

In order to obtain a spectrum of the 2,4,6-trimethylphenyl oxocarbonium ion, **1** in FSO_3H–SbF_5 (1:1 *M*, 25°), it was necessary to scan immediately after sample preparation. In this manner one could obtain chemical shift parameters which were in agreement with previously reported values.[5,13] Within minutes, however, four new singlets began to appear downfield at −7.51, −2.82, −2.76, and −2.70 ppm. With time these peaks were enhanced at the expense of the upfield signals for the oxocarbonium ion **1** (*i.e.*, at −7.46, −2.75, and −2.62 ppm). Rapid integration of the aromatic and aliphatic protons during this time revealed that considerable loss of aromatic protons occurred (~50% of theory) based on that expected for cation **1**. Within 15 min the homogeneous liquid sample solidified to a tan crystalline mass. These data suggest that rapid sulfonation is occurring. By analogy to the known sulfonation of anisole in $ClSO_3H$, this sulfonation product may be a sulfonyl fluoride.[23] It should be mentioned that the ionization of 2,4,6-trimethylbenzoyl chloride to cation **1** in neat FSO_3H is not troubled by these secondary reactions. No changes in the spectrum of cation **1**, prepared in this manner, were noted even after 16 hr at room temperature. Upon adding an excess of SbF_5 to this sample, however, a sulfonation product developed to the extent of ~43% over a period of 12 hr. At this time it is not known whether sulfonation is occurring on the oxocarbonium ion **1** or whether equilibrium concentrations of the acid chloride are involved in this transformation. The former is certainly possible in view of the evidence reported by Hart[24] for the sulfonation of triarylcarbonium ions in concentrated sulfuric acid. This appears to be the second reported observation of sulfonation products resulting from attempts to generate cations in a FSO_3H medium.[23]



(F)

The behavior of 2-, 3-, and 4-methoxybenzoyl chlorides in neat FSO_3H was somewhat complicated.

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[19] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

[20] R. L. Baird and A. A. Aboderin, *J. Amer. Chem. Soc.*, **86**, 252 (1964).

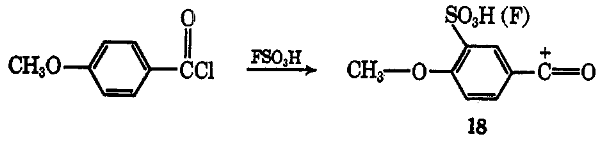
[21] H. Hart and R. H. Schlosberg, *ibid.*, **88**, 5030 (1966).

[22] N. C. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966).

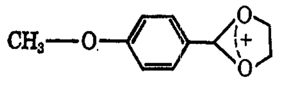
[23] B. G. Ramsey, *ibid.*, **88**, 5358 (1966).

[24] H. Hart and T. Sulzberg, *J. Org. Chem.*, **28**, 1159 (1963).

All three of the methoxy-substituted benzoyl chlorides appear to undergo complete monosulfonation over a period of 16 hr. When 4-methoxybenzoyl chloride is added to neat FSO_3H, a spectrum scanned within 5–7 min consists of multiplets at −8.90 to −8.12 ppm and −7.64 to −7.14 ppm accompanied by three upfield singlets at −4.24, −4.16, and −4.06 ppm. These singlets are designated A, B, and C in the order given above and are present in approximately the following relative amounts: $B \gg C > A$. After approximately 20 min the relative amounts become $B \gg A > C$ and after 3 hr the ratio is $A \gg B \cong C$. A considerably more simplified spectrum is obtained by storing the sample for 16 hr at room temperature. After this time the spectrum consists of a multiplet centered at −8.76, a doublet at −7.54, and a singlet at −4.26 ppm. These resonance signals are present in a ratio of 2:1:3. Based on previous aromatic proton assignments it appears as though monosulfonation at the *meta* position has occurred. According to the data available at this time, the sulfonated product is believed to be in the oxocarbonium ion form, **18**. This is based on the fact that by adding a stoichiometric excess of SbF_5 and allowing to equilibrate for 12 hr one observes a downfield shift of only 0.08 ppm for the methoxy group. This is in accord with a solvent shift rather than an ionization. Ultraviolet spectral data also corroborates this speculation. Fresh samples of 4-methoxybenzoyl chloride in FSO_3H gave λ_{max} at 232.6 and 302.5 mμ. The spectrum was unchanged after 12 hr at 25°. These data agree well with values obtained by Olah and coworkers[25] for 4-methoxyphenyl oxocarbonium in 33% oleum. Furthermore the related cations **19**[26] and **20**[19] exhibit methoxy resonance signals in approximately the same region at −4.08 and −4.38 ppm, respectively, in neat FSO_3H.



18



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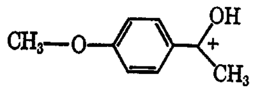
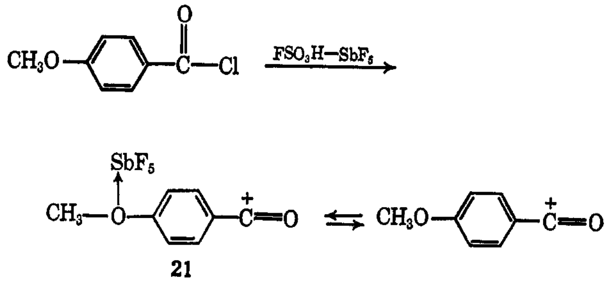


20

Analogous observations were made for 2- and 3-methoxybenzoyl chlorides. After 16 hr in neat FSO_3H, 2-methoxybenzoyl chloride gave an nmr spectrum consisting of a complex multiplet at −9.07 to −7.29 ppm, a major singlet at −4.44 ppm, and two minor singlets at −4.47 and −4.29 ppm. The aromatic to aliphatic proton ratio at this time was 3:3.27, indicating essentially complete monosulfonation. By adding a stoichiometric excess of SbF_5 the spectrum simplified to four doublets in the aromatic region at −8.95, −8.71, −8.55, and −7.82 ppm and a singlet in the aliphatic region at −4.47 ppm. The aromatic to aliphatic proton ratio remained the same. In the aromatic region the ratio of the most deshielded doublet (−8.95 ppm), the two intermediate doublets (−8.71, −8.55 ppm), and the upfield doublet was 1:1:1. Of the four possible monosulfonation products and based on previous aromatic proton assignments, these data are most consistent with sulfonation at positions either *ortho* or *para* to the methoxy groups.

3-Methoxybenzoyl chloride gave a spectrum consisting of a complex multiplet at −8.45 to −7.80 ppm accompanied by two minor singlets (−4.64 and −4.13 ppm) and two major singlets (−4.25 and −4.03 ppm). The ratio of aromatic to aliphatic protons was 3.12:3.00. Upon adding a stoichiometric excess of SbF_5 and scanning the spectrum reduced to a complex multiplet at −8.96 to −7.80 ppm and a singlet at −4.37 ppm. Although adding 4-methoxybenzoyl chloride to a 1:1 *M* mixture of $FSO_3H–SbF_5$ (25°) gave only a small amount of sulfonation even after 12 hr, ionization in this medium did not give a simple spectrum. Upon addition of acid chloride to the $FSO_3H–SbF_5$ medium and scanning within 15 min a spectrum was obtained which consisted of two doublets centered at −8.60 and −7.46 ppm accompanied by two singlets at −4.48 and −4.33 ppm. The aromatic to aliphatic proton ratio was 3.96:3.00 whereas the downfield to upfield singlet ratio was 1.00:0.85. Over a period of 12 hr the upfield singlet increased at the expense of the downfield singlet. The ratio of downfield to upfield singlet after 12 hr was 1.00:1.60. At this point the aromatic signals had not changed significantly from the original 15-min scan aromatic to aliphatic proton ratio was 3.81:3.00 thus indicating negligible sulfonation. The changes that occurred in the methoxy region are believed to be due to complexing of the methoxy group by SbF_5 thus yielding kinetically controlled mixtures of methoxy complexed oxocarbonium ion **21** and uncomplexed oxocarbonium as shown below. With time the complexed oxocarbonium presumably dissociates until a thermodynamically controlled equilibrium mixture is reached.



21

Similar observations were made for 3-methoxybenzoyl chloride. After allowing to equilibrate for 62 hr, 3-methoxybenzoyl chloride in $FSO_3H–SbF_5$ was observed as a multiplet at −9.01 to −7.98 ppm and a singlet at −4.35 ppm. The aromatic to aliphatic proton ratio was 3.25:3.00, indicating substantial monosulfonation.

The behavior of 2-methoxybenzoyl chloride in $FSO_3H–SbF_5$ was very complex. A spectrum scanned 20 min after sample preparation consisted of a multiplet at −9.20 to −7.27 ppm and −4.76 to −4.24 ppm. During a period of 62 hr the sample solidified to a black resinous product which was not further characterized.

Experimental Section

Materials.—All of the acid chlorides or carboxylic and precursors were obtained from commercial sources (Eastman, Ald-

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[25] G. A. Olah, C. U. Pittman Jr., R. Waack, and M. Doran, *J. Amer. Chem. Soc.*, **88**, 1488 (1966).

[26] D. A. Tomalia and H. Hart, *Tetrahedron Lett.*, **29**, 3389 (1966).

rich or Frinton Laboratories) except for 4-cyclopropylbenzoyl chloride. The preparation of which is described below. The acid chlorides were prepared in the usual manner from the respective carboxylic acids and thionyl chloride. Fluorosulfonic acid was obtained from Allied Chemical Co. and antimony pentafluoride was procured from Alfa Inorganic.

Nmr Spectra.—All spectra were recorded on a Varian A-60 nmr spectrometer equipped with a variable-temperature probe. Spectra were scanned within 15 min after sample preparation. The chemical shifts (δ) are reported in parts per million downfield from TMS using tetramethylammonium tetrafluoroborate (δ 3.10) as the secondary standard.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer Infracord Model 137-G using a AgCl cell. The cation samples in FSO_3H-SbF_5 caused substantial etching of the cell.

Ultraviolet Spectra.—Spectra were recorded on a Model 202 Perkin-Elmer recording spectrometer using 0.2-cm quartz absorption cells. Sample concentration were 10^{-2} to 10^{-3} *M*.

Sample Preparation.—Samples were prepared by adding ~0.1 g of the acid chloride in a dropwise manner to ~1.0 ml of FSO_3H-SbF_5 (1:1 *M*) at room temperature. A ratio of 1:1 by volume of sulfur dioxide was used for the low-temperature samples. The usual intense peak at −10.9 ppm and that of H_3^+O at −10.5 ppm were observed in all cases.

4-Cyclopropylbenzoyl Chloride.—Cyclopropylbenzene[27] was brominated according to the method of Levina and coworkers.[28] 4-Bromocyclopropylbenzene was obtained as a colorless liquid boiling at 97–98° (10 mm) (63%).

4-Cyclopropylbenzoic acid was prepared *via* the Grignard reagent and was obtained as a white crystalline solid melting at 156–157° (45%). Hart and Levitt[29] report a melting point of 157–158°. 4-Cyclopropylbenzoyl chloride was prepared by refluxing the carboxylic acid with 1 *M* excess of thionyl chloride for 2 hr. The acid chloride distilled as a colorless liquid, bp 89–90° (0.5 mm). The product gave an nmr spectrum consisting of two doublets centered at −7.93 and −7.09 ppm and two complex multiplets centered at −1.96 and −0.95 ppm in a proton ratio of 2:2:1:4, respectively.

Registry No.—**1**, 1571-83-1; **2**, 20122-33-2; **3**, 20122-34-3; **4**, 20122-35-4; **5**, 20122-36-5; **6**, 20122-37-6; **7**, 20122-38-7; **8**, 20122-39-8; **9**, 20122-40-1; **10**, 20122-41-2; **11**, 20122-42-3; **12**, 20122-43-4; **13**, 20122-44-5; **14**, 20122-45-6.

Acknowledgment.—The author would like to acknowledge the assistance of Mr. J. W. Lalk for the preparation of some of the acid chlorides.

(27) T. F. Corbin, R. C. Hahn, and H. Schechter, *Org. Syn.*, **44**, 30 (1964).

(28) R. Y. Levina, P. A. Gembitskii, and E. G. Treshchova, *Zh. Obshch. Khim.*, **33**, 371 (1963); *J. Gen. Chem.*, **33**, 364 (1963).

(29) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

The Alkylation of Difluoramine with Carbonium Ions[1]

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The acid-catalyzed reactions of difluoramine with olefins, alcohols, alkyl halides, ketones, and acetals yield organic difluoramino derivatives. These reactions appear to take place by reaction of a carbonium ion with difluoramine. Interpretation of the results is discussed in terms of carbonium ion stability and reactivity.

Previous reports of the chemistry of difluoramine from these laboratories have focused on its reactions with basic reagents, such as amines[2,3] and imines,[4] in which the fluorine–nitrogen bonds were broken. Recently, the addition of difluoramine to aldehydes and ketones was reported.[5] This reaction may be viewed as a special example of an alkylation reaction whereby a difluoramino group is attached to carbon. A preliminary report of other alkylations has also appeared.[6]

Results

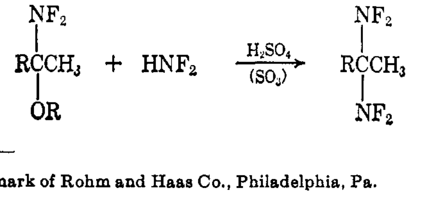
It has been found that a variety of compounds which react with acids to produce carbonium ions will alkylate difluoramine to produce new organic difluoramino compounds. The conditions required for alkylation depend on the ease of carbonium ion formation and the reactivity of the carbonium ion. Some comment will be made on the various factors involved during the discussion of these reactions. Some difluoramines prepared in this way are listed in Table I.

Olefins.—1,1-Dialkylethylenes, enol ethers and esters, and ketene acetals react with difluoramine in the presence of acid catalysts to produce the corresponding alkyl difluoramine. α,β-Unsaturated carbonyl compounds also add difluoramine readily.

The conditions of this addition reaction appeared to depend upon the nucleophilic character of the olefin. For example, ketene acetals and enol ethers reacted directly with difluoramine without added acid, enol esters required an added acid catalyst (a sulfonic acid ion-exchange resin, Amberlyst 15,[7] proved useful), and hydrocarbon olefins required concentrated sulfuric acid as catalyst.

Acrolein and methyl vinyl ketone reacted with difluoramine without catalyst to yield the conjugate addition products. Acrolein reacted further by addition to the carbonyl group. Acrolein diethyl acetal, on the other hand, reacted initially at the α-ether carbon atom, but with acid catalysis the bis product resulting from reaction at both carbonium ion centers was produced.

When the HNF_2–enol ether or enol ester products were treated with more difluoramine in the presence of 100% sulfuric acid or fuming sulfuric acid, the ether or ester function was replaced by a difluoramino group.



$$RC(NF_2)(OR)CH_3 + HNF_2 \xrightarrow[(SO_3)]{H_2SO_4} RC(NF_2)_2CH_3$$

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(1) This work was carried out under Army Ordnance Contract No. DA-01-021 ORD-5135.

(2) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Amer. Chem. Soc.*, **85**, 97 (1963).

(3) C. L. Bumgardner and J. P. Freeman, *ibid.*, **86**, 2233 (1964).

(4) W. H. Graham, *ibid.*, **88**, 4677 (1966).

(5) J. P. Freeman, W. H. Graham, and C. O. Parker, *ibid.*, **90**, 120 (1968).

(6) W. H. Graham and J. P. Freeman, *ibid.*, **89**, 716 (1967).

(7) Trademark of Rohm and Haas Co., Philadelphia, Pa.