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ISOMERIC FLUOROBENZYL AND FLUOROTROPYLIUM CATIONS

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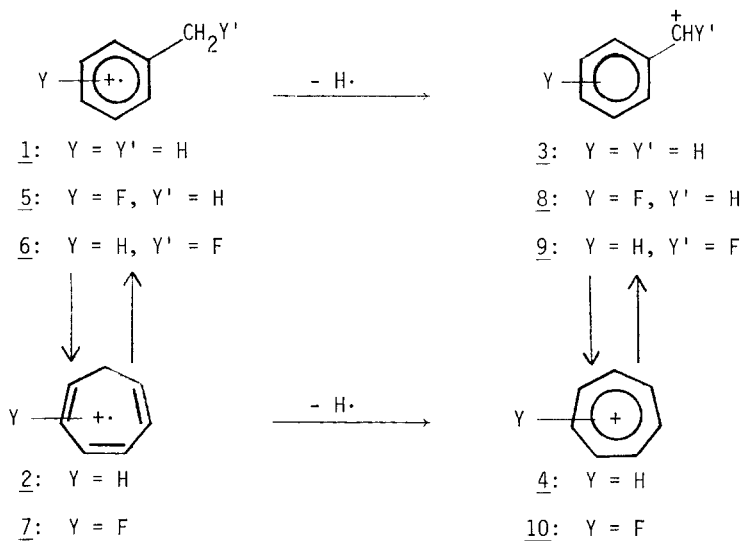
SUMMARY

The tendency for isomerization of toluene and cycloheptatriene molecular ions, and of benzyl and tropylium product ions, is substantially reduced by fluorine substitution, irrespective of position. This stabilization appears to be due to back-donation of electrons from fluorine, despite its high electronegativity.

INTRODUCTION

Although relatively few studies have been made of the electron-ionization (EI) mass spectra of fluoroorganic compounds [1,2], it is clear that their behavior can differ substantially from that of other halogenated compounds, R-X [2]. An example is the loss of H versus the losses of X and/or HX; in the mass spectra of α - and p -fluorotoluene, and α - and p -chlorotoluene, $[(M - H)^+]/[(M - X)^+]$ values are 50, 100, 0.02, and 0.2, respectively. However, the effects of m - and p -substitution of fluorine and chlorine (as well as a wide variety of other groups) on ion intensities in mass spectra of aromatic compounds are well correlated with Hammett σ constants [3], and the σ constants of m -F, p -F, m -Cl, and p -Cl are similar to each other (+0.34, +0.06, +0.37, +0.23, respectively) and to that of H (0.0). This study of the isomeric aromatic $C_7H_6F^+$ ions obtained from isomeric fluorotoluene and fluorocycloheptatriene molecular ions was also prompted by the numerous studies over many years on the unimolecular decomposition of ionized toluene (1) and cycloheptatriene (2) since the pioneering investigations by Meyerson [4]. The ratio of benzyl (3) to tropylium (4) ions produced from either 1 or

2 varies from 0.0 at threshold energy, to 1.0 for 15 eV electron ionization, to 0.5 at 70 eV, according to recent evidence [5] from collisional-activation mass spectra [6]. The Scheme offers a rationalization



Scheme

of these data. The equilibration $\underline{1} \rightleftharpoons \underline{2}$ requires less energy than H loss, so that at threshold energies either $\underline{1}$ or $\underline{2}$ precursors decompose through the lowest energy H loss pathway producing the more stable $\underline{4}$ ion. However, for $\underline{1} \rightleftharpoons \underline{2}$ the more stable $\underline{1}$ is favored, so that with increasing molecular ion internal energies H loss from the dominant $\underline{1}$ ion increases until equal amounts of $\underline{3}$ and $\underline{4}$ are produced. With further increases in the internal energy of the molecular ions, an increasing proportion of benzyl ($\underline{3}$) ions is formed with sufficient energy to undergo isomerization to tropylium ($\underline{4}$), decreasing the abundance ratio of $\underline{3}$ to $\underline{4}$ produced.

Isomerization of non-dissociating α -chlorotoluene molecular ions is indicated by photodissociation spectroscopy studies of Dunbar; possibly 70% have the ar-chlorotoluene structure [7]. The same study indicated only ~5% rearrangement of the initial molecular ion structure for ar-chlorotoluenes and 15% for α -fluorotoluene. However, for molecular ions of internal energies sufficient for dissociation, Williams [8] finds that ring expansion occurs for ar-fluorotoluenes ($\underline{5} \rightarrow \underline{7}$) and ar-chlorotoluenes, but not for ar-bromo- and ar-iodotoluenes. Thus it also appeared to be of particular interest to investigate the effect of ring- and α -fluorine substitution on these isomerization and H-loss reactions.

EXPERIMENTAL

Electron-ionization, metastable ion (MI), and collisional-activation (CA) mass spectra were measured on a tandem mass spectrometer (MS/MS) described elsewhere [9] consisting of a high-resolution Hitachi RMH-2 (ion source 150° C) as MS-I, a molecular-beam collision region (using for CA a helium pressure resulting in a 25% precursor-ion transmittance), and an electrostatic analyzer as MS-II. The reported spectra are the averages of several separate measurements, each the computer-averaged spectrum of 10-20 scans. For the $C_7H_6F^+$ CA spectra from 5, 6, and 7, and those with 15 eV-electron ionization, the regions m/z 76-82 and 87-96 were measured separately several times to increase the precision of these data. The data from 7 are of substantially lower precision because of sample limitations.

The α -fluorotoluene was obtained from Pfaltz and Bauer, and the aryl-fluorotoluenes from Aldrich. Fluorocycloheptatriene was prepared from diazomethane and fluorobenzene [10] as a mixture of the 1-, 2-, and 3-isomers whose individual mass spectra were obtained on a Finnigan 3300 gas chromatograph (GC)/MS. The mixed isomers, isolated by preparative GC, were ionized to produce the fluorotropylium ion 10 by H loss. The EI mass spectra of all these C_7H_7F compounds indicated them to be free of interfering non-isomeric impurities. The o-fluorotoluene- α, α - d_2 (purchased from Merck) contained 6% d_1 species (confirmed by NMR analysis); this impurity had no appreciable effect on the CA data of Table 2 (the CA losses of CH_2 , CH_3 , and CH_4 from $\alpha-F-C_6H_4-CH_3^+$ are <1% of the base peak).

RESULTS AND DISCUSSION

The EI mass spectra of o-, m-, p-, and α -fluorotoluene, and 1-, 2-, and 3-fluorocycloheptatriene are closely similar; hydrogen loss produces the base peak in each spectrum. This behavior resembles that already observed for the mass spectra of their unsubstituted analogs, the C_7H_8 isomers [4], but in addition the position of the fluorine atom also has little effect. If this is due to isomerization of the molecular ion to an equilibrated mixture of structures, 5 \rightleftharpoons 7 \rightleftharpoons 6, loss of hydrogen after ionization of any of the C_7H_7F isomers should produce a similar mixture of $C_7H_6F^+$ isomers.

The collisional activation (CA) mass spectrum (excluding products formed by low energy pathways) of an ionic species is characteristic of its structure; if two species produce different CA spectra, they must have different structures, or be composed of different mixtures of structures [6]. The CA mass spectra of the $C_7H_6F^+$ ions formed from *ar*-fluorotoluenes (5), α -fluorotoluene (6), and fluorocycloheptatriene (7) are significantly different (Table 1), so that the equilibration $\underline{5} \rightleftharpoons \underline{7} \rightleftharpoons \underline{6}$ is not complete before hydrogen loss. The most significant differences are in the peaks representing losses of CH_2 (m/z 95) and CHF (m/z 77). The $C_7H_6F^+$ ions from 6, consistent with their presumed structure $C_6H_5CHF^+$ (9), show the largest peak for CHF loss; these ions thus contain $\leq 40\%$ ($3.2/7.8$) of the isomeric 8 and 10 ions, and the latter two contain $\leq 30\%$ of 9 ions. Further, the CA spectra of the presumed 8 and 9 ions do not change when the ionizing electron energy is lowered from 70 to 15 eV, consistent with a change of $<15\%$ in the amount of 8 or 10 in the 9 ions, or of 9 in the 8 ions. This is in contrast with the behavior of the unsubstituted ions 1 and 2 [5], but is consistent with Dunbar's observation of only 15% isomerization of 6 [7].

The CA spectra of *o*-, *m*-, and *p*-fluorobenzyl ions (8) are the same within experimental error, and show only small (but reproducible) differences in comparison to the spectrum of the fluorotropylium ion 10. This could be due to isomerization of the 8 and 10 ions to a common structure (or mixture of structures) prior to collisional activation and/or close similarities in the CA spectra of the different 8 and 10 isomers. As a further test, the CA spectra of $C_7(H,D)_6F^+$ ions formed by D and H loss from *o*- $F-C_6H_4-CHD_2$ were measured (Table 2). These indicate that formation of the expected $F-C_6H_4-CHD^+$ and $F-C_6H_4-CD_2^+$ and their CA loss of $C(H,D)_2$ is accompanied by incomplete, although extensive, H/D scrambling ($\sim 72\%$ and $\sim 77\%$, respectively). Part of this could be due to the exchange in *o*-5 of α - and *o*-hydrogen atoms (a low energy process for toluene ions [9]) without F-position or skeletal isomerization; additionally, part of the H/D scrambling probably occurs after collisional activation of the $C_7(H,D)_6F^+$ ions. We thus conclude that there is an appreciable activation energy barrier to isomerizations changing the fluorine position in the fluorotoluene molecular ions 5 and 6 and in the fluorobenzyl ions 8 and 9, as well as the ring expansions to form 7 and 10, respectively.

The striking difference in $[(M - H)^+]/[(M - X)^+]$ in the mass spectra of these fluoroaromatic compounds versus their chloro counterparts can be explained [2] on the basis of the higher tendency for back-donation of

TABLE 1

Collisional activation mass spectra of $C_7H_6F^+$ isomers

m/z	Precursor C_7H_7F molecule				F-CHT
	<u>o</u> -F	<u>m</u> -F	<u>p</u> -F	<u>α</u> -F	
31	17	15	15	14	13
33	4	5	3	4	8
39	45	43	40	41	39
50	32	30	29	33	34
51	30	31	26	33	34
54.5	3	2	3	3	<5
57	100	100	100	100	100
59	17	25	21	26	28
62	36	38	37	33	42
63	58	62	59	57	70
68	10	8	10	7	13
69	13	13	13	13	13
70	9	10	7	7	6
74	14	13	13	13	17
75	16	15	15	13	20
77	2.3	3	3	7.7	2
81	58	57	59	55	58
83	(235)*	(255)	(226)	(217)	(259)
89	25	26	24	26	31
94	4.3	4	5	3.4	7
95	7.8	8	9	3.2	12
105	9	10	10	10	8
107	(251)	(272)	(256)	(251)	(214)
108	(129)	(131)	(126)	(136)	(72)

*Figures in parentheses represent abundances of product ions also formed by metastable ion decompositions.

TABLE 2

Collisional activation mass spectra of $C_7(H,D)_6F^+$ ions from labeled *o*-fluorotoluenes*

m/z	$F-C_6H_4-CH_2^+$	$F-C_6H_4-CHD^+$	$F-C_6H_4-CD_2^+$
93	13	9	5
94	32	22	8
95	56	42	33
96		27	36
97			18

*The precursor $C_7(H,D)_6F^+$ ions are formed, respectively, from *o*- $F-C_6H_4-CH_3$ by H loss, and from *o*- $F-C_6H_5-CHD_2$ by D loss and by H loss.

electrons by fluorine. This should also provide increased cation stabilization, lowering the tendency for the isomerizations $\underline{5} \rightleftharpoons \underline{7} \rightleftharpoons \underline{6}$ and $\underline{8} \rightleftharpoons \underline{10} \rightleftharpoons \underline{9}$, as observed. This behavior is quite similar to the additional stabilization observed in adding a methyl-substituent to ions $\underline{1} - \underline{4}$ [12]. The negative Hammett σ constants of *m*- CH_3 and *p*- CH_3 (-0.07 and -0.17, respectively) reflect directly this electron-donating ability, while for fluorine this is more than offset by its high electronegativity (σ : *m*-F, +0.34; *p*-F, +0.06).

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