Aryl Migration in Aromatic Amides during Mass Spectrometry

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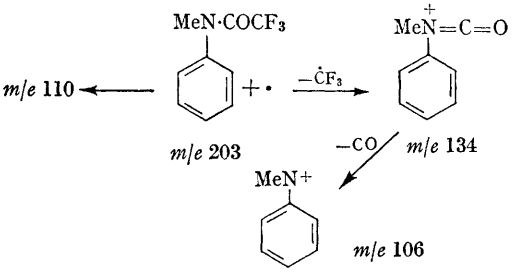
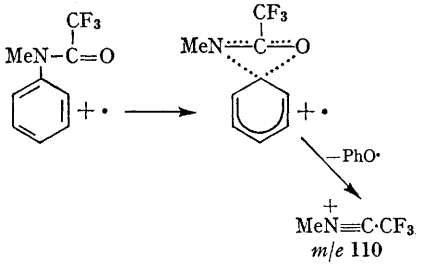
THE fragmentation of *N*-methyl-*N*-trifluoracetylaniline (I, Figure 1) proceeds "normally" with successive losses of CF_3 and CO to give the ion at *m/e* 106, but the process is accompanied by another involving rearrangement of the molecular ion to give an abundant ion at *m/e* 110 ($C_3H_3F_3N$).



The formation of the ion at *m/e* 110 from the molecular ion, marked by a strong metastable ion, indicated the elimination of a phenoxyl radical.



The origin of the ion at *m/e* 110 was amply confirmed in many subsequent experiments, some of which are described. Thus in *N*-acetyl-*N*-methylaniline the corresponding ion should appear at *m/e* 56, and an abundant ion (C_3H_6N) was found at this position although the rearrangement ion was not so prominent as in the case of the trifluoracetyl

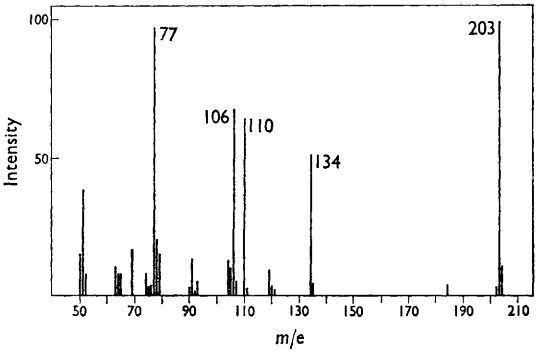


FIGURE 1

amides. With these *N*-acetyl amides, the normal loss of keten was the major process. At an intermediate electronegativity, as in *N*-chloracetyl-*N*-methylaniline, the rearrangement ion (chlorine doublet, *m/e* 90, 92), was also intermediate in abundance as shown in the Table. Similarly, varying the other groups attached to nitrogen produced changes in the prominence of this ion, and with *N*-trifluoracetyldiphenylamine the rearrangement ion at *m/e* 172 constituted by far the most intense fragment ion in the spectrum. In contrast, there was almost no ion from this process in the case of *N*-trifluoracetylaniline. Substitution of the phenyl ring in *N*-methyl-*N*-trifluoracetylaniline ($R{\cdot}C_6H_4{\cdot}NMe{\cdot}COCF_3$; R = *m*-, *p*- Cl, OMe, NO_2, Me) showed that the ion at *m/e* 110 was formed in each case with loss of the radical $R{\cdot}C_6H_4O$.

TABLE

Amide, $R^1R^2NCOR^3$	"Normal" fragment ion†	Rearrangement ion
R^1 = Ph; R^2 = H; R^3 = CF_3	113	<0·5
R^1 = Ph; R^2 = Me; R^3 = CF_3	51·4	65·0
R^1 = Ph; R^2 = Ph; R^3 = CF_3	11·6	86·0
R^1 = Ph; R^2 = Me; R^3 = Me	282	33
R^1 = 2,6-$Me_2{\cdot}C_6H_3$; R^2 = Me; R^3 = Me	21·4	246
R^1 = Ph; R^2 = Me; R^3 = CH_2Cl	82	86

† Produced by loss of CF_3, CH_2Cl, or CH_2CO from molecular ion. Intensities (%) are relative to height of molecular ion.

Measurements of the energy required for this rearrangement and the effects of these substituents upon it are being made. The relative intensities of the ions formed by this rearrangement process compared to those formed by "normal" fragmentation are shown in the Table.

Further evidence for the rearrangement mechanism described was provided by *N*-acetyl-*N*-methyl-2,6-dimethylaniline which, with methyl groups blocking the *ortho*-positions, showed a greatly enhanced intensity of the rearrangement ion at *m/e* 56. The rearrangement was not observed in aliphatic trifluoracetamides.

The possible analogous rearrangement of *S*-trifluoracetylthiophenol was not observed, only simple fragmentation.

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