Photonucleophilic Substitution in Aryl Fluorides: Photochemical Cine-substitution and Evidence for an Addition–Elimination Mechanism

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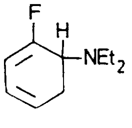
Summary Photosubstitution of aryl fluorides by primary and secondary amines can give both 'normal' and cine-substitution products, probably by an addition–elimination mechanism; *ortho*-type photoadducts are also produced in most cases, although *p*-difluorobenzene gives the *para*-adduct (**6**) with diethylamine.

The light-induced substitution of aryl fluorides by nucleophiles has been the subject of several publications;[1] *e.g.*, fluorobenzene and piperidine give *N*-phenylpiperidine.[1a] We now report the first examples of photochemical cine-substitution, and outline evidence that a major pathway for the photosubstitution of fluorine in aryl fluorides involves initial addition of the amine to the benzene ring[2,3] followed by elimination of hydrogen fluoride.

Irradiation of diethylamine in fluorobenzene (1 : 1 v/v, 254 nm, 20 °C, N_2) gives *NN*-diethylaniline and, by attack of the amine nitrogen on the *ortho*-, *meta*-, and *para*-positions, the *ortho*-type adducts (**1**), (**2**), and (**3**) in the initial ratios 0·75 : 0·35 : 0·25 : 1·0, respectively. (Analogous products have also been obtained from chlorobenzene and diethylamine: contrast with ref. 1a). Similar results were observed with t-butylamine and piperidine as the amine component, although the product ratios in both cases differed somewhat from those with diethylamine. The absence of adducts of the *ortho*- or *para*-type arising from attack of the amine nitrogen at the 1-position, and those containing a H–C–F group, prompted the suspicion that such adducts or their precursors are unstable and eliminate HF to yield the aniline. The photoreactions of difluorobenzenes with amines have provided further information.

Although all three difluorobenzenes gave the corresponding monofluoroaniline derivatives, cine-substitution products were also produced, together with adducts of the *ortho*-type, and one *para*-type from the *para*-isomer. Thus *m*-difluorobenzene and diethylamine gave the adducts (**4**) and (**5**) and *o*-, *m*-, and *p*-fluoro-*NN*-diethylanilines in the ratios 0·37 : 0·2 : 0·25 : 1 : 0·004, respectively. The behaviour of *o*-difluorobenzene was similar to that of the *meta*-isomer, and t-butylamine also gave 'normal' and cine-substitution products. All the substitution products and adducts appeared to be primary photochemical products, although the proportions of adducts of *ortho*-type showed variations with irradiation time consistent with varying degrees of photolability.[2b] On the other hand, the adduct (**6**) of *para*-type from *p*-difluorobenzene was essentially photostable.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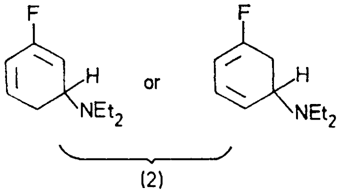
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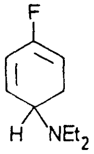
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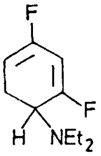
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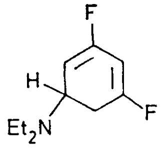
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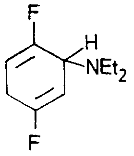
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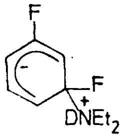
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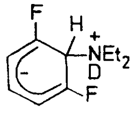
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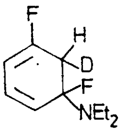
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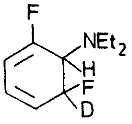
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In reactions of Et_2ND with the three difluorobenzenes, >0·85 atoms of deuterium were incorporated in the adducts, 0·5—0·6 in the 'normal' substitution products, and 0·3—0·4 in the cine-substitution products. The *NN*-diethylaniline produced from irradiation of Et_2ND with fluorobenzene also contained 0·45 atoms of deuterium.†

Although free-radical products, *e.g.* fluorinated tetrahydrobiphenyls,[3] are formed, their proportions relative to the adducts and substitution products decrease markedly in the series: benzene, fluorobenzene, difluorobenzenes. The overall chemical yields, however, increase in the same order.

The effect of solvent dielectric constant is interesting. In the case of benzene and primary and secondary amines, little effect is observed.[3,4] In contrast, mono- and difluorobenzenes gave markedly decreased chemical yields of substitution and addition products with solvents of increasing dielectric constant (cyclohexane, ether, acetonitrile, methanol), but the ratios were essentially unaffected.

Any major mechanistic contribution from a route involving aryne intermediates appears to be ruled out by the absence of effects of the aryne-traps, furan and tetracyclone (apart from internal filtering in the latter case), and by the general predominance of 'normal' over cine-substitution products. It is evident that substitution occurs largely by an addition–elimination mechanism, *viz.* either *via* zwitterionic Wheland-type intermediates [*e.g.* (**7**) and (**8**) from Et_2ND and *m*-difluorobenzene] and/or unstable chemical adducts [*e.g.* (**9**) and (**10**)]. The latter have not been detected, even at the shortest feasible irradiation times. Both they and the isolated adducts could arise by the 1-electron transfer mechanism previously discussed for benzene.[3] The zwitterions (**7**) and (**8**) could in principle arise by either 1- or 2-electron transfer processes. In practice the absence of a solvent polarity effect for additions to benzene suggests either a 1-electron process not involving an exciplex,[3] or that any exciplex involved is not markedly polar,[5] whereas the marked solvent effect now noted for the reactions of fluorobenzenes suggests a distinctly polar exciplex, quenchable by polar solvents,[5] which can react partly by 1-electron–proton transfer to give free radicals, and to a greater extent by 2-electron transfer to give either zwitterions or perhaps even four-centre additions of NR_2 and H to the aromatic ring related to those suggested by Porter *et al.*[6]

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† Irradiation of the products of these reactions in the presence of Et_2ND showed that no significant incorporation of deuterium by H–D exchange occurs. Exchange with HF or DF is considered very unlikely as these promptly yield the highly insoluble amine hydro(deuterio) fluorides.

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