A Mechanism for the Photosubstitution of Fluoro- and Methoxy-benzenes by Diethylamine

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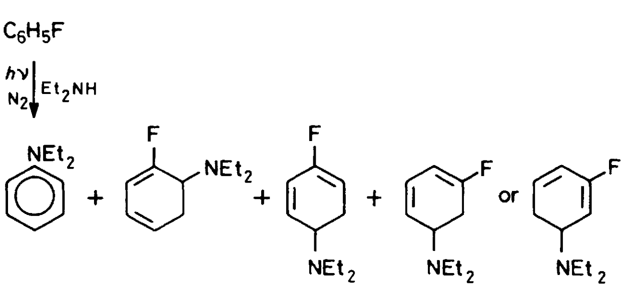
The photochemical reactions of fluoro- and methoxy-benzenes with diethylamine produce addition and substitution products. The proposed mechanism involves quenching of the singlet state by the amine to give an exciplex. Proton transfer within the exciplex leads to the amine adducts, some of which can undergo elimination to yield the substitution products.

The photoreaction of fluorobenzene with aliphatic amines has been studied by Barltrop *et al.*,[1] who isolated a substitution product (**1**), and by Gilbert and his co-workers,[2,3] who obtained addition products (**2**)—(**4**) as well as (**1**) [equation (1)].



(1)

(**1**) (**2**) (**3**) (**4**)

Barltrop and his co-workers[1] also investigated the reactions of anisole derivatives with amines. The highest chemical yield was obtained from the photosubstitution of 3,5-dimethylanisole with diethylamine to give a 35% yield of *N*,*N*-diethyl-3,5-dimethylaniline, based on starting material consumed.

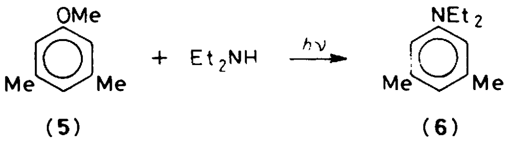
This study was begun with three objectives: to account for the difference in the product spread found by the previous workers; to determine whether this kind of photonucleophilic substitution[4—6] could be useful synthetically (for example in ring-closure reactions directed towards the synthesis of nitrogen heterocycles); and to elucidate the reaction mechanism.

Results and Discussion

When a mixture of fluorobenzene and diethylamine was irradiated for 24 h, the products were *N*,*N*-diethylaniline and a mixture of two adducts. The latter were not completely identified, but from their mass spectra they appear to be the same as two of those obtained by Gilbert and his co-workers.[3] Two separate work-up procedures were employed to study the behaviour of the addition products. One was analogous to the procedure used in ref. 3, and involved concentrating the product mixture by bubbling nitrogen through for several hours. The other procedure involved separation of the products into basic and neutral components by extraction, analogous to the method used in ref. 1. In both cases, the same product mixture was obtained. The proportions of the more volatile adducts were gradually reduced on removal of solvent, and this may be a reason why no adducts were observed by Barltrop and his co-workers. We will return to the issue of the adducts later.

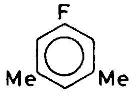
In our subsequent experiments we chose to work with 3,5-dimethylbenzene derivatives. First, 3,5-dimethylanisole gives a higher yield of substitution products than anisole itself, as already noted;[1] second, unsubstituted fluorobenzene has b.p. almost identical with that of common solvents such as cyclohexane and acetonitrile, and this makes it difficult to monitor the loss of reactant by g.l.c.

When a solution of 3,5-dimethylanisole (**5**) in diethylamine was irradiated for 15.5 h, the major product was *N*,*N*-diethyl-3,5-dimethylaniline (**6**), obtained in yields of about 12% based on starting material consumed [equation (2)]. Irradiation under nitrogen increased the yield of (**6**) to about 20%, at conversions of 70—80%. An irradiation of 1-fluoro-3,5-dimethylbenzene (**7**) with diethylamine under nitrogen gave a complex assortment of products, of which (**6**) appeared to be only a minor product (g.l.c. analysis). We were unable to increase the yields in these reactions to synthetically useful levels. The addition of solvents to the diethylamine, whether the solvent was polar or not, reduced the yield of (**6**).

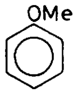


(2)

(**5**) (**6**)



(**7**)



(**8**)

The initial interaction between the amine and the aromatic substrate was investigated by studying the fluorescence quenching of (**5**), (**7**), and anisole (**8**) by a series of amines in cyclohexane solution (Table 1). The fluorescence quenching of (**5**) was also investigated in acetonitrile and in methanol. The following trends were noted. (*a*) The bimolecular quenching constants (obtained from K_{SV} and the fluorescence lifetime in the absence of amine) are all high, but fall short of the rate constant for diffusion (7×10^9 dm^3 mol^{-1} s^{-1} in cyclohexane[7]). (*b*) The quenching efficiency of 3,5-dimethylanisole is not strongly solvent dependent. (*c*) The quenching efficiency does not increase monotonically as the ionization potential of the amine decreases. This would have been expected for fluorescence quenching involving electron (or charge) transfer [equation (3)]. At least part of this phenomenon seems to be a steric effect, as seen from the relative quenching efficiencies of

$$^1ArX + R_3N \longrightarrow (R_3N^{\delta+}{\cdot}ArX^{\delta-}) \text{ or } R_3N^{+\cdot} + ArX^{-\cdot} \quad (3)$$

Table 1. Fluorescence quenching of anisole (**8**), 3,5-dimethylanisole (**5**), and 1-fluoro-3,5-dimethylbenzene (**7**)[a]

		K_{SV}/dm^3 mol^{-1}				
Amine	I.P.(eV)[b]	(**8**)	(**5**)	(**7**)	(**5**)[c]	(**5**)[d]
Propylamine	8.78	1.9	0.41	1.3	0.50	1.1
Piperidine	8.04	25	6.7	50	5.0	0.80
Diethylamine	8.01	17	2.9	37	3.0	1.1
Di-isopropylamine	7.73	2.8	1.1	6.6	0.34	0.32
Triethylamine	7.50	1.6	0.47	0.98	6.9	0.51
Lifetime (ns)		5.5	6.3	7.5		

[a] Concentrations were (**8**) 5.6 × 10^{-4}, (**5**) 3.0 × 10^{-4}, and (**7**) 3.3 × 10^{-4} mol dm^{-3} in cyclohexane. [b] Taken from ref. 8. The ionization potential (I.P.) for piperidine was estimated from the relative I.P.s of piperidine and diethylamine (from ref. 9). [c] 3.0 × 10^{-4} mol dm^{-3} in acetonitrile. [d] 3.0 × 10^{-4} mol dm^{-3} in methanol.

$$\mathrm{ArX} \xrightarrow{h\nu} {}^1\mathrm{ArX}$$

$${}^1\mathrm{ArX} \xrightarrow{k_1} \mathrm{ArX}$$

$${}^1\mathrm{ArX} \xrightarrow{k_2} \text{other processes}$$

$${}^1\mathrm{ArX} + \mathrm{Et_2NH} \xrightarrow{k_3} \underset{(\mathbf{9})}{[\mathrm{ArX}\cdots\mathrm{NHEt_2}]}$$

$$(\mathbf{9}) \xrightarrow{k_4} \text{product } (\mathbf{6})$$

$$(\mathbf{9}) \xrightarrow{k_5} \text{other processes}$$

Scheme.

the three secondary amines (piperidine > diethylamine > di-isopropylamine). (*d*) Quenching constants K_{SV} are such that relatively high concentrations of amine are needed to trap all the excited singlets. This is probably the reason why dilution of the amine with solvents depresses the product yields, since quantities of unidentifiable 'polymeric' material are formed whether or not the amine is present, and the material balance is poor (see also ref. 1).

We next studied the quantum yields in these reactions. The quantum yields for loss of aromatic starting material, φ_r, showed little change with amine concentration (diethylamine) when cyclohexane was the solvent. These quantum yields were: (**5**), aerated, $\varphi_r = 0.025$; (**5**), degassed, $\varphi_r = 0.046$; (**7**), aerated, $\varphi_r = 0.019$; (**7**), degassed, $\varphi_r = 0.027$. In the polar solvents methanol and acetonitrile, even lower quantum yields were found.

Quantum yields φ_p for formation of product (**6**) from (**5**) or (**7**) showed typical bimolecular behaviour, with $\varphi_p^{-1} \propto [\mathrm{Et_2NH}]^{-1}$. It is not inconsistent that φ_p should vary with [Et$_2$NH] while φ_r does not, because the chemical yields of product are low, and most of the photoexcited (**5**) gives products other than (**6**), whatever the amine concentration.

None of the previous workers had determined the excited state(s) responsible for these reactions. We have been able to show that the substitution product (**6**) is formed from the S_1 states of (**5**) and (**7**) as follows.

Let us assume the mechanism of the Scheme, where we denote as (**9**) the species formed (which we believe to be an exciplex) by the bimolecular interaction between the amine and the S_1 state of the aromatic substrate ArX. The rate constants k_2 and k_5 are composite and are first-order or pseudo-first-order. Application of the steady-state approximation to [^{1}ArX] and [(**9**)] gives equation (4) for the relationship between φ_p and [Et$_2$NH].

Table 2. Comparison of the intercept/slope parameter with K_{SV}

Substrate	Intercept	Intercept/slope (dm^3 mol^{-1})	K_{SV}/dm^3 mol^{-1}
(**5**)	120	2.8	2.9
(**7**)	230	39	37

$$\frac{1}{\varphi_p} = \left(1 + \frac{k_5}{k_4}\right)\left(1 + \frac{(k_1 + k_2)}{k_3[\mathrm{Et_2NH}]}\right) \qquad (4)$$

According to equation (4), a plot of $1/\varphi_p$ *vs.* $1/[\mathrm{Et_2NH}]$ should yield the parameter intercept/slope as $k_3/(k_1 + k_2)$. This is the same as the Stern–Volmer constant K_{SV} for fluorescence quenching (Table 1). Thus if the Scheme is to represent the reaction mechanism, there should be a reasonable concordance between the intercept/slope parameter and K_{SV}. Table 2 gives a comparison of these parameters. The excellent agreement between the intercept/slope parameter and K_{SV} conclusively shows that S_1 is the excited state responsible for the substitution reaction. The high intercepts are associated with $(1 + k_5/k_4)$ in the Scheme and they explain the low overall photoefficiency of substitution.

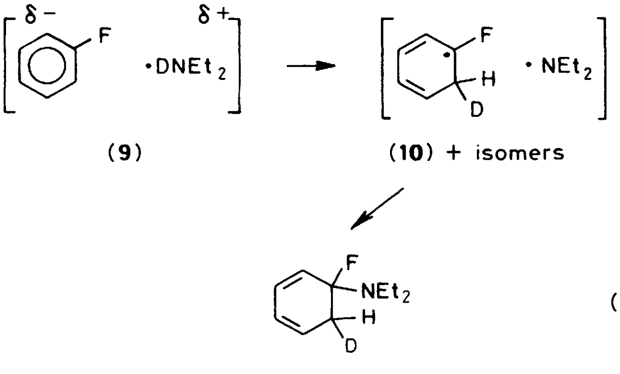
Additional support for a singlet-state reaction was obtained from xenon quenching studies. Conventional sensitization by triplet sensitizers such as acetone or benzophenone is not possible owing to the very high triplet energies of fluoro- and methoxy-benzenes.[8] Tables 3 and 4 (Experimental section) show the effect of xenon on the fluorescence quenching and reactions of (**5**) and (**7**) with diethylamine. The reduction of the yield of (**6**) in the presence of the heavy-atom quencher xenon paralleled the fluorescence quenching, consistent with a singlet-state reaction.

In an attempt to detect intermediates we examined the reactions of (**6**) and (**8**) with diethylamine using microsecond flash photolysis. In aerated cyclohexane, the single transient we observed between 280 and 500 nm only appeared after repetitive flashing of (**5**) or (**7**) with diethylamine and was identical with the transient obtained by flashing (**6**) itself. Hence this transient is not a reaction intermediate. In degassed cyclohexane, (**5**) and (**7**) each gave a complex series of transients in the absence of diethylamine, and no further study was attempted.

Evidence to support the identification of (**9**) (Scheme) as an exciplex was obtained through a deuterium-incorporation study. Fluorobenzene, 1-fluoro-3,5-dimethylbenzene, and 3,5-dimethylanisole were all irradiated with Et$_2$ND (compare refs. 10—12). In the case of fluorobenzene the adducts and the substitution product were all examined by g.l.c.–mass spectrometry, comparative with an experiment using Et$_2$NH. As expected, each adduct incorporated one deuterium per molecule. The substitution product was monodeuteriated to the extent of 83%.

In the case of the 3,5-dimethylphenyl compounds, the yields of adducts were very small, and in these cases the substitution product and the recovered reactants were examined. The substitution products were again monodeuteriated (80% for X = OCH$_3$; 89% for X = F) and deuterium was also incorporated into the 'unchanged' starting material (10% for X = OCH$_3$; 40% for X = F).

These observations show that the addition and 'substitution' are related processes. The initial reaction is proton transfer within the exciplex [equation (5)], this process being disfavoured in polar solvents where radical ion diffusion can occur. Back transfer of hydrogen from (**10**) accounts for incorporation of deuterium into the reactant and a low



(9) (10) + isomers (11) (5)

photoefficiency, while the loss of HF from (11) with a normal kinetic isotope effect explains the 80—90% rate of incorporation of deuterium into the substitution product. Examination of the structures of the confirmed adducts[3] shows that the only adducts that have so far been isolated (2)—(4) are those that cannot rearomatize by loss of HF and overall substitution.

One point that must be noted is that Barltrop *et al.*[1] observed that the reaction between *p*-fluorotoluene and piperidine afforded *N*-*p*-tolylperidine as the only substitution product. This must mean that substitution (as opposed to addition) products only are formed following protonation of (9) *ortho* or *para* to the substituent already present. This permits coupling of $^{\bullet}NR_2$ at the carbon atom already bearing the substituent.

In conclusion, we have established that the mechanisms of addition and substitution between diethylamine and photoexcited monosubstituted benzenes of the classes under study proceed from the excited singlet state of the aryl substrate. Quenching of this excited state by amine affords an exciplex, the initial reaction of which is proton transfer. This accords well with previous studies on photoreduction of arenes by amines,[10] and photodechlorination of aryl chlorides by amines.[11,12] Overall substitution occurs by way of the amine adduct of the aromatic compound; if HF (or CH_3OH) elimination is not possible the adduct may be isolable (*cf.* also ref. 13 for methoxynaphthalene–amine photoreactions). This mechanistic pathway makes it unlikely that synthetically useful substitutions following this route await discovery.

Experimental

M.p.s were determined with a Mel-temp apparatus. ^{1}H N.m.r. spectra were obtained with a Varian EM360L spectrometer. Samples were dissolved in deuteriochloroform, with tetramethylsilane as internal standard. U.v.–visible spectra were recorded with a Perkin-Elmer Lambda 3 spectrophotometer.

Fluorescence measurements were made at room temperature for samples in 1 × 1 cm square quartz cuvettes, with a Perkin-Elmer LS-5 fluorescence spectrophotometer. Quenching constants were determined by the Stern–Volmer method. The complete experimental method has been described previously.[14] Fluorescence lifetimes were recorded at 25 °C for solutions in aerated cyclohexane, with a PRA 2000 fluorescence lifetime instrument.

Flash photolysis experiments were performed with a PRA FP 1000 instrument operating with a flash energy of *ca.* 60 J and a flash duration of 10 μs. For experiments conducted in the absence of O_2, the solutions were degassed by two freeze–pump–thaw cycles.

Preparative-scale photolyses were conducted in a 350 cm^3 quartz immersion well equipped with a Hanovia 450 W medium-pressure mercury lamp. Aerated samples were stirred with a magnetic stirrer. For reactions under N_2, the gas was bubbled through during and for 20—30 min prior to irradiation, using nitrogen that was deoxygenated by bubbling through a solution of chromium(II) chloride.[15]

Kinetic-scale photolyses were carried out in duplicate using quartz ampoules of 8 mm o.d., with a 2.0 cm^3 sample size. The photolysis equipment was a Rayonet RPR photoreactor equipped with 16 low-pressure mercury lamps with emission maxima at 254 nm. A 'merry-go-round' was used to ensure equal illumination of the samples. Photolysed samples were analysed for substrate disappearance and product formation by g.l.c. using a Carle 211 gas chromatograph equipped with a 6 ft × $\frac{1}{8}$ in stainless steel column packed with 10% SE-30 on Chromosorb W. All samples were analysed at least in duplicate using dodecane, pentadecane, 4-methylanisole, or *N*,*N*-diethylaniline as external standard.

G.l.c.–mass spectrometry results were obtained using a VG MM 12000 analytical mass spectrometer interfaced with a Hewlett-Packard 5790 gas chromatograph equipped with a 60 m quartz capillary column of J&W DB-5 fused silica. G.l.c.–mass spectrometry of preparative-scale samples was performed with a VG 7070F mass spectrometer interfaced with a temperature-programmable Perkin-Elmer Sigma III gas chromatograph equipped with a 6 ft glass column of 3% OV-1 or 2.5% SE-30 on Chromosorb W.

Cyclohexane, acetonitrile, and methanol were Fisher ACS spectroanalysed solvents. Purity of starting materials was checked by g.l.c. The amines were freshly distilled over KOH prior to use. [*N*-$^{2}H_{1}$]Diethylamine, 98% atom purity, was obtained from KOR isotopes.

Authentic *N*,*N*-diethyl-3,5-dimethylaniline was prepared by refluxing 3,5-dimethylaniline with 2 equiv. of iodoethane and sodium hydroxide in water for 5 h. The crude material obtained was recrystallized from light petroleum (b.p. 30—60 °C) to give white plates, m.p. 44.5—45 °C (lit.,[1] 46—47 °C); δ 6.25 (3 H, s), 3.27 (4 H, q *J* 7 Hz), 2.23 (6 H, s), and 1.12 (6 H, t, *J* 7 Hz).

1-Fluoro-3,5-dimethylbenzene was prepared by the method of Schiemann[16] from 3,5-dimethylaniline. The fluoroborate salt was thermally decomposed to give a colourless liquid, b.p. 146 °C (lit.,[17] 145 °C); δ 6.67 (2 H, s), 6.50 (1 H, s), and 2.27 (6 H, s).

Irradiation of Fluorobenzene–Diethylamine.—A mixture of fluorobenzene (30.0 cm^3) and diethylamine (30.0 cm^3) was irradiated under N_2 for 24 h with a 75 W low-pressure mercury lamp to give a yellow solution. Half of this solution was concentrated by bubbling nitrogen through for several hours; the other half was separated into neutral and basic fractions by extraction. G.l.c. of the separate work-up fractions indicated that the same product mixture was formed. G.l.c.–mass spectrometry of the basic fraction indicated the presence of *N*,*N*-diethylaniline as well as two components identified from their mass spectra as the addition products; one had *m*/*z* (%) 170 (9.6), 169 (84.6, M^+), 154 (32.4), 98 (17.2), 97 (100), 96 (18.7), and 95 (14.3); the other had *m*/*z* (%) 170 (5.1), 169 (41.6, M^+), 154 (37.1), 98 (9.3), 97 (100), 96 (13.3), and 95 (12.5). This extract was stable to chromatography on silica gel although repeated concentration decreased the relative amount of the more volatile addition products.

Irradiation of 3,5-*Dimethylanisole–Diethylamine.*—A solution of 3,5-dimethylanisole (2.0 g) and diethylamine (290 cm^3) was irradiated for 15.5 h. Concentration and extraction followed by chromatography afforded *N*,*N*-diethyl-3,5-dimethylaniline (0.18 g, 8.4%). G.l.c. analysis revealed 24% starting material. The experiment was repeated except that analysis was performed only by g.l.c.; in this case an 8.8% yield was obtained, with 23%

Table 3. 3,5-Dimethylanisole[a] plus xenon

Run	[Et$_2$NH]/mol dm^{-3}	P_{Xe}/atm	Int.[b]	% Loss[c]	% Yield[d]
1	0	0	61.2	6.1	0
2	0	1	23.7	7.0	0
3	0.24	0	25.5	11.3	3.4
4	0.24	1	15.8	7.5	2.4

[a] Irradiation of degassed 3,5-dimethylanisole (4.95 × 10^{-3} mol dm^{-3}) in cyclohexane for 5 min. [b] Fluorescence intensities determined at 280/296 nm. [c] % Loss of 3,5-dimethylanisole by g.l.c. [d] % Yield of *N*,*N*-diethyl-3,5-dimethylaniline by g.l.c.

Table 4. 1-Fluoro-3,5-dimethylbenzene[a] plus Et$_2$NH–xenon

Run	[Et$_2$NH]/mol dm^{-3}	P_{Xe}/atm	Int.[b]	% Loss[c]	% Yield[d]
1	0	0	78.5	13.6	0
2	0	1	47.8	14.6	0
3	0.023	0	33.8	22.2	4.9
4	0.023	1	27.2	18.6	4.2

[a] Irradiation of degassed 1-fluoro-3,5-dimethylbenzene (5.4 × 10^{-3} mol dm^{-3}) in cyclohexane for 10 min. [b] Fluorescence intensities at 272/285 nm. [c] % Loss of substrate by g.l.c. [d] % Yield of *N*,*N*-diethyl-3,5-dimethylaniline by g.l.c.

starting material. Irradiation under nitrogen gave a 14.6% yield with 19.5% starting material as shown by g.l.c.

Irradiation of 1-*Fluoro*-3,5-*dimethylbenzene–Diethylamine*.—A solution of 1-fluoro-3,5-dimethylbenzene (1.83 g) and diethylamine (290 cm^3) was irradiated under nitrogen for 15.5 h. Concentration and extraction of the basic components into HCl gave a thick dark brown liquid, which was composed of about a dozen compounds. A peak attributed to product (**6**) was only a minor component.

Quantum Yield Determinations.—Quantum yields were determined using the method of Bunce *et al.*[18] A 5 min irradiation of a solution of 3,5-dimethylanisole (5.15 × 10^{-3} mol dm^{-3}) and diethylamine (8.59 × 10^{-2} mol dm^{-3}) in cyclohexane resulted in a 12.7% loss of substrate; a 5.55 × 10^{-3} mol dm^{-3} solution of azoxybenzene in 95% ethanol suffered a 7.95% loss; this gave φ_r = 0.025.

A 10 min irradiation of 1-fluoro-3,5-dimethylbenzene (5.13 × 10^{-3} mol dm^{-3}) and diethylamine (8.60 × 10^{-2} mol dm^{-3} in cyclohexane resulted in a 17.3% loss of substrate; a 4.99 × 10^{-3} mol dm^{-3} solution of azoxybenzene in 95% ethanol suffered a 15.6% loss; this gave φ_r = 0.019.

Effect of Xenon on Reactions.—This is shown in Tables 3 and 4.

Flash Photolysis.—*Aerated solutions*. Repetitive flashing of 3,5-dimethylanisole (3.66 × 10^{-3} mol dm^{-3}) or 1-fluoro-3,5-dimethylbenzene (5.13 × 10^{-3} mol dm^{-3}) with diethylamine (4.4 × 10^{-2} mol dm^{-3}) in cyclohexane gave a transient with $\lambda_{max.}$ *ca.* 300 nm, τ *ca.* 10 ms. A solution of *N*,*N*-diethyl-3,5-dimethylaniline (1.0 × 10^{-4} mol dm^{-3}) in cyclohexane gave this transient with τ 5.2 ms from 300 to 325 nm.

Degassed solutions. Solutions of 1-fluoro-3,5-dimethylbenzene (5.0 × 10^{-3} mol dm^{-3}) and 3,5-dimethylanisole (2.93 × 10^{-3} mol dm^{-3}) in cyclohexane were degassed by two freeze–pump–thaw cycles. A complex series of transients was observed for both substrates between 300 and 500 nm.

Table 5. Irradiation of (**5**) (5.37 × 10^{-3} mol dm^{-3}) in cyclohexane for 5 min[a]

10[Et$_2$NH]/mol dm^{-3}	% Yield (**6**)
0	0
1.1	0.97
2.1	1.8
3.2	2.2
5.4	2.5
8.6	2.7

[a] Loss of (**5**) constant at *ca.* 16%.

Table 6. Irradiation of (**5**) (4.72 × 10^{-3} mol dm^{-3}) in degassed cyclohexane for 5 min[a]

10[Et$_2$NH]/mol dm^{-3}	% Yield (**6**)
0	0
0.80	3.0
1.6	4.3
2.4	5.5
3.2	5.6
4.8	6.5

[a] Loss of (**5**) constant at *ca.* 16%.

Table 7. Irradiation of (**7**) (5.5 × 10^{-3} mol dm^{-3}) in cyclohexane for 10 min[a]

10[Et$_2$NH]/mol dm^{-3}	% Yield (**6**)
0	0
2.0	1.8
4.0	2.4
6.0	2.8
8.0	3.0
10	3.1

[a] Loss of (**7**) constant at *ca.* 18%.

Kinetics.—Data are given in Tables 5—7.

Comparative Study with Et$_2$ND *and* Et$_2$NH.—In all cases, the concentration of Et$_2$NH was 0.14M and of Et$_2$ND 0.13M. Samples were in cyclohexane solution and were degassed by two freeze–pump–thaw cycles. Samples were irradiated for 10 min except for 3,5-dimethylanisole which was irradiated for 5 min. In all cases g.l.c.–mass spectrometry revealed a component with *m*/*z* (%) 166 (9.8), 83 (46.6), 82 (100), 67 (42.9), and 55 (54.0), identified as bicyclohexyl.

Fluorobenzene–Et$_2$NH. G.l.c.–mass spectrometry showed two components: (1) *m*/*z* (%) 169 (13.8), 154 (19.9), 98 (8.3), 97 (100), 96 (18.4), 95 (14.9), and 77 (18.7) (addition product); (2) *m*/*z* (%) 150 (3.1), 149 (27.0), 135 (10.4), 134 (100), 106 (50.9), and 77 (37.4) (substitution product).

Fluorobenzene–Et$_2$ND. G.l.c.–mass spectrometry showed two components: (1) *m*/*z* (%) 170 (13.4), 155 (20.7), 99 (26.2), 98 (100), 97 (18.3), 96 (16.5), and 78 (16.5) (deuteriated adduct); (2) *m*/*z* (%) 151 (6.1), 150 (27.5), 136 (19.8), 135 (100), 134 (19.9), 107 (49.8), and 78 (32.6) (deuteriated substitution product).

1-*Fluoro*-3,5-*dimethylbenzene*–Et$_2$NH. G.l.c.–mass spectrometry showed two components: (1) *m*/*z* (%) 125 (4.3), 124 (49.4), 123 (22.4), 110 (7.8), and 109 (100) (starting material); (2) *m*/*z* (%) 178 (3.7), 177 (28.8), 163 (12.3), 162 (100), and 134 (25.8) (substitution product).

1-*Fluoro*-3,5-*dimethylbenzene*–Et$_2$ND. G.l.c.–mass spectrometry showed two components: (1) *m*/*z* (%) 125 (6.3), 124 (43.8), 123 (19.8), 110 (12.8), and 109 (100) (starting material partially deuteriated); (2) m/z (%) 179 (4.9), 178 (28.8), 177 (6.7), 164 (12.3), 163 (100), 162 (14.1), and 135 (25.8) (deuteriated substitution product).

3,5-*Dimethylanisole*–Et_2ND. G.l.c.–mass spectrometry showed two components: (1) m/z (%) 137 (11.0), 136 (100), 135 (10.1), 121 (36.6), 105 (16.4), 93 (14.0), 92 (10.1), 91 (96.4), and 77 (45.5) (starting material); (2) m/z (%) 164 (12.8), 163 (100), 162 (27.5), and 135 (23.2) (deuteriated substitution product).

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support through an operating grant to N. J. B. and a postgraduate scholarship to S. R. C.

References

1 J. A. Barltrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc. C*, 1967, 1142.
2 D. Bryce-Smith, A. Gilbert, and S. Krestonosich, *J. Chem. Soc., Chem. Commun.*, 1976, 405.
3 A. Gilbert and S. Krestonosich, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1393.
4 J. Cornelisse and E. Havinga, *Chem. Rev.*, 1975, **75**, 353.
5 E. Havinga and J. Cornelisse, *Pure Appl. Chem.*, 1976, **47**, 1.
6 J. Cornelisse, G. Lodder, and E. Havinga, *Rev. Chem. Intermed.*, 1979, **2**, 231.
7 J. G. Calvert and J. N. Pitts, Jr., 'Photochemistry,' Wiley, New York, 1966.
8 S. L. Murov, 'Handbook of Photochemistry,' Dekker, New York, 1973.
9 D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, 1975, **97**, 4137.
10 N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, 1973, **95**, 5783.
11 O. M. Soloveichik and V. L. Ivanov, *J. Org. Chem. USSR* (*Engl. Transl.*), 1974, **10**, 2416.
12 N. J. Bunce, *J. Org. Chem.*, 1982, **47**, 1948.
13 L. O. Ruzo, N. J. Bunce, and S. Safe, *Can. J. Chem.*, 1975, **53**, 688.
14 N. J. Bunce, Y. Kumar, L. Ravanal, and S. Safe, *J. Chem. Soc., Perkin Trans. 2*, 1978, 880.
15 A. J. Gordon and R. A. Ford, 'The Chemist's Companion,' Wiley, Toronto, 1972, p. 438.
16 G. Balz and G. Schiemann, *Ber.*, 1927, **60B**, 1186.
17 N. Löfgren, B. Lundqvist, and S. Lindström, *Acta Chem. Scand.*, 1955, **9**, 1079.
18 N. J. Bunce, J. LaMarre, and S. P. Vaish, *Photochem. Photobiol.*, 1984, **39**, 531.

Received 9th May 1985; *Paper* 5/769