Photochemical Reactions of Substituted Benzenes with Aliphatic Amines

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The products arising from the irradiation of diethylamine and t-butylamine with toluene, chlorobenzene, anisole, benzonitrile, benzyl fluoride, benzotrifluoride (α,α,α-trifluorotoluene), m-fluorobenzotrifluoride (α,α,α,m-tetrafluoro-toluene), p-fluorotoluene, m-fluorotoluene, p-fluoroanisole, m-fluoroanisole, and 1,3-bis(trifluoromethyl)benzene, and of triethylamine with toluene, benzotrifluoride and 1,3-bis(trifluoromethyl)benzene, all at 254 nm, are described. Reaction pathways involving both substitution and 1,2- and 1,4-acyclic addition processes are observed and which predominates depends upon the arene substituent. The novel acyclic adduct, $Me_2C{=}CH{-}CH{=}CH{-}CH{=}NBu^t$, is obtained from toluene and t-butylamine and, contrary to previous reports, chlorobenzene yields arene–amine 1 : 1 adducts as well as the amine α-substitution product (16); benzonitrile gives aniline derivatives with the primary and secondary amines.

PHOTONUCLEOPHILIC substitution of arenes by aliphatic amines has been described for several systems [1-3] but it has been observed that with benzene itself, although minor amounts of NN-dialkylanilines are formed from secondary amines, the major photochemical reaction involves acyclic addition of the N–H of primary and secondary amines and the α–C–H of tertiary amines to the arene.[4-6] Thus the 1,2- and 1,4-adducts (1) and (2) are formed from benzene and primary or secondary aliphatic amines and the 1,4-product (3), for example, from triethylamine. The photoaddition reactions are inhibited by polar solvents but that of tertiary amines is accelerated by methanol or other proton donors.[5] The mechanism for the process is considered to involve excited-state complexes and electron- and proton-transfer steps followed by combination of radicals within a solvent cage. We have recently reported that fluoro-benzene and the difluorobenzenes also yield 1 : 1 acyclic photoadducts with aliphatic amines but photonucleo-philic substitution to form aniline derivatives competes effectively with the addition process and from the latter arenes both the cine and ' normal ' substitution products are observed.[7] Formation of the cine and at least a proportion of the ' normal ' substitution product is con-sidered to arise via an addition–elimination mechanism involving unstable 1 : 1 acyclic adducts and/or their immediate precursors.

In order to obtain more information on the factors which may influence the relative efficiencies of photo-addition and -substitution in arene–amine systems and to assess further if the two processes are related mechan-istically, we have investigated the photoreactions of toluene, chlorobenzene, anisole, and benzonitrile with diethylamine. Benzyl fluoride and benzotrifluoride (α,α,α-trifluorotoluene) were also examined in this reaction to ascertain if substitution in the side-chain by the amine was competitive with reaction at the nucleus; p-fluoro-benzotrifluoride and m- and p-fluoro-toluenes and -anisoles were studied to assess the extent to which aryl fluoride could divert or modify the photoreactions observed between diethylamine and the monosubstituted

derivatives. Additionally, most of the above arenes were irradiated in the presence of t-butylamine but since reaction efficiencies of systems involving tertiary amines tend to be very low, and the presence of methanol is required,[5] the photoreactions of only three arenes with triethylamine were studied in detail.

RESULTS

The results of our present study into the modes of reaction of S_1 arenes with aliphatic amines are summarised in the Table. The chemical yields from most systems were generally low and in some cases only the major reaction products were characterised. The spectroscopic features of the photoadducts of aliphatic amines and benzene which allow structural assignments to be made have been pre-viously discussed [5] and hence are not argued further here; relevant data are presented in the Experimental section. In the present systems, the components of the mixture from irradiation were separated by preparative g.l.c. with purities of 90—95%, the ' impurities ' being isomeric products as judged by combined m.s.–g.l.c. and analytical data. In some cases inseparable mixtures of isomers were indicated from spectroscopic properties. For example such data from the major fraction collected from the irradiation of toluene and diethylamine were consistent with a 1,4-acyclic addition product with the aryl methyl group now residing on an ethenylic bond. Expansion of the ^1H methyl resonance of the ethyl groups of the sample in C_6D_6, however, clearly showed the presence of two overlapping triplets in a 1 : 1 ratio. Multiple mass scanning through this component eluted from a gas chromatograph demonstrated the absence of non-isomeric impurities and hence structures (8) and (9) were assigned to the components of the mixture. Similar examination of the spectroscopic properties of reaction components from the irradiation of toluene–t-butylamine, chlorobenzene–t-butylamine and chlorobenzene–diethyl-amine, showed the presence of an isomeric mixture in each case. In other systems which gave greater yields of product, repeat cycle preparative g.l.c. was realistic and gave components sufficiently pure for meaningful analytical data to be obtained. As in the case of the fluorobenzene–amine photoreactions,[7] the decision between 1,2- and 1,4-acyclic addition products [i.e. type (1) or (2)] was made essentially from the ultraviolet spectra of the adducts;

thus 1 : 1 adducts which had their maximum absorption in the 245—265 nm region were deduced to have the cyclohexa-1,3-diene unit as in (1), whereas the other adducts having their longest wavelength absorption at *ca.* 220 nm

structures.[5,7] The positions of the substituents on the adducts were determined from a more detailed analysis of the [1]H n.m.r. spectra. For example, structures (14) and (15) were assigned to the separated two 1 : 1 adduct isomers

Products from irradiation of aliphatic amines with substituted benzenes at 254 nm

Arene	Amine	Products [a]	Ratio [b]	Relative retention time [c]
Toluene [d]	t-Butylamine	(4) + (5) 2 : 1 mixture	0.85	0.65
		$\overset{\displaystyle Me}{\underset{\displaystyle Me}{Me-\overset{\textstyle \vert}{\underset{\textstyle \vert}{C}}-N{=}CH{-}CH{=}CH{-}CH{=}CMe_2}}$ (6)	1.00	1.00
Toluene	Diethylamine	(7)	0.45	0.85
		(8) + (9) 1 : 1 mixture	1.00	1.00
		(10)	0.19	1.10
		NN-diethyl-m-methylaniline	0.15	1.95
Toluene	Triethylamine [e]	(11)		
		[7 minor products constitute 40% of mixture but each <9% of (11)]		
Chlorobenzene	t-Butylamine	N-t-butylaniline	1.00	1.00
		(12) + (13) 1 : 1 mixture	0.50	1.70
		(14)	0.10	2.00
		(15)	0.28	2.90
Chlorobenzene	Diethylamine	(16)	0.27	0.47
		NN-Diethylaniline	1.00	1.00
		(17)	0.45	1.20
		(18) + (19) 1 : 1 mixture	0.65	1.40
		(20)	0.25	1.60
Anisole	Diethylamine	NN-Diethylaniline		
Benzonitrile [d]	t-Butylamine	N-t-Butylaniline		
	Diethylamine	NN-Diethylaniline		
Benzyl fluoride [d,f]	t-Butylamine	PhCH=NBu[t]	0.5	0.8
		PhCH₂NHBu[t]	1.0	1.0
Benzyl fluoride [f]	Diethylamine	PhCH₂NEt₂		
Benzotrifluoride [f]	t-Butylamine	(21)	0.7	0.4
		(22)	0.2	0.6
		PhCF=NBu[t]	1.0	1.0
		(Five other products, each <10% of the major and sum total <10% of the mixture)		
Benzotrifluoride [d,f]	Diethylamine	(23) [h]	1.0	1.0
		(24) [h]	0.2	1.2
		PhCONEt₂	0.9	2.5
		PhCF₂NEt₂	0.5	2.9
Benzotrifluoride [f]	Triethylamine	PhCF₂CH(Me)NEt₂		
m-Fluorobenzotrifluoride [f]	t-Butylamine	m-FC₆H₄CF=NBu[t]	1.0	1.0
		m-CF₃C₆H₄NHBu[t]	0.25	1.15
		(6 minor products, total <25% of major product and none constituted >7% of major product)		
m-Fluorobenzotrifluoride [d,f]	Diethylamine	m-CF₃C₆H₄NEt₂		
p-Fluorotoluene [d,f]	t-Butylamine	(25)	0.6	0.9
		(26)	1.0	1.0
		p-MeC₆H₄NHBu[t]	0.2	1.1
p-Fluorotoluene [d,f]	Diethylamine	(27) [h]	1.0	1.0
		p-MeC₆H₄NEt₂	0.95	2.75
m-Fluorotoluene [f,g]	t-Butylamine	Mixture of three 1 : 1 adducts, Me and F on ethenylic bonds in all	1.0	1.0
		m-MeC₆H₄NHBu[t]	0.55	1.3
m-Fluorotoluene [d,f,g]	Diethylamine	(28) [h]	1.0	1.0
		m-MeC₆H₄NEt₂	0.7	3.8
p-Fluoroanisole	Diethylamine	p-FC₆H₄NEt₂		
m-Fluoroanisole [d,g]	Diethylamine	(29) [h]	1.0	1.0
		m-FC₆H₄NEt₂	0.4	1.15
1,3-Bis(trifluoromethyl)benzene [d,f]	t-Butylamine	m-CF₃C₆H₄CF=NBu[t]		
1,3-Bis(trifluoromethyl)benzene [d,f,g]	Diethylamine	m-CF₃C₆H₄NEt₂		
1,3-Bis(trifluoromethyl)benzene [f,g]	Triethylamine	m-CF₃C₆H₄CF₂CH(Me)NEt₂		

[a] Variable and minor amounts of neutral products observed from systems in which acyclic addition products observed. [b] Determined from preparative irradiation involving equal volumes of the reactants: in some cases ratios varied with time as the 1,2-adducts have varying photolabilities. [c] 10% Apiezon L on Universal B support packed g.l.c. columns. [d] Undetermined minor amounts of other products also formed. [e] Equal volume of methanol added before irradiation. [f] Amine hydrofluoride also formed. [g] Very low yields of volatile products. [h] Assignment of orientation of substituents tentative.

or at shorter wavelength were assigned the 1,4-acyclic addition structure as in (2). Support for these assignments was provided by i.r. and [1]H n.m.r. spectroscopy and by comparison of these data with those of adducts of proven

from chlorobenzene and t-butylamine as follows. There are four 1,2-adduct isomers which may be formed from these addends and which have three ethenyl protons: these have structures (12), (13), (14), and (15). The methine proton

resonance of one of the components appeared as a doublet of triplets (J 8 and 3 Hz): this pattern would not arise for this proton from an isomer of structure (12). The methylene protons resonated at δ 2.2—2.6 as a multiplet but if the component had structure (13), this resonance would be expected to be essentially a broadened doublet arising from major coupling with the methine proton. Couplings within this multiplet were determined as 8 and 4 Hz. Irradiation in the methine signal collapsed a doublet feature (J 3 Hz) in the three-proton ethenyl resonance into a singlet. Such a transformation would not be expected for an isomer of
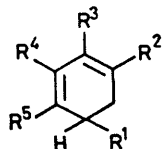
(1) $R^1 = NR^6R^7$ (where $R^6 =$ alkyl, $R^7 =$ H or alkyl), $R^2 = R^3 = R^4 = R^5 =$ H
(7) $R^1 = NEt_2$, one of R^2, R^3, R^4, or $R^5 =$ Me, the others $=$ H
(10) $R^1 = NEt_2$, one of R^2, R^3, R^4, or $R^5 =$ Me, the others $=$ H
(12) $R^1 = NHBu^t$, $R^2 = R^3 = R^4 =$ H, $R^5 =$ Cl
(13) $R^1 = NHBu^t$, $R^2 =$ Cl, $R^3 = R^4 = R^5 =$ H
(14) $R^1 = NHBu^t$, $R^4 =$ Cl, $R^2 = R^3 = R^4 =$ H
(15) $R^1 = NHBu^t$, $R^3 =$ Cl, $R^2 = R^4 = R^5 =$ H
(17) $R^1 = NEt_2$, $R^3 =$ Cl, $R^2 = R^4 = R^5 =$ H
(18) $R^1 = NEt_2$, $R^2 =$ Cl, $R^3 = R^4 = R^5 =$ H
(19) $R^1 = NEt_2$, $R^5 =$ Cl, $R^2 = R^3 = R^4 =$ H
(20) $R^1 = NEt_2$, $R^4 =$ Cl, $R^2 = R^3 = R^5 =$ H
(21) $R^1 = NHBu^t$, $R^5 = CF_3$, $R^2 = R^3 = R^4 =$ H
(23) $R^1 = NEt_2$, $R^5 = CF_3$, $R^2 = R^3 = R^4 =$ H
(24) $R^1 = NEt_2$, $R^5 =$ H, R^2, R^3, or $R^4 = CF_3$
(31) $R^1 = NHBu^t$, $R^2 =$ Me, $R^3 = R^4 = R^5 =$ H

structure (15) but would arise from the isomer with an 'isolated' ethenyl proton vicinal to the methine as in structure (14). Structure (13) was discounted for the second component since again the methylene ^{1}H n.m.r. signal had methylene–methine (8 Hz) and methylene–ethenyl (4 Hz) couplings. Since structure (14) has been assigned, this only leaves the decision between structures (12) and (15) for this 1 : 1 adduct. The methine proton appeared as a triplet of doublets and hence structure (12) with a chlorine atom vicinal to the methine was discounted. The ethenyl resonance of this component appeared as a one proton low field triplet, which was coupled (3.5 Hz) to the methylene protons, and a higher field two proton broad doublet; these features are entirely consistent with the isomer of structure (15). Similar analyses were employed to assign positions of substituents in isomeric adducts from other systems. The coincidence of the t-butyl and N–H ^{1}H n.m.r. signals in several of the products is remarkable but was established by exchange experiments with D_2O.

DISCUSSION

Inspection of the data in the Table reveals several interesting and unusual features of the present arene–amine systems particularly when comparisons are made with the previously reported results for the photochemical reactions of benzene and other substituted derivatives with aliphatic amines.[1,5,7,8,9]

With the present systems, there appears to be little selectivity in the position of attack of the amine onto the arene although it is most noteworthy that, as was observed with fluorobenzenes and aliphatic amines,[7] from none of the present systems were 1 : 1 adducts isolated which reflected amine attack at the 1-position

and in all the adducts the substituents from the arene always resided on the ethylenic bonds (*i.e.* no adduct had the structural moiety –CH=CH–CHR– where R is the arene substituent). Amine attack at the 1-position of chlorobenzene, anisole, benzonitrile, and the fluorobenzenes may lead directly to the aniline derivatives by conventional nucleophilic displacement,[2,10] but in the case of toluene it is difficult to rationalise the absence of such adducts and those with a –CHMe– grouping. It has been suggested that such adducts and/or their precursors from fluorobenzenes are unstable and may lead to both normal or cine substitution products. Although with the present fluorobenzenes the minor reaction components could not in practise be identified, we obtained no evidence for the formation of cine-substitution compounds from any system. Nevertheless the type of products formed from *p*- and *m*-fluoro-toluenes were closely similar to those from *p*- and *m*-difluorobenzenes[7] but in the former case fluorination reduced product yields compared with toluene whereas with benzene and the fluorobenzenes, reaction efficiency increased with fluorine substitution.[7] If it is assumed that all of the aniline originates by direct nucleophilic displacement from chlorobenzene and that cine-substitution is a minor process then the 1-position of this arene is that favoured for attack. However, in contrast to the corresponding reactions with fluorobenzene, in the present case reaction at the other three positions of chlorobenzene appears to occur with approximately equal efficiency and thus there is no correlation between the present results with chlorobenzene and the calculated charge density for the first excited singlet state of this arene.[11]

From our present study no clear pattern emerged which allowed the factor(s) dictating the relative ease of substituent displacement by the amines or their addition to the benzene nucleus to be recognized conclusively. Photoinduced replacement of aryl methoxy-groups by nucleophiles is a well documented reaction [10] and the formation of aniline derivatives in the present system was expected. It is, however, noteworthy that no fluorine displacement was observed with the fluoro-anisoles and that whereas the *p*-isomer reaction was specific, that of *m*-fluoroanisole gave several products of which the major was the 1,4-acyclic addition product (29).

It has earlier been reported that chlorobenzene and fluorobenzene give aniline derivatives on irradiation in the presence of amines, the formation of adducts not being described: benzonitrile was also reported not to react in this system.[1] In contrast, we have observed that although such substitution products are the major components from both primary and secondary amines with chlorobenzene, several 1 : 1 adducts are also formed and that the nitrile group of benzonitrile is photo-substituted, albeit somewhat inefficiently by t-butyl-amine and diethylamine.

From the structures of the 1 : 1 adducts from chlorobenzene and the amines it is clear that these systems show a marked preference for 1,2- compared with 1,4-

acyclic addition whereas with benzene and toluene, the reverse is observed. There appears to be no obvious reason for this feature but as we have noted elsewhere,[7] preferred orientations adopted by the addends in intermediate excited-state complexes may well dictate the subsequent mode of reaction.

Attack of a photoexcited arene on the α–CH of a tertiary amine is reflected in the 1 : 1 adduct of benzene and triethylamine [5] and in the substitution product (33) from the same amine and 1,4-dicyanobenzene.[8] However, such a product as (16) from a secondary amine has not previously been described, although subsequent to our preliminary account of this reaction [12] with chlorobenzene, other workers have observed similar products from 1,4-dicyanobenzene and primary and secondary amines.[9] In contrast to these latter observations, however, we have isolated NN-diethylaniline as the major product from benzonitrile and diethylamine and obtained no evidence which suggested arene reaction at the α-amine position.

The acyclic product (6) from toluene and t-butylamine is most noteworthy, as the formation of such a compound
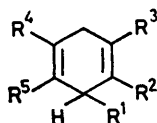
(2) R¹ = NR⁶R⁷ (where R⁶ = alkyl, R⁷ = H or alkyl),
       R² = R³ = R⁴ = R⁵ = H
(3) R¹ = CH(Me)NEt₂, R² = R³ = R⁴ = R⁵ = H
(4) R¹ = NHBuᵗ, R² = Me, R³ = R⁴ = R⁵ = H
(5) R¹ = NHBuᵗ, R³ = Me, R² = R⁴ = R⁵ = H
(8) R¹ = NEt₂, R² = Me, R³ = R⁴ = R⁵ = H
(9) R¹ = NEt₂, R³ = Me, R² = R⁴ = R⁵ = H
(11) R¹ = CH(Me)NEt₂, R² = Me, R³ = R⁴ = R⁵ = H
(22) R¹ = NHBuᵗ, R² = CF₃, R³ = R⁴ = R⁵ = H
(25) R¹ = NHBuᵗ, R² = Me, R⁴ = F, R³ = R⁵ = H
(26) R¹ = NHBuᵗ, R² = F, R⁴ = Me, R³ = R⁵ = H
(27) R¹ = NEt₂, R² = F, R⁴ = Me, R³ = R⁵ = H
(28) R¹ = NEt₂, R² = F, R⁵ = Me, R³ = R⁴ = H
(29) R¹ = NEt₂, R² = F, R⁵ = OMe, R³ = R⁴ = H

from these photoreactions is quite unprecedented. Evidence has been presented to show that the hexatriene (30) is formed as an unstable secondary photoproduct from the 1,2-adduct of benzene and t-butylamine,[5] and the involvement of the corresponding 1,2-adduct (31) in the toluene case is attractive since its ring opening followed by a 1,7-hydrogen migration would lead directly to (6). Such processes may well occur during the isolation (preparative g.l.c.) of (6) and this does indeed appear to be the case, for treatment of an ethereal solution of the crude irradiation product with N-phenyl-maleimide [5] produced a crystalline compound which was deduced from spectroscopic and analytical data to have structure (32), no component corresponding to (6) being detected in the remaining mixture. The absence of acyclic products analogous to (6) from both fluorotoluenes and t-butylamine may simply be a consequence of preferential formation of photostable 1,4-adducts rather than photo and/or thermally labile 1,2-adducts, and ring opening of the other 1,2-adducts reported here was not experienced during their isolation by preparative g.l.c.

As may be expected, α-fluorotoluenes photoreact with amines by displacement of the fluorine: this is the exclusive mode of reaction with benzyl fluoride and t-butylamine and diethylamine; however from benzotrifluoride 1 : 1 adducts are also formed in approximately equivalent amounts to the substitution products from these two amines, although again in this case only displacement of fluorine occurs with the tertiary amine. Fluorine substitution is understandable in terms of a

(6)   (16)

(30)   (32) R = Me   (33)
               (34) R = H
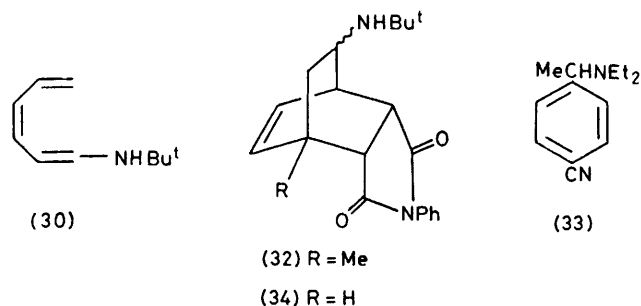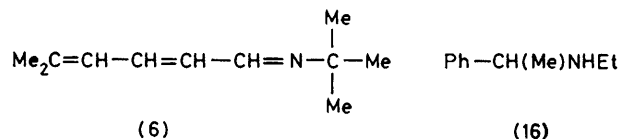
photonucleophilic displacement reaction but the formation of the seemingly primary product PhCF=NBuᵗ from benzyl fluoride and t-butylamine is not so readily explained. The thermal synthesis of imidoyl fluorides has been described by Merritt and Johnson and the spectroscopic properties of the Z- and E-isomers of PhCF=NBuᵗ were reported.[13] From these data we deduce that the product obtained in the photoprocess is the E-isomer. However the compound that we isolated did not yield benzonitrile, isobutylene, and t-butyl fluoride at 25 °C: this thermal decomposition was described for the product of the thermal synthesis.[13] Formation of NN-diethylbenzamide from benzotrifluoride and diethylamine is considered to arise simply by hydrolysis of the αα-difluorobenzyl-NN-diethyl-amine by trace amounts of water either during the irradiation or on work-up:[14] the amide was greatly favoured from irradiation of this system in the presence of methanol.

In general, the use of arene–amine photoreactions as synthetic procedures is severely restricted by their low chemical and quantum (ca. 0.01) yields and the formation of multicomponent mixtures. Reaction of the amine at the fluorinated side-chain of the arene is comparatively efficient and with benzotrifluoride and triethylamine a 24 h irradiation of 5.0 ml of an equivolume solution yielded 0.1—0.2 g, dependent on the light source, of 1-phenyl-1,1-difluoro-2-NN-diethylaminopropane.

The ultraviolet spectra of mixtures of the arene–amine systems described here were additive of the components and hence ground-state complexes having charge-transfer absorptions were not formed; excited-state interactions between the S_1 arene and S_0 amine were however

deduced from fluoescence quenching studies. Thus, with the exception of the anisoles, the fluorescence of the arenes was efficiently quenched (K_{SV} values of 35—80 l mol^{-1}) by the amines in cyclohexane solution. However, in the present systems broad structureless emission attributable to fluorescence from an exciplex was observed at room temperature only for m-fluorotoluene, p-fluorotoluene, and benzonitrile ($\lambda_{max.}$ 370, 380, and 470 nm respectively) with triethylamine at high reactant concentrations in iso-octane solution and using the triangular cell technique.[15],* The efficiency of product formation of the present arene–amine systems was decreased with increasing polarity of added diluent and methanol greatly inhibited the reactions involving primary and secondary amines: the solvent inhibition effects were, however, much less pronounced for the products of fluorine substitution in the α-fluorotoluenes than for 1 : 1 adduct formation. The interpretation of similar solvent effects and mechanistic considerations of arene–amine interactions have been previously discussed [5,7] and the present results are in general agreement with the earlier proposals. Thus we suggest that the arene–amine reactions proceed by way of an excited-state complex which may yield the 1 : 1 adducts *via* either a 1-electron–proton-transfer radical mechanism or by reaction of the addends initially to form zwitterionic species. The polarity of the exciplex and which of the two decay pathways is preferred may depend upon the nature of the arene substituent. The aniline derivatives may arise by a conventional photonucleophilic substitution reaction and/or from unstable adducts and/or their precursors such as zwitterionic species.

To summarise, the type of photoproduct resulting from excited-state interaction between aliphatic amines and benzenoid compounds is very dependent upon the arene substituent and reflects acyclic 1,2- and 1,4-addition of, and/or substitution in the nucleus or side-chain by, the amine. The addition process is observed for t-butylamine and diethylamine with toluene, chlorobenzene, benzotrifluoride, p-fluorotoluene, and m-fluorotoluene and a novel secondary acyclic product is formed between t-butylamine and toluene. Replacement of an arene substituent by the amine occurs with chlorobenzene, benzonitrile, the anisoles, fluorotoluenes, and m-fluoro-benzotrifluoride and reaction is also observed in the side-chain for the α-fluorotoluenes studied; only for the triethylamine–benzotrifluoride system, however, is the reaction sufficiently efficient and selective to consider the process synthetically useful.

EXPERIMENTAL

The irradiation source for all experiments comprised Hanovia 15 W low-pressure mercury lamps. All solutions were nitrogen-degassed before irradiation. Preparative experiments involved irradiation of equivolume mixtures of

* Benzene is reported to show exciplex emission with triethyl-amine under such conditions [15] and we have also observed broad structureless emission for fluorobenzene, m-difluorobenzene, and p-difluorobenzene with triethylamine at 370, 395, and 400 nm, respectively in iso-octane solutio n.

the reactants in sealed quartz tubes for 24 h. The effect of solvent on the reactions was investigated using equivolumes of the reactants in an equal volume of the solvent (cyclohexane, diethyl ether, acetonitrile, and methanol; total volume 1 ml). The temperature of the irradiated solution was between 20 and 25 °C and formation of products was monitored by g.l.c. using 10% Apiezon L on Universal B support. The standard work-up procedure involved filtration of the amine hydrofluoride where applicable and removal of the starting materials by bubbling nitrogen through the irradiated mixture at 20 °C for several hours or rotary evaporation of the solution at water pump vacuum and recovery of the starting materials. These procedures gave a viscous brown oil which was subjected to preparative g.l.c. on columns packed with Apiezon L on Universal B support. Generally the products could be isolated with 90—95% purity but at the expense of a low efficiency of recovery: the amounts of fractions realistically obtained were of the order of 20—50 mg. In some cases subsequent spectroscopic examination of the separated components indicated the presence of two isomers. Systems which gave reasonable yields of product (*e.g.* benzotrifluoride and triethylamine) were subjected to repeat cycle preparative g.l.c. in order to obtain the purity necessary for meaningful analytical data.

The aniline derivatives obtained in this work were identified by comparison of their spectroscopic and chromatographic properties with those of authentic materials. The spectroscopic properties of the types of 1 : 1 adducts of arenes and amines isolated in the present study are well-documented and the structures of the adducts reported here were deduced by spectroscopic analysis and comparison of these data with those previously published.[5,7] As with the corresponding benzene–amine adducts, with the exception of (31), the cyclic 1,3-diene derivatives reported here did not yield crystalline 1 : 1 : 1 Diels–Alder adducts with N-phenylmaleimide.[5]

Data Relevant to the Structural Assignments of the 1 : 1 *Arene–Amine Adducts and Substitution Products.*—^{1}H N.m.r. spectra were recorded for solutions CCl$_4$ (60 and 100 MHz) except where stated otherwise, i.r. spectra for liquid smears, and u.v. spectra for solutions in cyclohexane. The purity of the separated components (90—95%) rendered accurate calculation of absorptivities meaningless but the absorptions at *ca.* 250 nm quoted for the 1,2-adducts are estimated to have ε values of the order of 8 000 l mol^{-1} cm^{-1}.

Toluene and t-butylamine. Irradiation of the reactants (100 ml) as above gave *ca.* 1.5 g of crude product. Compounds (4) and (5) had M^+ 165, $\lambda_{max.}$ 220 nm, δ 5.6—5.8 (2 H, complex m), 5.3—5.5br (1 H, s), 3.15—3.45 (1 H, t with further minor splittings), 2.3—2.7 (2 H, m, doubly allylic CH$_2$), 1.6—1.85 (3 H, two overlapping m's, approx. ratio 2 : 1 deduced from integral of signal spin-decoupled from methine), and 1.10 (10 H, s, Bu^t and N–H), $\nu_{max.}$ at 3 340 w (N–H), 1 645m and 1 620m (C=C str.), 1 385m and 1 365s (Bu^t, ratio *ca.* 1 : 2), and 700s cm^{-1} (=C–H); compound (6) [Found: M^+, 165.1498 (g.l.c. purity > 99% following preparative g.l.c. recycle). C$_{11}$H$_{19}$N requires M, 165.1517] had $\lambda_{max.}$ 251, 258, 263, 271, and 281 nm, δ 7.8 (1 H, d J 8 Hz, R^1–CH=N–R^2), 5.8—7.2 (3 H, overlapping multiplets), 1.85br (6 H, s), and 1.15 (9 H, s), $\nu_{max.}$ at 3 020—2 860 (5 bands s), 1 680m, 1 620s, 1 590m, 1 140m, 980s, and 870m cm^{-1}.

Formation of the 1 : 1 : 1 *adduct* (32). Treatment of a solution of the crude irradiation mixture (1.5 g) in diethyl

ether (50 ml) with N-phenylmaleimide (0.5 g) gave, after standing for 3 days at room temperature, an insoluble brown solid (*ca.* 0.3 g): the absence of (6) was now noted in the chromatogram of the solution. Thimble extraction of the solid with n-hexane gave a white solid (m.p. 173—175 °C) which from the following data was assigned the toluene–t-butylamine–N-phenylmaleimide 1 : 1 : 1 adduct structure (32) (Found: M^+, 338.198 4. $C_{21}H_{26}N_2O_2$ requires M, 338.199 3), δ(CDCl$_3$) 7.5—7.1 (5 H, m, Ph), 6.25—6.1 (2 H, m, =CH), 3.4—3.2 (1 H, m), 3.1—2.8 (3 H, m), 2.1—1.9 (2 H, m), 1.8br (3 H, s, CH$_3$), and 1.25 (10 H, s, Bu^t and NH), $\nu_{max.}$ 3 360br (N–H stretch), 1 715 (C=O in 5-membered imide ring), and 695 cm^{-1} (*cis* ethylene). The spectroscopic data are closely similar to those reported for compound (34).[5] The position of the methyl group in (32) was deduced from the n.m.r. spectrum and the fact that the position of attack of the amine must have been at the 3-position of toluene to allow the formation of the acyclic compound (6) from the 1,2-photoadduct (31).

Toluene and diethylamine. Irradiation of the reactants (100 ml) as above gave *ca.* 1 g of crude product. Compound (7) had M^+ 165, $\lambda_{max.}$ 250 nm, δ 5.5—5.9 (3 H, m), 3.2—2.8 (1 H complex, m), 2.1—2.8 (6 H, overlapping m and q doubly allylic CH$_2$ and CH$_2$Me), 1.9br (3 H, s =CCH$_3$), and 1.05 (6 H, t, CH$_3$ of Et); compounds (8) and (9) had M^+ 165, $\lambda_{max.}$ 220 nm, δ 5.3—5.8 (3 H, m), 3.4—3.8 (1 H, t with further minor splittings), 2.1—2.8 (6 H, overlapping multiplets), 1.75br (3 H, s with minor splittings), and 1.0 (6 H, two overlapping t, J 7 Hz, ratio *ca.* 1 : 1) (¹H n.m.r. spectrum recorded in C$_6$D$_6$ essentially the same as that reported above except for the methyl resonance centred at δ 1.75 becoming split into two signals of approximately equal intensity); compound (10) had M^+ 165, $\lambda_{max.}$ 250 nm, δ 5.4—5.8 (3 H, m), 3.2—3.6 (1 H, complex, m), 2.2—2.6 (6 H, overlapping m and q), 1.95br (3 H, s), and 1.05 (6 H, t). Isolated (7) and (10) contained variable amounts (5—10%) of the non-separated mixture [(8) + (9)], as evidenced by g.l.c. analysis and a low intensity triplet resonance overlapping with the ¹H n.m.r. signal centred at δ 1.05 in each isomer.

Toluene and triethylamine. Irradiation of a 1 : 1 : 1 v/v/v solution (120 ml) of toluene, triethylamine, and methanol gave the crude product (*ca.* 2.0 g). Compound (11) had M^+ 193 (very weak; base ion at m/e 100), $\lambda_{max.}$ 220 nm, δ 5.2—5.8 (3 H, complex m), 2.1—3.1 (8 H, overlapping multiplets), 1.7br (3 H, s), and 0.9 (9 H, overlapping t and d), minor amounts (*ca.* 5%) of other compounds present as shown by low intensity signals overlapping with the latter two resonances on expansion, $\nu_{max.}$ 3 020m, 2 950s, 2 910s, 2 860s, 2 800s, 1 445s, 1 380s, 1 200s, 930m, 780m, and 685m cm^{-1} (Found: C, 80.5; H, 12.1; N, 7.05. C$_{13}H_{23}N$ requires C, 80.83; H, 11.92; N, 7.25%).

Chlorobenzene and t-butylamine. Irradiation of the equivolume solution (100 ml) gave *ca.* 2.0 g of crude product. Both in this experiment and that involving diethylamine the basic products were extracted from the mixture which also contained chlorobiphenyls (as judged by combined m.s.-g.l.c.) by shaking the ethereal solution (100 ml) of the crude product with 2M-hydrochloric acid (3 × 100 ml). The combined aqueous extract was basified with 2M-sodium hydroxide solution and shaken with diethyl ether (4 × 25 ml). The ethereal solution was dried (magnesium sulphate) and gave a viscous orange oil in each case (*ca.* 0.7 g). Separation of the components was achieved on the combined products of several experiments. Compounds (12) and (13) had, M^+ 185, $\lambda_{max.}$ 260 nm, δ 5.6—6.1 (3 H, com-

plex m), 3.2—3.5 (1 H, 6 lines), and 2.4—2.7 (2 H, m) and 1.00 (10 H, two sharp singlets approx. ratio 1 : 1) (Bu^t and NH); compound (14) had M^+ 185, $\lambda_{max.}$ 260 nm, δ 5.6—5.9 (3 H, m), 3.1—3.4 (1 H, m), 2.2—2.6 (2 H, m), and 1.0 (10 H, s, Bu^t and NH), $\nu_{max.}$ 3 340w, 2 970s, 2 930s, 2 900s, 2 870s, 1 635m, 1 390s, 1 365s, 1 225s, 1 205s, and 780m cm^{-1} [the presence of minor amounts of (12) and (13) in (14) was indicated by g.l.c.]; compound (15) had M^+ 185 $\lambda_{max.}$ 260 nm, δ 5.8—6.0 (3 H, m), 3.5—3.9 (1 H, m), 2.6—2.9 (2 H, m), 2.2 (1 H, s NH, removed with D$_2$O), and 1.1 (9 H, s, Bu^t). That (15) as isolated was contaminated by *ca.* 2% of (14) was indicated by g.l.c. and a small sharp singlet at δ 1.0 in the ¹H n.m.r. spectrum.

Chlorobenzene and diethylamine. Compound (16) had M^+ 149, δ 7.25br (5 H, m), 3.7 (1 H, q, J 7 Hz), 2.45 (2 H, q, J 7 Hz), 1.3 (3 H, d, J 7 Hz), 1.05 (3 H, t, J 7 Hz), and 0.95 (1 H, s NH), $\nu_{max.}$ 3 300w, 3 060m, 3 030m, 2 960s, 2 920s, 2 900s, 2 870s, 2 820s, 1 600s, 1 135s, 750s, and 700s cm^{-1} (Found: C, 80.25; H, 10.25; N, 9.15. C$_{10}H_{15}N$ requires C, 80.54; H, 10.07; N, 9.39%); compound (17) had M^+ 185, $\lambda_{max.}$ 260 nm, δ 6.0—6.2br (1 H, t), 5.6—5.8br (2 H, d), 3.3—3.6 (1 H, t), 2.3—2.8 (6 H, m), and 1.05 (6 H, t) [the presence of small amounts (5—10%) of (18) and (19) in (17) as isolated was shown by g.l.c.]; compounds (18) and (19) had M^+ 185, $\lambda_{max.}$ 260 nm, δ 5.6—6.0 (3 H, m), 3.6—3.9 (1 H, m), 2.3—2.9 (6 H, overlapping multiplets), and 1.05 [6 H, overlapping 2 t (*ca.* 1 : 1 ratio)]; compound (20) had M^+ 185, $\lambda_{max.}$ 260 nm, δ 5.7—5.9 (3 H, m), 3.4—3.9 (1 H, t of d), 2.2—2.7 (6 H, overlapping multiplets), and 1.0 (6 H, t) [the presence of small amounts (5%) of (18) and (19) in (17), as isolated, was indicated by t.l.c. and a low intensity triplet resonance overlapping with this last signal on expansion], $\nu_{max.}$ 3 040w, 2 970s, 2 930s, 2 900m, 2 870m, 2 820w, 1 630m, 1 580w, 1 460m, 1 440m, 1 370s, and 800s cm^{-1}.

Products from benzyl fluoride and amines. (a) *t-Butyl-amine.* Equivolume solutions (8 ml) of the reactants gave *ca.* 0.4 g of the crude product. Starting materials were recovered and recycled. The products were identified as the N-t-butylimine of benzaldehyde and benzyl-t-butylamine by comparison of their spectroscopic and chromatographic properties with those of authentic materials.

(b) *Diethylamine.* Equivolume solutions (8 ml) of the reactants gave *ca.* 0.4 g of crude benzyldiethylamine, identified by comparison of chromatographic and spectroscopic properties with those of authentic material.

Benzotrifluoride and t-butylamine. Irradiation of an equivolume solution (90 ml) gave *ca.* 2 g of crude product. Compound (21) had M^+ 219, $\lambda_{max.}$ 250 nm, δ at 5.9—6.4 (3 H, m with s at δ 6.0), 3.3—3.5vbr (1 H, s), 2.2—2.4 (2 H, m), and 1.1 (s with small s at δ 1.15, total 10 H), $\nu_{max.}$ 3 340w, 2 970s, 2 930m, 2 900m, 1 665m, 1 370s, 1 365s, 1 320s, 1 220s, 1 160s, and 1 020s cm^{-1}. Compound (22) had M^+ 219, $\lambda_{max.}$ 230 nm, δ 6.25br (1 H, s), 5.57 (2 H, s), 3.6—3.9 (1 H, complex m), 2.6—2.9br (2 H, d), and 1.1 (s with small s at δ 1.05, total 10 H), $\nu_{max.}$ 3 350w, 2 970s, 2 930m, 2 900m, 2 870m, 1 700w, 1 600w, 1 390s, 1 365s, 1 290s, 1 170s, and 1 120s cm^{-1}; PhCF=NBu^t had δ 7.7—8.0 (2 H, m), 7.25—7.45 (3 H, m), and 1.4 (9 H, s), and $\nu_{max.}$ 1 720s, 1 585w, 1 390m, 1 365m, 1 215s, 1 000s, 770s and 690s cm^{-1}.[13] The presence of small amounts (5—10%) of (22) in (21) and (21) in (22) from preparative g.l.c. was shown by the ¹H n.m.r. spectra, particularly in the δ 5.5—6.4 and 3.3—3.9 regions: this was confirmed by analytical g.l.c.

Benzotrifluoride and diethylamine. Irradiation of an equivolume solution (40 ml) of the reactants gave *ca.* 1 g of crude product. *NN*-Diethylbenzamide was identified by comparison of the spectroscopic and chromatographic properties of the photoproduct with those of authentic material. Compound (23) had M^+ 219, $\lambda_{max.}$ 250 nm, δ 6.2br (1 H, s), 6.0 (2 H, s), 3.5—4.0 (1 H, complex m), 2.2—2.8 (6 H, overlapping q with m), and 1.0 (6 H, t) (on expansion of this last signal a minor overlapping triplet was evident), $v_{max.}$ at 3 050w, 2 975s, 2 940m, 2 880m, 2 820m, 1 640w, 1 165s, and 1 120s cm^{-1}; compound (24) had M^+ 219, $\lambda_{max.}$ 250 nm, δ 5.8—6.2 (3 H, m), 3.7—3.9 (1 H, m), 2.6—2.8 (6 H, m), and 1.1 (6 H, t) (on expansion of this last signal a minor overlapping triplet was evident); PhCF$_2$-NEt$_2$ had M^+ 199, δ 7.2—7.7 (5 H, m), 2.9 (4 H, q, J 7 Hz), and 1.2 (6 H, t, J 7 Hz), $v_{max.}$ at 3 090—3 040w (3 bands), 2 980—2 850m (4 bands), 1 385m, 1 300s, 1 175s, 1 115s, 1 050s, 785m, and 695s cm^{-1}.

Benzotrifluoride and triethylamine. Irradiation of an equivolume solution (5 ml) of the reactants gave *ca.* 0.5 g of crude product from which *ca.* 0.2 g of the substitution compound could be isolated. PhCF$_2$CH(Me)NEt$_2$ had M^+ 227 (Found: C, 68.5; H, 8.5; N, 6.6. $C_{13}H_{19}F_2N$ requires C, 68.72; H, 8.37; N, 6.17; F, 16.74%), δ 7.3 (5 H, s with minor splittings), 2.5—3.5 [1 H, complex m, overlapping with δ 2.4 (4 H, q, J 7 Hz)], 1.1 (3 H, d, J 7 Hz), and 0.9 (6 H, t, J 7 Hz).

m-Fluorobenzotrifluoride and t-butylamine. Irradiation of an equivolume solution (10 ml) of the reactants gave *ca.* 0.4 g of crude product: the starting materials were recovered for recycling. m-FC$_6$H$_4$CF=NBu^t had M^+ 197 (abundant ions at m/e 121, 95, 76, and 57), $v_{max.}$ at 3 080w, 2 970s, 2 930m, 2 900m, 2 870m, 1 720vs, 1 600s, 1 495s, 1 395m, 1 365s, 1 260s, 1 220s, 855m, 790s, and 710m cm^{-1}, δ 7.0—7.9 (4 H, complex m) and 1.4 (9 H, s).

m-Fluorobenzotrifluoride and diethylamine. Irradiation of an equivolume solution (8 ml) of the reactants gave *ca.* 0.4 g of crude product: the starting materials were recycled. Only the major product was isolated and this was deduced to be *NN*-diethyl-*m*-trifluoromethylaniline, M^+ 217, δ 7.4—6.55 (4 H, m), 3.4 (4 H, q, J 7 Hz), and 1.2 (6 H, t, J 7 Hz), $v_{max.}$ 2 980s, 2 940s, 2 900m, 2 880m, 1 610m, 1 510m, 1 450m, 1 325s, 1 170s, 1 130s, 1 325s, 850m, 780s, and 700m cm^{-1}.

p-Fluorotoluene and t-butylamine. Irradiation of an equivolume solution (10 ml) of the reactants gave *ca.* 0.5 g of crude product. Compound (25) had M^+ 183, $\lambda_{max.}$ 220 nm, δ 5.05—5.5 (2 H, m), 3.4—3.8 (1 H, m), 2.6—2.9 (2 H, m), 1.8br (3 H, s), and 1.1 (10 H, s, Bu^t and NH), $\lambda_{max.}$ at 3 340w, 1 715s, 1 670m, 1 390m, 1 370s, 1 365s, 1 230s, 1 170s, 1 150s, 810m, and 785m; compound (26) had M^+ 183, $\lambda_{max.}$ 220 nm, δ 4.95—5.6 (2 H, m), 3.4—3.8vbr (1 H, s), 2.4—2.8 (2 H, m), 1.7br (3 H, s), and 1.1 (10 H, s, Bu^t and NH), $v_{max.}$ at 3 340w br, 1 715s, 1 670m, 1 390s, 1 380s, 1 365s, 1 230s, 1 170s, 1 145s, 940m, 815m, and 785s cm^{-1}. The presence of (25) in (26) and (26) in (25) in amounts of *ca.* 5—10% from preparative g.l.c. was shown by analytical g.l.c.

p-Fluorotoluene and diethylamine. Irradiation of an equivolume solution (10 ml) of the reactants gave *ca.* 0.5 g of crude product. Compound (27) had M^+ 183, $\lambda_{max.}$ 220 nm, δ 5.0—5.7 (2 H, m), 3.7—4.1 (1 H, m), 2.2—3.0 (6 H, overlapping m with q), 1.8br (3 H, s), and 1.1 (6 H, t), $v_{max.}$ at 3 050w, 3 030w, 2 980—2 820s (4 bands), 1 715s, 1 670m, 1 450—1 380s br (2 bands), 1 165s, 950m, 820m, and 785m

cm^{-1}. The presence of minor amounts (*ca.* 5%) of impurities in (27), as isolated, was indicated by g.l.c. and very low intensity spurious signals in the ^{1}H n.m.r. spectrum.

m-Fluorotoluene and t-butylamine. Irradiation of an equivolume solution (10 ml) of the reactants gave *ca.* 0.4 g of a very viscous brown oil, much of which was insoluble polymeric material. The inseparable mixture of the 1 : 1 adducts had M^+ 183 (scan through g.l.c. component), $\lambda_{max.}$ 220 and 250 nm, δ 4.95—5.5 (2 H, m), 3.4—3.8br (1 H, q), 2.4—2.8 (2 H, m), 1.8br (3 H, s), and 1.1 (10 H, 3 very close s).

m-Fluorotoluene and diethylamine. Irradiation of an equivolume solution (10 ml) of the reactants gave *ca.* 0.3 g of crude product but much of this was insoluble polymeric material. Compound (28) had M^+ 183, $\lambda_{max.}$ at 225 nm, δ 5.0—5.7 (2 H, m), 3.5—3.9 (1 H, m), 2.3—2.8 (6 H, overlapping m and q), 1.75br (3 H, s), and 1.05 (6 H, t). The presence of minor amounts (*ca.* <10%) of impurities in (28), as isolated, was indicated by g.l.c. and low intensity spurious signals in the n.m.r. spectrum.

m-Fluoroanisole and diethylamine. Irradiation of an equivolume solution (10 ml) of the reactants gave *ca.* 0.3 g of crude product but much of this was insoluble polymeric material. Compound (29) had M^+ 199, $\lambda_{max.}$ at 220 nm, δ 5.4 (1 H, 2 t, J 16 and 3 Hz), 4.65—5.05 (1 H, m), 3.7—4.1 (1 H, m), 3.5 (3 H, s), 2.4—2.8 (6 H, overlapping m and q), and 1.0 (6 H, t). Isomeric impurities in (29) were detected by combined m.s.–g.l.c.: on expansion of the resonance centred at δ 1.0 a minor overlapping triplet was evident.

1,3-Bis(trifluoromethyl)benzene and the aliphatic amines. In each case irradiation of equivolume solutions of the arene and the three amines gave *ca.* 0.4 g of crude product but much polymeric material was formed. m-CF$_3$C$_6$H$_4$CF=NBu^t had M^+ 247 (very weak) (abundant ions at m/e 232 and 171), δ 7.3—8.2 (4 H, complex m), and 1.4 (9 H, s), $v_{max.}$ at 1 720vs, 1 610w, 1 590w, 1 250s, 1 220s, 1 165s, 1 125s, 900m, 810s, and 700m cm^{-1}; m-CF$_3$C$_6$H$_4$CONEt had M^+ 245, δ 7.6br (4 H, s with minor splittings), 3.3 (4 H, q), and 1.2 (6 H, t), $v_{max.}$ at 1 640vs, 1 335s, 1 170s, and 1 130s cm^{-1}; m-CF$_3$C$_6$H$_4$CF$_2$CH(Me)NEt$_2$ had M^+ 295, δ 7.4—7.8 (4 H, m), 2.4—3.6 [1 H, complex m overlapping with δ 2.4 (4 H, q)], 1.2 (3 H, d), and 0.9 (6 H, t), $v_{max.}$ 1 620w, 1 450m, 1 385m, 1 340s, 1 170s, 1 130s, 900m, 800s, and 700s cm^{-1}.

Aniline derivatives from anisole, p-fluoroanisole, and benzonitrile. The amounts of crude product from irradiation of equivolume solutions of each of the above arenes with diethylamine and t-butylamine for 24 h were as follows: 2 g from anisole and diethylamine (100 ml), 0.3 g from *p*-fluoroanisole and diethylamine (8 ml), 0.5 g from benzonitrile and diethylamine (100 ml), and 0.5 g from benzonitrile and t-butylamine (100 ml).

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