Excited State Substitution and Addition Reactions of Aryl Fluorides with Aliphatic Amines

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Fluorobenzene and the difluorobenzenes undergo photochemical reaction with t-butylamine and diethylamine to give both 1 : 1 adducts and substitution products but only the latter are formed from hexafluorobenzene and diethylamine. Both *cine* and ' normal ' substitution products are observed from the difluoro-compounds and the mechanism to account for this is considered to involve a polar excited-state complex between the addends and an addition–elimination process rather than benzyne intermediates. 1,2-Acyclic amine photoadducts are produced from most systems but the corresponding 1,4-isomers are the major adducts from p-difluorobenzene and that from diethylamine is unique in undergoing thermal retro-addition to the starting materials rather than conversion into the aniline derivative.
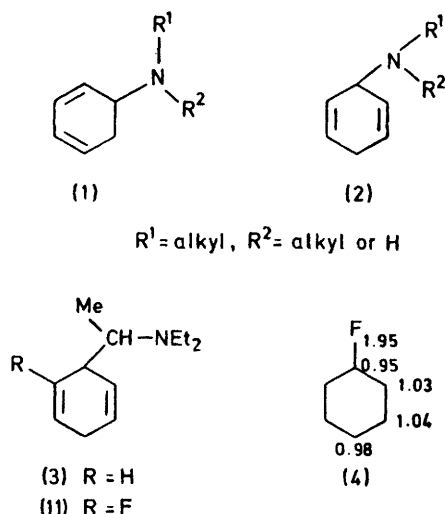
PHYSICAL aspects of excited-state interaction between arenes and amines are well documented [1] and in recent years the chemical reaction resulting from such interaction has been described.[2,3] In particular, S_1 benzene undergoes 1,2- and 1,4-acyclic addition of the N–H bond of primary and secondary amines to give the 1 : 1 adducts (1) and (2) respectively; [4,5] the 1,4-adduct (3) is formed from triethylamine and benzene.[5,6] These addition reactions have been extended to naphthalene [7] and anthracene,[8] and the mechanism is considered to involve both polar and radical intermediates with an initial step being electron transfer from the amine to the arene.[5] In order to obtain further information concerning this process, we have studied the photoreactions of

(1)   (2)

R¹ = alkyl, R² = alkyl or H

(3) R = H
(11) R = F

(4)

aliphatic amines with fluorobenzenes. Light-induced substitution of aryl fluorides by nucleophilic reagents has been the subject of several publications [3,9] but photoaddition products analogous to (1), (2), and (3) were not reported to be formed. Our present investigation gave the opportunity to assess the relationship between the photo-addition and -substitution processes and we now report details of the first photochemical *cine*-substitution reaction,[10] and present evidence which shows that a major route to the substitution products

from amines and aryl fluorides involves an addition–elimination mechanism.

RESULTS AND DISCUSSION

The systems chosen for study were combinations of fluorobenzene, the three difluorobenzenes, and hexa-fluorobenzene with t-butylamine, diethylamine, and triethylamine. Mechanistic investigations involved the mono- and difluoro-benzenes with diethylamine and its *N*-deuterio-derivative since, in general, product mixtures from this amine were conveniently separated chromatographically. The photoreaction of triethylamine was only examined in detail with fluorobenzene since this amine gave low yields of multicomponent mixtures with the arenes. The results are summarised in the Table. The ratios of products given are those determined from preparative 24 h irradiations. It should be noted, however, that while the substitution products were generally photostable, the 1 : 1 adducts displayed varying degrees of photolability; [5] all products from all systems were, however, observed following the shortest feasible exposure times. The structures of the 1 : 1 adducts were assigned on the basis of their spectroscopic properties. In particular adducts whose absorption maxima occurred in the 248—255 nm region were assigned the 1,2-acyclic adduct structure (1) whereas the other adducts which had their longest wavelength absorption at 220 nm or at shorter wavelengths were deduced to have structure (2). Such deductions for each adduct were supported by the i.r. spectra and confirmed by ¹H n.m.r. spectroscopy. Spectroscopic features relevant to the assignment of structures to the 1 : 1 adducts and substitution products are given in the Experimental section. Unambiguous assignment of the position of the fluorine atom in the 1 : 1 adducts from fluorobenzene and t-butylamine and diethylamine could not be made from the spectral properties alone, and in these cases the relative positions of the amino and fluorine substituents were deduced from the structure of the aromatic products formed in quantitative yields by dehydrogenation of the separated adducts with 10% Pd–C in refluxing toluene.

The adducts from fluorobenzene and the primary and

secondary amines reflect 2-, 3-, and 4-attack but neither from this system nor from any of the others in the present investigation were adducts isolated which either had involved reaction at the 1-position or which had a CHF grouping, whether in a cyclohexa-1,3- or -1,4-diene. The adduct photolability resulted in time-variable ratios of products but at the shortest feasible irradiation times, the ratio of attack of diethylamine on fluorobenzene was $0.5 : 0.36 : 0.2 : 0.8$ respectively for the 1-, 2-, 3-, and 4-positions, assuming that all the NN-diethylaniline
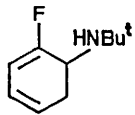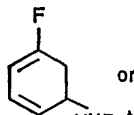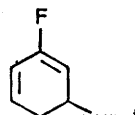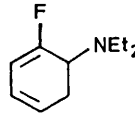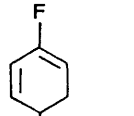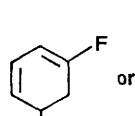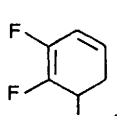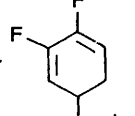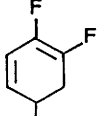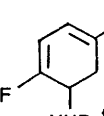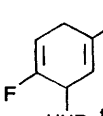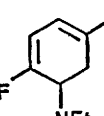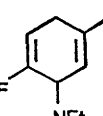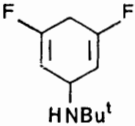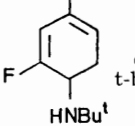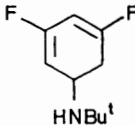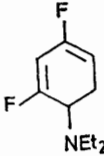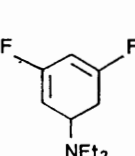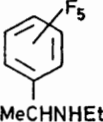
Products from Irradiation of Aryl Fluorides with Aliphatic Amines

Arene	Amine	Products (→Elution sequence on Apiezon L g.l.c. columns)				
Fluorobenzene	t-butylamine	(5)	(6)* or	(7)	N-t-butylaniline	
	Ratio	0.5	0.1	1.0	0.5	
Fluorobenzene	diethylamine	(8)	(9)	(10) or	NN-diethylaniline	
	Ratio	0.3	0.8	0.2	0.7	
Fluorobenzene	triethylamine	At least seven products formed of which (11) constituted 50% and was the only product isolated; NN-diethylaniline detected by m.s.–g.l.c. (10% of major product)				
o-Difluorobenzene	t-butylamine	(12) or	o-fluoro-N-t-butylaniline	(13)	m-fluoro-N-t-butylaniline	
	Ratio	0.25	1.0	0.6	0.2	
o-Difluorobenzene	diethylamine	(14)	o-fluoro-NN-diethylaniline		m-fluoro-NN-diethylaniline	
	Ratio	0.4	1.0		0.3	
p-Difluorobenzene	t-butylamine	(15)	(16)	p-fluoro-N-t-butylaniline	m-fluoro-N-t-butylaniline	
	Ratio	0.2	1.0	0.45	0.1	
		Two minor products were also formed from this system but together were <5% of the total product mixture				
p-Difluorobenzene	diethylamine	(17)*	(18)	p-fluoro-NN-diethylaniline	m-fluoro-NN-diethylaniline	
	Ratio	0.15	0.8	1.0	0.08	

TABLE (*Continued*)

						p-fluoro-N-t-butylaniline	m-fluoro-N-t-butylaniline
m-Difluorobenzene	t-butylamine	(19) *	(20)	o-fluoro-N-t-butylaniline	(21)		
Ratio		0.03	0.45	0.05	0.8	0.1	1.0

also 1 : 1 adduct minus hydrogen formed in a relative yield of 0.04

					p-fluoro-NN-diethylaniline	m-fluoro-NN-diethylaniline
m-Difluorobenzene	diethylamine	(22)	(23)	o-fluoro-NN-diethylaniline		
Ratio		0.2	0.4	0.2	0.05	1.0

		pentafluoro-NN-diethylaniline	(24)	2,3,4,6-tetra-fluoro-NN-diethylaniline	2,3,4,5-tetra-fluoro-NN-diethylaniline
Hexafluorobenzene	diethylamine				
Ratio		1.0	0.08	0.1	0.2

* Structure is tentative as amounts realistically available were too small to obtain product sufficiently pure for detailed spectroscopic analysis.

resulted from direct nucleophilic displacement. The calculated charge densities for the first excited singlet state of fluorobenzene are shown in (4) [11] from which it may be deduced that the attack of a nucleophile on this S_1 arene would occur at the positions in the order $1 \approx 4 > 2 \approx 3$. Our experimental results show some measure of agreement with this prediction but this weakens with respect to the 1-attack since this product could arise from both direct and *cine*-substitution (see below). However, neither in this nor the other systems discussed here do we have any experimental evidence which suggested that at least part of the 'normal' substitution product did not occur by a conventional photonucleophilic displacement reaction.[9,12] The 1 : 1 adduct isolated from fluorobenzene and triethylamine

was that expected by analogy with the corresponding benzene–amine system [5] but the formation of NN-diethylaniline from the former reaction is difficult to rationalise. It has been observed by Japanese workers

that p-dicyanobenzene and triethylamine yield p-cyanoethylbenzene *via* (25) and (26); [13] similar alkylated compounds are also formed from primary and secondary amines.[14] Such products were not detected from irradiation of the present aryl fluoride–amine systems although (24), analogous to the intermediate (26), was isolated from hexafluorobenzene and diethylamine. The form-

ation of NN-diethylaniline from fluorobenzene and triethylamine may occur *via* elimination of ethyl fluoride from a Wheland-type intermediate (27), analogous to those discussed below, to account for the substitution products from aryl fluorides.

The most important result of our present study is that for the first time in photonucleophilic substitution reactions, products arising from *cine*-substitution have been isolated and identified. There are two pathways which could account for our observations and these involve either addition of the amine to a photo-produced benzyne intermediate or addition of the S_1 arene to the amine followed by elimination of HF from unstable adducts and/or their precursors. The general predominance of 'normal' over the *cine*-products would tend to argue against the major involvement of a benzyne mechanism unless a significant proportion of the former product arose by straightforward light-induced

nucleophilic displacement. To differentiate between the two mechanisms, we have investigated the extent of deuterium incorporation in the photoproducts from irradiation of fluorobenzene and the difluorobenzenes with *N*-deuteriodiethylamine and the effect on the adduct : substitution product ratio of the presence of a benzyne trap in the irradiated solution.

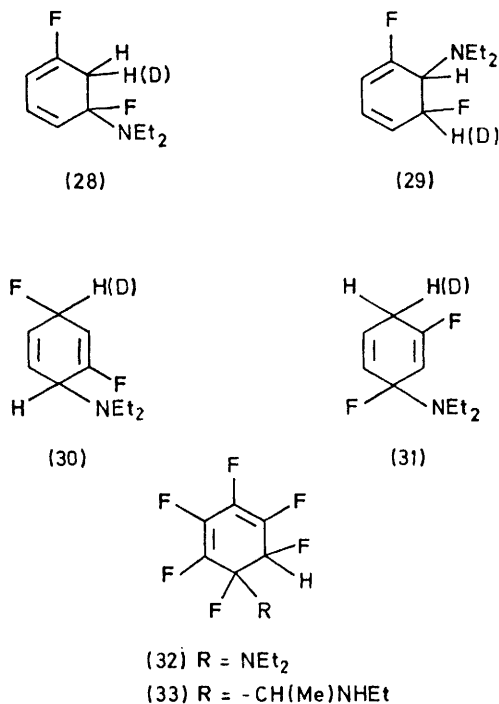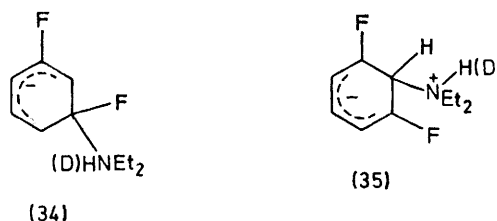Irradiation of each fluorobenzene with 85% isotopically pure *N*-deuteriodiethylamine gave the same types of product noted in the Table. The extent of deuterium incorporation was determined for *NN*-diethylaniline and the 1 : 1 adducts from fluorobenzene to be 0.5 and >0.8 atoms respectively. The 1 : 1 adducts from the difluorobenzenes each had >0.85 atom of deuterium incorporated, the 'normal' substitution products had 0.5—0.6 atoms and the *cine*-substitution products 0.3—0.4 atoms. Control experiments involving irradiation of the non-deuteriated products in the presence of the deuteriated amine showed that no significant incorporation of deuterium occurred by H–D exchange, and exchange involving HF or DF was considered very improbable as these promptly produced the highly insoluble amine hydro(deuterio)fluoride. The low deuterium incorporation into the *cine*-substitution product is inexplicable in terms of a benzyne route which should have resulted in essentially 1.0 atom incorporation in both substitution products. This deduction was confirmed from irradiation of the systems in the presence of

(28)

(29)

(30)

(31)

(32) R = NEt$_2$
(33) R = -CH(Me)NHEt

furan and tetracyclone which gave the 1 : 1 adducts and substitution products in the same relative yields as in the absence of these benzyne traps. Hence it is evident that the substitution products and in particular the *cine*-

isomer arose largely, if not exclusively, by an addition–elimination mechanism.

It is significant that adducts resulting from either 1,2- or 1,4-attack which reflect reaction of the amine at the 1-position or adducts which have the CHF moiety [*e.g.* (28) and (31), and (29) and (30), respectively, from *m*-difluorobenzene and diethylamine] were not observed. The lack of these types of adducts suggested that they or their precursors were the addition compounds which undergo elimination to yield the ' normal ' and *ortho cine*-substitution products from these systems. Any adducts formed between hexafluorobenzene and diethylamine must have both the above structural features and thus it is noteworthy that only substitution products arose from this system. Pentafluoro-*NN*-diethylaniline may have resulted from a conventional

(34)

(35)

photonucleophilic displacement reaction or like (24) may have arisen by HF elimination from unstable intermediates such as (32) and (33) respectively or the 1,4-diene isomers but both 2,3,4,5- and 2,3,4,6-tetrafluoro-*NN*-diethylaniline require loss of a fluorine molecule. Pentafluoro-*NN*-diethylaniline and the 2,3,4,5-tetrafluoro-derivative may have the same precursor but the genesis of the 2,3,4,6-isomer remains obscure as it appears to have no obvious adduct precursor, was a primary photoproduct, and did not result from photorearrangement of either the 2,3,4,5- or the (undetected) 2,3,5,6-isomer. The photoaddition of amines to benzene is a non-concerted process [5] and hence both *cis* and *trans* isomers of the adducts (28), (29), (30), and (31) would be expected from *m*-difluorobenzene and diethylamine. Thus the formation of both deuterium- and non-deuterium-incorporated ' normal ' substitution products may be accounted for by the 1,2- and 1,4-elimination of both HF and DF from such unstable intermediates as (28) and (31) respectively. Formation of the *ortho cine*-substitution product containing deuterium may likewise be rationalised [*i.e.* elimination of HF from (29) or (30)] but for that with no deuterium incorporation, which constitutes approximately 60—70% of this product, it is necessary to postulate a 1,1-elimination of DF followed by a hydrogen shift. This elimination process does have some literature precedent,[15] but under the present experimental conditions is not expected to be a highly favoured process, and it may well be that the elimination occurs from precursor species such as zwitterionic Wheland-type intermediates (34) and (35), although again with (35) at some point a hydrogen shift is necessary.

The effect of solvent on the product formation from the

aryl fluorides and diethylamine was examined using cyclohexane, diethyl ether, methanol, and acetonitrile. In each case the ratio of adducts to substitution products was essentially constant suggesting that the formation of the two types of product is mechanistically related. In all cases, however, as the polarity of the solvent increased, the total yield of products decreased and methanol, with the exception of the fluorobenzene–triethylamine system, was a particularly poor solvent (cf. ref. 5).

The present results are consistent with previous mechanistic considerations for benene–amine adduct formation.[5] In all systems the arene fluorescence was quenched efficiently by the amine and values for K_{SV} in cyclohexane were determined to be in the range 35—65 l mol^{-1}: in the case of fluorobenzene and diethylamine in methanol, however, the value was considerably reduced to 3.8 l mol^{-1}. In no case was additional emission at longer wavelengths than that of the arene observed, but we consider that our results are best understood and rationalised in terms of formation of an S_1 arene and S_0 amine complex. In polar solvents, formation of solvent-separated and more strongly solvated radical anions and cations is promoted which decreases product formation. In non-polar solvents proton-transfer, within the exciplex, from the amine to the arene yields a radical pair which on primary combination gives the isolated adducts and those discussed above which may be the precursors of the cine and 'normal' substitution products. The efficiency of formation of the adducts and substitution products increased in the order benzene < fluorobenzene < difluorobenzenes, and the total quantum yield from hexafluorobenzene and diethylamine was 0.15, which is approximately two- to three-fold higher than those of the other systems. We interpret these observations in terms of greater stabilisation of the exciplex with increased fluorine substitution. Collapse of the exciplex could result directly in the formation of Wheland-type intermediates [e.g. (34) and (35)] by a 2-electron-transfer process as well as yielding radicals by 1-electron- and proton-transfer sequences: the zwitterionic species may well be the direct precursors of all the observed products. It is consistent with this proposal that although we have observed free-radical products (e.g. fluorinated tetra-hydrobiphenyls) from these systems, the amounts are very minor compared to those from benzene as arene and in view of this and the failure to observe the unstable adducts, we consider that reaction of the polar exciplex by a 1-electron–proton transfer–radical mechanism contributes less to the overall process than a 2-electron transfer and the formation of zwitterions. Unlike benzene–amine 1:1 adducts, those observed from aryl fluorides reflect that 1,2 not 1,4 is the preferred mode of reaction. There is no simple rationale for this and minor structural or electronic features of the addends may be sufficient to promote or inhibit particular orientations of interaction complexes; this is reflected in the structures of the product.

We refer in conclusion to the unexpected behaviour of (18) on pyrolysis. Thermal cis-1,4-elimination of hydrogen from cyclohexa-1,4-dienes to yield benzene derivatives is an 'allowed' process [16] and has been described for amine–benzene 1,4-adducts.[5] Samples of (18) obtained by preparative g.l.c. always contained traces of the starting materials, suggesting that the thermal reversal of the photo-process occurred readily. The retro-reaction has been confirmed and samples of (18) at 140 °C for 40 min result in essentially quantitative conversion into diethylamine and p-difluorobenzene; there seems no ready explanation for the retro-addition in this particular case, whereas from similar systems aniline derivatives are formed.

EXPERIMENTAL

The irradiation source in all experiments comprised Hanovia 15-W low-pressure mercury-arc lamps. For preparative experiments (24 h irradiation) equivolume mixtures of the reactants (60 or 400 ml total volume) were flushed with nitrogen before and during irradiation in a water-cooled quartz reactor ($T = 20$—25 °C). Small-scale experiments and investigation of solvent effects and the presence of benzyne traps were carried out in small sealed quartz tubes (400 μl or 1 ml capacity) following nitrogen degassing. The solvent effects were investigated using equivolumes of the reactants in an equal volume of the solvent. Reactions were monitored by g.l.c. using 10% Apiezon L on Universal B support. The standard work-up procedure involved filtration of the amine hydro-(deuterio)fluoride from the irradiated mixture and removal of the starting materials by bubbling nitrogen through the solution at room temperature for several hours. The products were isolated by preparative g.l.c. on columns packed with Apiezon L on Universal B support. Dehydrogenation of the separated 1:1 adducts (200 μl) to the aromatic compounds was accomplished by refluxing their solutions in toluene (10 ml) with 10% Pd–C (0.1 g) for 24 h; the reaction was essentially quantitative.

Data Relevant to the Structural Assignments of the 1:1 Adducts and Substitution Products.—I.r. spectra were recorded as liquid smears, ^{1}H n.m.r. spectra for solutions in CCl_4 (60 MHz), and u.v. spectra for solutions in cyclohexane. The samples of 1:1 adducts and substitution products used in the spectroscopic analysis were >90% pure except where indicated; absorptions at ca. 250 nm quoted below for the 1,2-acyclic adducts are all estimated to have ε values of the order of 8 000 l mol^{-1} cm^{-1}. The aniline derivatives, with the exception of those from hexafluorobenzene, were identified by comparison (spectroscopic and chromatographic properties) with authentic materials or compounds synthesised by unambiguous routes.

(a) Fluorobenzene and t-butylamine products. Compound (5) had M^+ 169, $λ_{max.}$ 254 nm, δ 5.4—5.9 (3 H, complex m), 3.2—3.5 (1 H, m), 2.3—2.6 (2 H, t with further splitting), and 1.1 (10 H, s, NH and Bu^t), and $ν_{max.}$ at 3 350w (N–H), 1 705s (C=C of cyclohexadiene with F substituent), 1 150s (C–F str.), and 745s cm^{-1} (C–H on C=C out-of-plane deformation). Dehydrogenation gave o-fluoro-N-t-butyl-aniline (cf. major product from o-difluorobenzene and t-butylamine). Compound (6) had M^+ 169. Very small amounts were obtained which were insufficiently pure for spectral analysis but the adduct dehydrogenated in the mixture to m-fluoro-N-t-butylaniline; 1,2-adduct structure

proposed by analogy with (10) from diethylamine and fluorobenzene. Compound (7) had M^+ 169, $\lambda_{max.}$ 254 nm, δ 5.7—5.9 (2 H, dd, J 1.5 Hz), 5.2—5.6 (1 H, dt, J 17.2 and 3.5 Hz), 3.6—4.0 (1 H, m), 2.6—3.0 (2 H, m), and 1.2 (10 H, NH and Bu^t); $\nu_{max.}$ 3 350w (N–H), 1 710s (C=C of cyclohexadiene with F substituent), 1 150s (C–F str.), and 740s cm^{-1} (C–H on C=C out-of-plane deformation). De-hydrogenation of (7) gave p-fluoro-N-t-butylaniline (*cf.* major substitution product from p-difluorobenzene and t-butylamine).

(b) *Fluorobenzene and diethylamine.* In this case the adduct mixture was quantitatively dehydrogenated to a mixture of the NN-diethylfluoroanilines by refluxing in toluene for 5 h. The ratio of anilines was the same as that of the adducts and the former were separated by preparative g.l.c. Compound (8) had M^+ 169, $\lambda_{max.}$ 250 nm, δ 5.4—5.8 (3 H, m), 3.4—3.8 (1 H, dt, J 8.5 and 6.5 Hz), 2.3—2.9 (6 H, m and q, J 7 Hz), and 1.05 (6 H, t, J 7 Hz); $\nu_{max.}$ 1 680s (C=C of cyclohexadiene) and 1 150 cm^{-1} (C–F str.). Dehydrogenation gave NN-diethyl-o-fluoroaniline. The adducts (9) and (10) (M^+ 169, m.s.–g.l.c.) could not be adequately resolved by preparative g.l.c. and were collected as one fraction (ratio 4 : 1 respectively). Dehydrogenation of this fraction gave p- and m-fluoro-NN-diethylaniline quantitatively in the ratio 4 : 1, respectively. The 4 : 1 (9) : (10) mixture showed $\lambda_{max.}$ 250 nm, δ 5.0—5.9 (3 H, m), 3.5—4.2 (1 H, m), 2.2—2.9 (6 H, m + q, J 7 Hz), and 1.0 (6 H, t, J 7 Hz).

(c) *Fluorobenzene and triethylamine.* As with other tertiary amine–benzene 1,4-adducts, the M^+ ion for compound (11) was not discernible but typical fragmentation to ions of m/e 100 (base ion), 72, and 44 occurred; [17] $\lambda_{max.}$ no absorption above 225 nm, δ 5.5—5.8 (2 H, m), and 5.0 and 5.3 (1 H total 2 × m), 2.2—2.9 (8 H, overlapping m with br s at 2.8), and 1.0 (9 H, d + t, J 7 Hz); $\nu_{max.}$ 1 715s (C=C of cyclohexadiene with F substituent) and 1 145s cm^{-1} (C–F str.).

(d) o-*Difluorobenzene and t-butylamine.* Compound (12) had M^+ 187; $\lambda_{max.}$ 250 nm; δ 5.4—5.9 (2 H, m) 3.2—3.6 (1 H, m), 2.4—2.8 (2 H, m), and 1.1 (10 H, Bu^t and NH). Compound (13) had M^+ 187, $\lambda_{max.}$ 250 nm, δ 5.4—5.7 (2 H, m), 3.9—4.2 (1 H, m), 2.8—3.1 (2 H, m), and 1.1 (10 H, Bu^t and NH); $\nu_{max.}$ 3 350w (N–H), 1 760 and 1 720m (C=C stretching, substituted with F), and 1 195 and 1 110s cm^{-1} (C–F str.).

(e) o-*Difluorobenzene and diethylamine.* Compound (14) had M^+ 187, $\lambda_{max.}$ 250 nm, δ 5.5 (2 H, m), 4.1 (1 H, m), 2.5 (6 H, m + q, J 7 Hz), and 1.0 (6 H, t, J 7 Hz).

(f) p-*Difluorobenzene and t-butylamine.* Compound (15) had M^+ 187, $\lambda_{max.}$ 250 nm, δ 5.1—5.5 (2 H, t, with minor splitting, J 7.5 Hz), 3.3—3.7 (1 H, 7 lines, $J \approx$ 4 Hz), 2.2—3.1 (2 H, m), and 1.2 (1 H, s, N–H), and 1.1 (9 H, s, Bu^t); $\nu_{max.}$ 3 350w (N–H), 1 700 and 1 650 (C=C str with F substitution), 1 160s (C–F str.), and 725s cm^{-1} (C–H on C=C out-of-phase deformation). Compound (16) had M^+ 187; no absorption at longer wavelength than 225 nm; δ 4.9—5.7 (2 H, m), 3.7—4.2 (1 H, br with 7 lines super-imposed), 2.6—3.0 (2 H, m), and 1.10 (10 H, s, Bu^t and NH); $\nu_{max.}$ 3 350w (N–H), 1 695s (C=C str), 1 165vs (C–F str.), and 735s cm^{-1} (C–H on C=C out-of-plane deformation).

(g) p-*Difluorobenzene and diethylamine.* Compound (17) had M^+ 187, $\lambda_{max.}$ 250 nm, and was very photolabile. Compound (18) had M^+ 187, no absorption at longer wavelength than 225 nm, δ 4.9—5.6 (2 H, 2 × m centred at 5.1 and 5.4), 4.0—4.4 (1 H, m), 2.8—3.1 (2 H, m), 2.6 (4 H, q,

J 7 Hz), and 1.1 (6 H, t, J 7 Hz); $\nu_{max.}$ 1 690 (C=C stretch with F substitution), 1 160s (C–F str.), and 730 cm^{-1} (C–H on C=C out-of-plane deformation).

(h) m-*Difluorobenzene and t-butylamine.* Compound (20) had M^+ 187; $\lambda_{max.}$ 250 nm; δ 5.2—5.6 (1 H, overlapping d of dd, J 12.5, 7, and 2 Hz), 4.7—5.1 (1 H, complex m), 3.2—3.6 (1 H, 6 lines), 2.2—2.7 (2 H m), and 1.10 (10 H, Bu^t and NH); $\nu_{max.}$ 3 350w (N–H), 1 685 and 1 630s (C=C stretch with F substitution), 1 220 and 1 095 (s) (C–F str.), and 785m cm^{-1} (C–H on C=C out of plane deformation). Compound (21) had M^+ 187, $\lambda_{max.}$ 250 nm, δ 5.0—5.5 (2 H, complex m), 3.8—4.2 (1 H, complex m, J 7 and 4 Hz), 2.5—3.0 (2 H, m), and 1.10 (10 H, Bu^t and NH); $\nu_{max.}$ 3 350 w (N–H, 1 720 s (C=C str. with F substitution), and 1 195 and 1 110s cm^{-1} (C–F str.). Compound (19) had M^+ 187; amounts available were very small and aromatic impurities were always present; δ 4.8—5.2 (2 H, dd J_{HF} 10 Hz), 2.5—4.1 (3 H, series of complex m), and 1.10 (10 H, Bu^t and NH), deduced to be a 1,4-adduct as the two possible 1,2-isomers with two ethenyl protons positively assigned.

(i) m-*Difluorobenzene and diethylamine.* Compound (22) had M^+ 187, $\lambda_{max.}$ 250 nm; δ 5.3—5.8 (1 H, overlapping d of dd, J 12.5, 8, and 2 Hz), 4.7—5.2 (1 H, complex m), 3.3—3.8 (1 H, 6 lines), 2.4—2.8 (6 H, m with q, J 7 Hz), and 1.0 (6 H, t, J 7 Hz). Compound (23) had M^+ 187; $\lambda_{max.}$ 250 nm; δ values 5.1—5.6 (2 H, m), 3.9—4.3 (1 H, 7 lines), 2.4—2.9 (6 H, m + q, J 7 Hz), and 1.05 (6 H, t, J 7 Hz).

(j) *Hexafluorobenzene and diethylamine.* (24) had M^+ 239, δ 4.30 (1 H, q, J 7 Hz), 2.60 (4 H, q, J 7 Hz), 1.50 (3 H, d), and 1.10 (6 H, t). Pentafluoro-NN-diethylaniline, M^+ 239; only ethyl resonances in ^{1}H n.m.r. spectrum; $\nu_{max.}$ 2 980m, 2 940m, 2 880m, 2 850w, 1 520s, 1 500s, 1 480m, 1 455m, 1 380m, 1 195m, and 1 040m cm^{-1}. NN-Diethyl-2,3,4,5-tetrafluoroaniline had M^+ 221, δ 6.2—6.8 [1 H, m pattern matched that for o-H with $J_{HF\text{-}ortho}$ 12.8, $J_{HF\text{-}meta}$ 7.2 (both values), and $J_{HF\text{-}para}$ 2.4 Hz[18]], 3.2 (4 H, q, J 7 Hz), and 1.1 (6 H, t, J 7 Hz). NN-Diethyl-2,3,4,6-tetrafluoro-aniline had M^+ 221 and δ values as for the 2,3,4,5-isomer but the one aromatic proton resonated as six poorly resolved and overlapping doublets (pattern matched that for m-H with $J_{HF\text{-}ortho}$ 12.5 and *ca.* 10.5, $J_{HF\text{-}meta}$ *ca.* 5, and $J_{HF\text{-}para}$ 1.7 Hz).

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