The Synthesis of Di- and Tri-arylamines through Halogen Displacement by Base-activated Arylamines: Comparison with the Ullmann Condensation

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In dipolar aprotic solvents, nitranions derived from anilines of enhanced N-acidity displace fluorine from activated aromatic compounds at room temperature. Diarylamines thus produced are free from tri-arylamines, which are formed at higher temperatures when diarylamines, after N-deprotonation by potassium t-butoxide or by the heavier alkali metal carbonates, similarly displace activated fluorine. Certain diarylamines can also be prepared by chlorine displacement in the presence of alkali metal carbonates. It is confirmed that such carbonates play only an auxiliary role in the Ullmann (copper-assisted) diarylamine synthesis conducted in dipolar aprotic solvents; they may indeed impede the reaction in some instances.

Diarylamines are readily formed by the reaction of activated fluoroarenes with arylamines containing electron-releasing groups;[1] the corresponding displacement of fluorine, nitro groups,[2] and the other halogens by arylamines containing electron-withdrawing groups requires activation of the amine by a base capable of effecting partial or complete removal of a proton from the acidic NH_2 group (Scheme 1).

$R^1, R^2 =$ electron-withdrawing groups

M = an alkali metal

X = halogen or nitro group
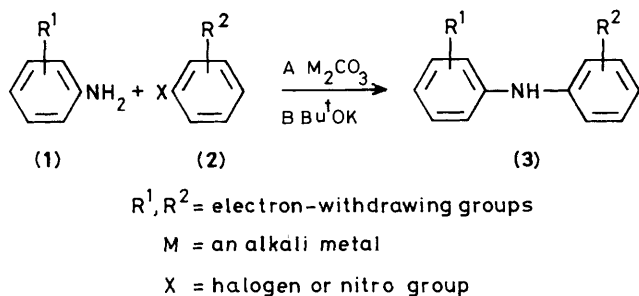
Scheme 1. *Conditions:* In dimethyl sulphoxide (DMSO): (A) at 120—150 °C; (B) at 20—25 °C

The reaction of Scheme 1A (M = potassium), already discussed for nitro group displacement,[2] fulfils the normal criterion for such S_NAr reactions[3] by proceeding with decreasing facility in the series X = F, $NO_2 \gg$ Cl > Br > I, so that, for practical purposes, bromine and iodine displacement are lacking in synthetic utility.

The reaction of Scheme 1B, proceeding through the NH^- anion, is accompanied by concurrent hydrogen-displacement from a ring position of the electrophilic reagent (2) when the activating (R^2) or leaving (X) group is nitro,[4] except when X is readily displaced.[2] Fluorine appears to satisfy this last condition, and Scheme 1B (X = F) has been found to afford the most convenient route to many diarylamines (3a—n) (Table 1), some of which have previously been prepared by the Ullmann condensation, or by other routes. In the absence of an excess of fluoroarene (2), triarylamines (4) were formed in no more than trace amounts, so it is a reasonable conclusion, in harmony with electronic and steric considerations,[5] that the anion of the diarylamine (3) is markedly less reactive than the anion of the arylamine (1). Unsymmetrical diarylamines (3; $R^1 \neq R^2$) were prepared by alternative routes, and the respective yields obtained from 21 of these reactions under standard conditions (24 h at room temperature) (Table 1) probably reflect the relative rates of reaction, since no complicating factors entered, and

suggest control by the reactivities of both the aryl fluoride and the substituted aniline. Yields were generally higher when fluorine was activated by an *ortho*- or *para*-nitro group, no significant difference between the isomers being apparent,[6] than when activation was by *o*- or *p*-CN or by *p*-COPh. Nitroanilines were generally less reactive than those with –CN or –COPh substituents, perhaps because of greater charge-delocalisation and correspondingly reduced electron density at the reacting NH^- centre.[5a] These trends were illustrated by average yields obtained from the fluoroarenes (2; X = F, $R^2 = o$- and *p*-NO_2) with the anilines (1; $R^1 = o$- and *p*-NO_2) of 68% (4 reactions) and with (1; $R^1 = o$- and *p*-CN; *p*-COPh) of 75% (6 reactions). From the fluoroarenes (2; X = F, $R^2 = o$- and *p*-CN; *p*-COPh) were recovered yields of 28% (6 reactions) and 64% (5 reactions) respectively with these substituted anilines.

In contrast to the uncomplicated synthesis of diarylamines (3) according to Scheme 1B, the reaction of Scheme 1A (X = F, M = potassium) has been found[2] in certain instances to afford triarylamines (4) (Scheme 2) as major products even in the presence of an excess of the arylamine (1).

$R^1, R^2, R^3 =$ electron-withdrawing groups

M = an alkali metal
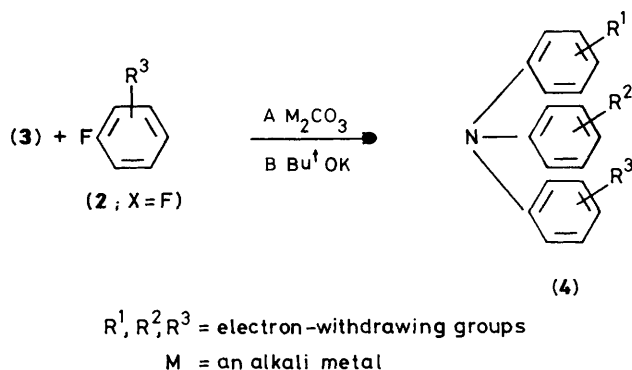
Scheme 2. *Conditions:* In DMSO at 120—150 °C

This preferential formation of triarylamine (4) suggests that carbonate activation of the diarylamine (3) entails full deprotonation to the nitranion (Scheme 3B), which may be expected to be more reactive than the hydrogen-bonded carbonate adduct (hypothetically represented in Scheme 3A) of the less acidic arylamine (1) (unless steric limitations enter, as in the nitro group[2] and, perhaps, chlorine displacement, and in fluorine displacement when *ortho*-substituents are present in the diarylamine).

Table 1. Diarylamines $R^1C_6H_4NHC_6H_4R^2$ prepared from $R^1C_6H_4NH_2$ and $R^2C_6H_4F$ according to Scheme 1B (X = F)

Compound	R^1	R^2	Yield (%, 24 h)	M.p. (°C) (lit.)	Formula	C	H	N	NH	Other
(3a)	p-NO$_2$	p-NO$_2$	63[a]	217—218 (218—219)[d]	$C_{12}H_9N_3O_4$	—	—	—	3 315	1 495, 1 320br (NO$_2$)
(3b)	o-NO$_2$	o-NO$_2$	68	169—170 (169)[e]	$C_{12}H_9N_3O_4$	—	—	—	3 290	1 510br, 1 330 (NO$_2$)
(3c)	o-NO$_2$	p-NO$_2$	74	223—224 (224—224.4)[f]	$C_{12}H_9N_3O_4$	—	—	—	3 320	1 500, 1 335 (NO$_2$)
	p-NO$_2$	o-NO$_2$	66							
(3d)	p-CN	p-CN	51	255—256 (240—246)[g] (265—266)[h]	$C_{14}H_9N_3$	—	—	—	3 350	2 210 (CN); 820
(3e)	o-CN	o-CN	65	137—138	$C_{14}H_9N_3$	76.6 (76.7)	4.1 (4.1)	19.0 (19.2)	3 375	2 215, 2 205 (CN)
(3f)	o-CN	p-CN	68	156—157	$C_{14}H_9N_3$	76.6 (76.7)	4.1 (4.1)	19.0 (19.2)	3 320	2 210 (CN)
	p-CN	o-CN	60							
(3g)	p-NO$_2$	p-CN	30	214—215	$C_{13}H_9N_3O_2$	65.2 (65.3)	3.8 (3.8)	17.45 (17.6)	3 305	2 215 (CN); 1 500, 1 320br (NO$_2$)
	p-CN	p-NO$_2$	83[k]							
(3h)	o-NO$_2$	o-CN	42	140—141 (115—116)[i]	$C_{13}H_9N_3O_2$	65.5 (65.3)	3.95 (3.8)	17.5 (17.6)	3 310	2 220 (CN); 1 505br, 1 345 (NO$_2$)
	o-CN	o-NO$_2$	83							
(3i)	o-NO$_2$	p-CN	20[b]	179—180	$C_{13}H_9N_3O_2$	65.4 (65.3)	3.7 (3.8)	17.4 (17.6)	3 315	2 220 (CN); 1 500, 1 350 (NO$_2$)
	p-CN	o-NO$_2$	67							
(3j)	o-CN	p-NO$_2$	91	190	$C_{13}H_9N_3O_2$	65.3 (65.3)	3.7 (3.8)	17.5 (17.6)	3 330	2 210 (CN); 1 495, 1 330 (NO$_2$)
	p-NO$_2$	o-CN	43							
(3k)	p-PhCO	p-NO$_2$	68	211—212	$C_{19}H_{14}N_2O_3$	71.7 (71.7)	4.55 (4.4)	8.7 (8.8)	3 300	1 630 (CO); 1 500, 1 335 (NO$_2$)
	p-NO$_2$	p-PhCO	20							
(3l)	p-PhCO	o-NO$_2$	55[c]	118	$C_{19}H_{14}N_2O_3$	71.8 (71.7)	4.4 (4.4)	8.8 (8.8)	3 340	1 645 (CO); 1 505, 1 495, 1 345 (NO$_2$)
	o-NO$_2$	p-PhCO	13							
(3m)	p-PhCO	p-PhCO	74	241—242 (244)[j]	$C_{21}H_{19}NO_2$	—	—	—	3 290	1 645, 1 630 (CO)
(3n)	p-PhSO$_2$	p-CN	50	205—206	$C_{19}H_{14}N_2O_2S$	68.1 (68.25)	4.1 (4.2)	8.2 (8.4)	3 345	2 215 (CN); 1 325, 1 145 (SO$_2$)

[a] 77% After 72 h. [b] 31% After 55 h. [c] 77% After 92 h. [d] Beilsteins Handbuch, 4th edn., H, 12, 716. [e] A. Eckert and K. Steiner, *Monatsh. Chem.*, 1914, 35, 1153. [f] Beilsteins Handbuch, 4th edn., H, 12, 715. [g] J. N. Ashley, H. J. Barber, A. J. Ewins, G. Newbery, and A. D. H. Self, *J. Chem. Soc.*, 1942, 103. [h] K. Yoshida and T. Fueno, *J. Org. Chem.*, 1972, 37, 4145. [i] O. Tsuge and H. Samura, *J. Heterocycl. Chem.*, 1971, 8, 707; the purity or identity of their material is open to doubt. [j] H. R. Snyder and C. T. Elston, *J. Am. Chem. Soc.*, 1955, 77, 364; J. M. Birchall and D. H. Thorpe, *J. Chem. Soc. C*, 1967, 2071. [k] From a reaction at 125—130 °C (5.5 h), with an excess (4.5 equiv.) of Bu^{t}OK, was isolated the amide (3; R^1 = p-CONH$_2$, R^2 = p-NO$_2$) in 43% yield. This was also obtained from (3g) by the action of 95% H$_2$SO$_4$ at room temperature (20h), and formed yellow crystals (AcOH–H$_2$O), m.p. 225—226 °C (Found: C, 60.8; H, 4.2; N, 16.1. $C_{13}H_{11}N_3O_3$ requires C, 60.7; H, 4.3; N, 16.3%); $\nu_{max.}$ 3 410, 3 325, 3 280 (NH$_2$, NH); 1 640 (CO); 1 500, and 1 350 cm^{-1} (NO$_2$).

A :

B :
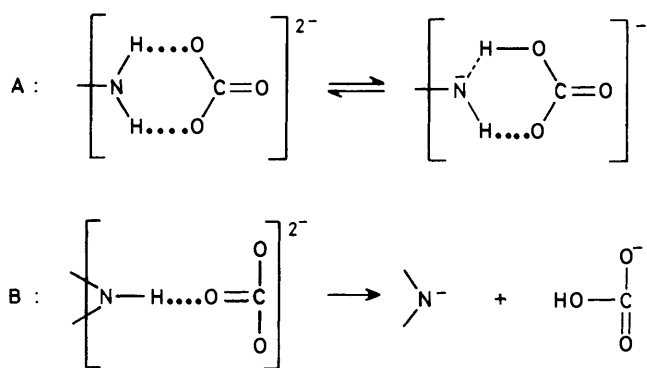
Scheme 3.

In carbonate-mediated reactions, in Scheme 2A as in Scheme 1A (X = NO$_2$),[2] the effectiveness of M$_2$CO$_3$ tended to increase with the atomic number of the cation M. Thus, yields of tris-(p-nitrophenyl)amine (4a) obtained from the diarylamine (3a) under comparable conditions in dimethylformamide (DMF) (3 mol equiv. of M$_2$CO$_3$, 130 °C, 5.5 h) were 12, 42, 86, and 86% respectively for M = Li, Na, K, and Cs. Even in refluxing pyridine, Cs$_2$CO$_3$[7] mediated the reaction between (1; R^1 = p-

CN) and (2; R^2 = p-NO$_2$) with preferential formation of triarylamine (4e),[2] whereas K$_2$CO$_3$ and Rb$_2$CO$_3$ were ineffective.

The triarylamines (4) listed in Table 2 were conveniently prepared according to the reaction of Scheme 2A from the diarylamine (3) or, by a combination of Scheme 1A and 2A, from the arylamine (1). In the theoretically equivalent reaction of Scheme 2B, interaction between fluoroarene (2; X = F) and Bu^{t}OK[8] did not appear to be important, but there was a certain disadvantage, particularly when using p-cyano compounds, in the necessity to exclude all traces of water, which effected hydrolysis both of nitrile to amide and of fluoroarene (2; X = F) to diaryl ether; this type of side-reaction was less apparent, but not entirely absent, in the reaction of Scheme 2A. Steric factors may influence the rate of the reactions of Scheme 2; thus the two o-nitro groups in o,o'-dinitrodiphenylamine (3b) strongly impeded reaction with p-fluoronitrobenzene, whereas o,p'-dinitrodiphenylamine (3c) reacted more readily with o-fluoronitrobenzene to give the same triarylamine (4c). A fully unsymmetrical triarylamine such as (4k) could be prepared by any one of 3 routes.

Chlorine Displacements.—Reaction was much slower than with fluorine or the nitro group, but diarylamine formation could be achieved when R^2 in (2; X = Cl) was strongly activating. When R^2 = NO$_2$, the reaction of Scheme 1B was inapplicable

Table 2. Triarylamines (4) prepared from $R^1C_6H_4NHC_6H_4R^2$ with $R^3C_6H_4F$ according to Scheme 2, or formed in the reaction of Scheme 1A

Compound	R^1	R^2	R^3	Route	Temp. (°C)	Reaction time (h)	Yield (%)	Solvent for cryst.[c]	M.p. (°C) (lit.)
(4a)	p-NO₂	p-NO₂	p-NO₂	2A (K, Cs)[a]	130	5.5	86	Y	396
				1A (K)	135	5	42		(396)[d]
(4b)	o-NO₂	p-NO₂	p-NO₂	2A (K)	125—130	4	76	Y, Z	223—224
				1A (K)	125—130	4.3	76		
	p-NO₂	p-NO₂	o-NO₂	2B	125—130	4	74		
(4c)	p-NO₂	o-NO₂	o-NO₂	2A (K)	125—130	2.5	65	Z	138—139
	o-NO₂	o-NO₂	p-NO₂	2A (Cs)[a]	135—150	23	<20		
(4d)	o-NO₂	o-NO₂	o-NO₂	2A (K)	145	16.5	44	Y, Z	213—214
(4e)	p-NO₂	p-NO₂	p-CN	2A (K)	140—145	5	30—40	Y	376—378
	p-CN	p-NO₂	p-NO₂	1A (K)	125—130	5.5	75		
				1A (Cs)[b]	Reflux	6	35		
(4f)	p-NO₂	p-CN	p-CN	2A (K)	140	6.3	44	Y	346—348
	p-CN	p-CN	p-NO₂	2A (K)	135—140	6.8	46		(346)[e]
(4g)	p-CN	p-CN	p-CN	2A (K)	135—140	22	ca. 50	Z	346—348
									(342)[e]
(4h)	o-CN	o-CN	o-CN	2A (K)	130—140	17	27	Y	238—239
				2A (Cs)[a]	135—140	22	45		
(4i)	p-NO₂	p-NO₂	p-PhCO	2A (K)	145—150	21	33	Z	199—200
	p-PhCO	p-NO₂	p-NO₂	1A (K)	130—135	6	34		
(4j)	p-PhCO	p-PhCO	p-PhCO	1A (K)	150	5.5	15	Y	176—177
				2B	140—145	12	ca. 20		(176—177)[f]
(4k)	p-NO₂	o-NO₂	p-PhCO	2A (K)	135—140	5	45	Y	157—158
	p-PhCO	p-NO₂	o-NO₂	2A (K)	135—140	5	80		
	o-NO₂	p-PhCO	p-NO₂	2A (K)	135—140	5	84		

Compound	Formula	Found (%) (Required) C	H	N	$\nu_{max.}$ (cm⁻¹)
(4a)	$C_{18}H_{12}N_4O_6$	—	—	—	1 500, 1 490, 1 335 (NO₂)
(4b)	$C_{18}H_{12}N_4O_6$	56.9 (56.85)	3.2 (3.2)	14.7 (14.7)	1 505br, 1 490, 1 340 (NO₂)
(4c)	$C_{18}H_{12}N_4O_6$	56.8 (56.85)	3.2 (3.2)	14.6 (14.7)	1 515br, 1 340 (NO₂)
(4d)	$C_{18}H_{12}N_4O_6$	56.9 (56.85)	3.1 (3.2)	14.7 (14.7)	1 510, 1 335br (NO₂)
(4e)	$C_{19}H_{12}N_4O_4$	63.0 (63.3)	3.4 (3.4)	15.5 (15.55)	2 220 (CN); 1 500, 1 340 (NO₂)
(4f)	$C_{20}H_{12}N_4O_2$[g]	—	—	—	2 215 (CN); 1 500, 1 320 (NO₂)
(4g)	$C_{21}H_{12}N_4$[h]	—	—	—	2 215 (CN)
(4h)	$C_{21}H_{12}N_4$[i]	78.8 (78.7)	3.6 (3.8)	17.4 (17.5)	2 220 (CN)
(4i)	$C_{25}H_{17}N_3O_5$	68.6 (68.3)	4.0 (3.9)	9.4 (9.6)	1 650 (CO); 1 490, 1 340 (NO₂)
(4j)	$C_{39}H_{27}NO_3$	—	—	—	1 645 (CO)
(4k)	$C_{25}H_{17}N_3O_5$	68.1 (68.3)	3.9 (3.9)	9.5 (9.6)	1 645 (CO); 1 520, 1 500, 1 490, 1 335 (NO₂)

[a] In DMF. [b] In pyridine. [c] Y = MeOH or DMF–MeOH; Z = AcOH or AcOH–H₂O. [d] Beilsteins Handbuch, 4th edn., H, **12**, 717. [e] A. P. T. Easson, *J. Chem. Soc.*, 1961, 1029. [f] C. J. Fox and A. L. Johnson, *J. Org. Chem.*, 1964, **29**, 3536; B. Staskun, *J. Org. Chem.*, 1968, **33**, 3031. [g] Found: M^+ (100%), m/z 340.0957. Calc. 340.0960. Also peak at m/z 358 (1.7%) (amide). [h] Found: M^+ (100%), m/z 320.1062. Calc. 320.1062. Also peak at m/z 338 (4%) (amide). [i] Found: M^+, m/z 320.1065. Calc. 320.1062.

owing to concurrent hydrogen displacement,[4] but the reaction of Scheme 1A could be utilised (Table 3) since no hydrogen displacement occurred and, in this case, triarylamine formation was minimal (≯ 3%). Yields generally increased with the atomic number of M in the mediating carbonate, M_2CO_3. Dimethyl sulphoxide appeared to be superior as a solvent to DMF, while pyridine was ineffective. Somewhat higher yields were obtainable by an increase in time, temperature, and amount of K_2CO_3, and therefore this may be considered a useful synthetic procedure when compounds of sufficient activation are employed. Since, however, the reaction rate of carbonate-mediated displacement by arylamines (1) depends, as a limiting factor, on the acidity of an amino-proton, arylamines (1) containing sub-

stituent groups (*e.g.* R^1 = CN or PhCO) less strongly electron-withdrawing than nitro are not very effective in the displacement of a chloro group.

The foregoing syntheses are logical developments of the uncatalysed displacement of highly activated chlorine discovered by Jourdan.[9]

The Ullmann Condensation.—The Ullmann (copper-assisted) diarylamine synthesis is known[10] to involve a mechanism in which halogen displacement usually proceeds with decreasing facility in the series X = I > Br > Cl ≫ F. Since the dinitro-diphenylamines (3b) and (3c) had been prepared by this route, their preparations from (1; R^1 = o-NO₂) and (2, X = I, R^2 =

Table 3. Diarylamines $R^1C_6H_4NHC_6H_4R^2$ prepared from $R^1C_6H_4$-NH_2 (2.5 equiv.) and $R^2C_6H_4Cl$ in presence of M_2CO_3 (3 mol equiv.) according to Scheme 1A (X = Cl)

Compd.	R^1	R^2	Temp. (°C)	Reaction time (h)	M	Yield (%)
(3a)	p-NO_2	p-NO_2	145—150	5	Na	19
					K	71[a]
					Cs	90[a]
(3b)	o-NO_2	o-NO_2	135	5	Li	1
					Na	9
					K	45[b,c]
					Rb	73
					Cs	75[c]
(3c)	o-NO_2	p-NO_2	140	5.5	Li	3
					K	61[d,e]
					Cs	86[e]
	p-NO_2	o-NO_2	125—130	5.5	K	45
					Cs	66
(3h)	o-NO_2	o-CN	150	5.5	K	10
					Cs	29

[a] Accompanied by triarylamine (4a) (1—2%). [b] 62% Yield after 6 h at 145 °C (8 mol equiv. K_2CO_3). [c] In experiments where X = Br, the yield was very low with K_2CO_3 and little better (< 13%) with Cs_2CO_3 (11 h at 140—145 °C). [d] In another experiment, the yield after 5.3 h at 140 °C was 58%, compared with 17% in DMF and 0% in pyridine (at reflux). [e] In experiments where X = Br, a yield of 27% obtained with K_2CO_3 was increased to 65% by the use of Cs_2CO_3 (4 mol equiv.) (5 h at 135 °C).

Table 4. Diarylamines $R^1C_6H_4NHC_6H_4R^2$ prepared from $R^1C_6H_4$-NH_2 (2.5 equiv.) and $R^2C_6H_4I$ in the presence of Cu (1 equiv.) and M_2CO_3 (4 mol equiv. in DMSO, 4 h at 135—140 °C; 3 mol equiv. in pyridine, 4 h at reflux)

Compd.	R^1	R^2	Solvent	M	Yield (%)
(3c)	o-NO_2	p-NO_2	DMSO	Li	80
				Na	70—75
				K	50[a]
				Rb	40
				Cs	35—40
			Pyridine	Li	75—80
				Na	90
				K	80
				Rb	80
				Cs	< 30
(3b)	o-NO_2	o-NO_2	DMSO	Li	70—75
				Na	70
				K	65—70[b]
				Rb	50
				Cs	40—45

[a] In the absence of Cu, the yield was 4% (5 h, 115—125 °C). [b] In the absence of Cu, the yield was 1.5% (5 h, 130—135 °C).

p- and o-NO_2) were re-examined, conditions being similar to those used for the carbonate-mediated reaction (Scheme 1A; X = Cl) except that copper powder (1 equiv.) was added. The results (Table 4) uphold the accepted view that the function of carbonate in the Ullmann condensation is merely to remove hydrogen halide. With (2; X = I, R^2 = p-NO_2) the particular carbonate cation utilised was not however unimportant, since, in contrast to the findings for the Jourdan-type reactions, yields and product quality decreased in the order M = Li > Na > K > Rb, Cs. This suggests the possibility that the Ullmann condensation is impeded by the heavier carbonates in some undetermined manner. In pyridine solution, product yields were uniformly high where M = Li, Na, K, and Rb, but decreased sharply where M = Cs. In reactions of (2; X = I, R^2 = o-

NO_2) in DMSO a similar trend was apparent, but to a lesser degree than with p-iodonitrobenzene, the effect of the heavier carbonates being apparent in decreasing yields: M = Li, Na, K > Rb > Cs. In this case, the readiness of the ortho-group to form an intermolecular hydrogen bond with the amino group (recognised as a facilitating factor in the Ullmann condensation [10b]) may assume greater importance. Nevertheless, in this type of reaction the choice of neutralising agent would lie between sodium and lithium carbonates, rather than K_2CO_3.

Experimental

M.p.s were determined on an Electrothermal melting point apparatus or on a Mel-Temp apparatus (above 300 °C). I.r. spectra, which were recorded for all products using a Perkin-Elmer 157G spectrophotometer (KBr), were utilised in identifications and comparisons. For mass spectra, an A.E.I. MS 902 instrument (at 70 eV) or an A.E.I. MS 30 was employed. Commercial materials were generally utilised, but 4-aminodiphenyl-sulphone was prepared by a standard procedure.[11] Solvents were routinely dried and stored over molecular sieve. Alkali metal carbonates were dehydrated on platinum foil, then powdered before use.

Reactions of Table 1.—The aniline (0.5 mmol) and the fluoro-arene (0.5 mmol) were dissolved in DMSO (1.5 ml) at room temperature. On the addition of potassium t-butoxide (1.05 mmol) strong colours developed, which generally intensified during the course of the reaction and were discharged on final dilution with water (100 ml). The filtered products were washed with dilute hydrochloric acid and water, and crystallised from aqueous methanol or acetic acid. Coloured compounds were (3g) (golden yellow), (3h) (orange), (3i) (orange), (3j) (pale yellow), (3k) (yellow), and (3l) (orange). Yields are based on material of satisfactory purity obtained in the time recorded, and do not represent maximum obtainable yields. Reactions were conducted in groups of 4 to ensure comparability.

Reactions of Table 2.—These were set up in a similar manner to those of Table 1, but with oil-bath heating (without thermostatic control). For comparability studies, reactions were conducted in pairs. In carbonate-mediated reactions (according to Schemes 1A and 2A) the amounts of carbonate used were 3 mol equiv. (M = Cs) and 3—6 mol equiv. (M = K). The fluoroarene was used in excess (up to 100%) in reactions according to Scheme 2A, but not in reactions according to Scheme 1A, where, in the production of (4a), (4b), and (4e), 2.5 equiv. of the aniline were employed for 1 equiv. of the fluoroarene. The isolation and crystallisation of products proved straightforward, except in the hindered preparation of (4c) from o,o'-dinitrodiphenyl-amine (3b), but the slow-running triarylamine (4c) was readily separated from starting material (3b) on a preparative t.l.c. plate [SiO_2; light petroleum (b.p. 60—80 °C)–MeOH–$CHCl_3$, 5:1:1]. Coloured compounds were (4b), (4c), (4d), (4e), (4i), and (4k), which usually crystallised in yellow prisms.

Chlorine Displacement (Table 3).—The procedure corresponded to that used for some of the compounds of Table 2 (route of Scheme 1A), 2.5 equiv. of the aniline being employed for 1 equiv. of chloroarene.

Copper-assisted Reactions (Table 4).—These were conducted under the conditions used for chlorine displacement, but with the addition of copper bronze (B.D.H.). The reaction mixture was filtered before final dilution with water, and the crude products were crystallised as in previous preparations.

References

1 R. L. Lantz and P. Obellianne, *Bull. Soc. Chim. Fr.*, 1956, 311; J. J. Kulagowski and C. W. Rees, *Synthesis*, 1980, 215.

2 J. H. Gorvin, *J. Chem. Soc., Chem. Commun.*, 1985, 238.

3 J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968, pp. 137—156.

4 H. Iida, M. Yamazaki, K. Takahashi, and K. Yamada, *Nippon Kagaku Kaishi*, 1976, 138 (*Chem. Abstr.*, 1976, **84**, 134795f).

5 (*a*) F. G. Bordwell and D. L. Hughes, *J. Am. Chem. Soc.*, 1984, **106**, 3234; (*b*) *ibid.*, 1986, **108**, 5991.

6 N. S. Nudelman and S. Cerdeira, *J. Chem. Soc., Perkin Trans. 2*, 1986, 695; J. H. Gorvin and D. P. Whalley, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1364.

7 For references to the use of caesium salts in organic synthesis, see B. Strijtveen and R. M. Kellogg, *J. Org. Chem.*, 1986, **51**, 3664.

8 D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, 1960, **82**, 6412.

9 F. Jourdan, *Chem. Ber.*, 1885, **18**, 1444.

10 For reviews, see (*a*) R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, 1965, **19**, 95; (*b*) J. Lindley, *Tetrahedron*, 1984, **40**, 1433 (Tetrahedron Report No. 163).

11 F. Ullmann and G. Pasdermadjian, *Chem. Ber.*, 1901, **34**, 1155.