

Aromatic Substitution by Phenylnitrenium and Naphthylnitrenium Ions formed from Phenyl Azide and 1-Azidonaphthalene in the Presence of Trifluoromethanesulphonic Acid

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Aromatic *N*-substitution by phenylnitrenium ions generated from phenyl azide in the presence of a catalytic amount of trifluoromethanesulphonic acid gave diarylamines (in especially good yield in the reaction with biphenyl or naphthalene), whereas naphthylnitrenium ions from 1-azidonaphthalene react with benzene to afford a *C*-substitution product, 1-amino-4-phenylnaphthalene.

It has been reported that nitrenium ions are intermediates in the reactions of *N*-hydroxy- and *N*-chloro-aniline derivatives under neutral conditions.¹ The phenylnitrenium ion is formed in the decomposition of phenyl azide in strongly acidic media² or acetic acid.³ We have recently established the mechanism of an aromatic *N*-substitution by the phenylnitrenium⁴ or ethoxycarbonylnitrenium ions,⁵ formed from phenyl azide or ethyl azidoformate in the presence of trifluoroacetic acid (TFA). We have now examined *N*-substitution by the phenylnitrenium ion using trifluoromethanesulphonic acid (TFSA) instead of TFA, and aromatic *C*-substitution by the naphthylnitrenium ion from 1-azidonaphthalene. We also discuss the differences between the reactivities in the presence of TFSA and TFA.

Reactions of phenyl azide with benzene, toluene, cumene, chlorobenzene, bromobenzene, and biphenyl in the presence of TFSA (5% v/v) at room temperature for a few minutes gave the 2- and 4-substituted diarylamines (**1**) and (**2**) respectively in fairly good yields (Table 1 and Scheme 1). The products are preferentially substituted at the *ortho*- and *para*-positions. Products of *C*-substitution, 2- and 4-aminobiphenyl (**3a**) and (**4a**),[†] and 4-amino-4'-phenylbiphenyl (**4f**), were isolated in the

[†] The value for the substitution ratio, (**1a**):(**3a**):(**4a**) is almost the same in the presence of TFSA and TFA, suggesting that the two reactions proceed *via* a common intermediate, the phenylnitrenium ion.

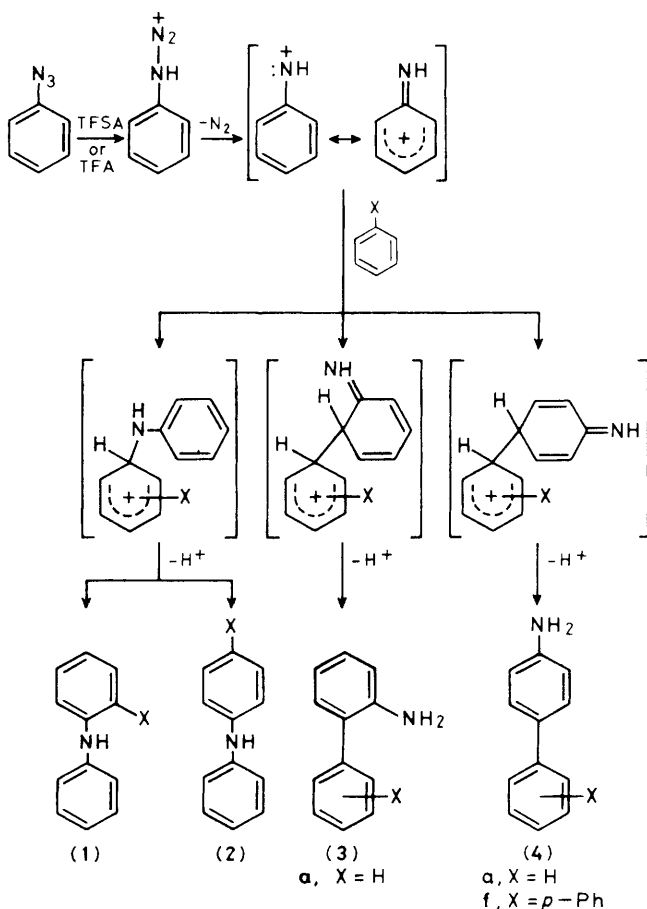
reactions with benzene and biphenyl, respectively (Table 1 and Scheme 1).

3-Nitrodiphenylamine was not detected in the reaction with nitrobenzene, but 4-nitrodiphenylamine (5) was formed in the

Table 1. Reactions of aryl azides with the aromatic compounds PhX in the presence of TFSA (5% v/v) at room temperature.

Ar of ArN ₃	[ArN ₃]/M	X in PhX	% Yield ^{a,b}	
			(1)	(2)
Ph	0.25	a, H	73 (66) ^f	
Ph	0.25	b, Me	15 (35)	22 (47)
Ph	0.25	c, Pr ⁱ	31 (32)	44 (44)
Ph	0.25	d, Cl	19 (16)	55 (65)
Ph	0.25	e, Br	16 (9)	46 (20)
Ph	0.28	f, Ph ^c	24 (18) ^g	68 (43) ^h
4-O ₂ NC ₆ H ₄ ^d	0.25	a, H		
Ph	0.36	Naphthalene ^e		i
1-Naphthyl	0.11	a, H		j

^a Yields in parentheses refer to the reaction in the presence of TFA (30% v/v). ^b Yields are based on azide decomposed. ^c Substrate concentrations: 2.6 M in CH₂Cl₂-TFSA (2% v/v), and 1.1 M in CH₂Cl₂-TFA. ^d The azide was decomposed in the presence of TFSA (10% v/v). ^e Concentration of naphthalene as substrate was 1.5 M in CH₂Cl₂-TFSA, or 0.82 M in CH₂Cl₂-TFA containing phenyl azide (0.25 M). ^f +8.2(7.0)% of (3) and 8.0(6.7)% of (4). ^g +3(6)% of (4). ^h 44% of (5). ⁱ 78(42)% of (6). ^j 82(62)% of (7).



Scheme 1

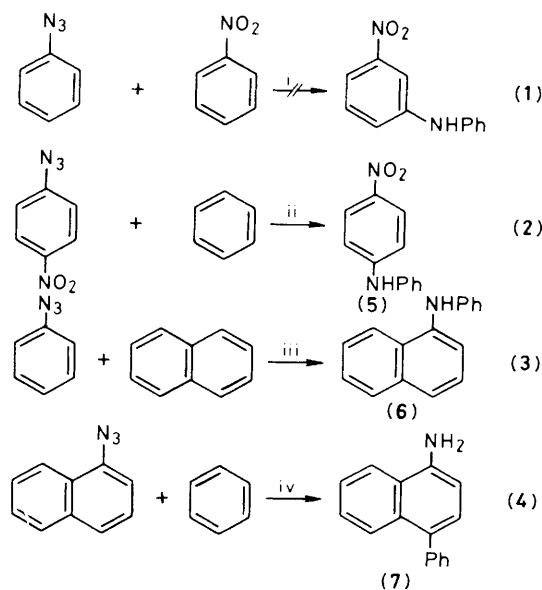
reaction of 4-nitrophenyl azide[‡] with benzene [Table 1 and equations (1) and (2)].

The reaction of phenyl azide with naphthalene gave *N*-phenyl-1-naphthylamine (6) in good yield, whereas the reaction of 1-azido-naphthalene with benzene yielded no (6) but the *C*-substitution product 1-amino-4-phenylnaphthalene (7) [Table 1 and equations (3) and (4)].

Phenyl azide, 4-nitrophenyl azide, and 1-azidonaphthalene are completely decomposed in the presence of TFSA (1–10% v/v) at room temperature. The decomposition proceeds *via* the conjugate acids of the azides.

Partial rate factors, f_p , for the *para*-position of toluene, cumene, chlorobenzene, and bromobenzene were determined for the formation of diarylamines in the presence of TFSA (5% v/v) containing phenyl azide (<1/10 molar ratio of PhN₃ to aromatic component). The correlation between log f_p and σ^+ gives a linear plot with $\rho = -4.5$ which is identical with that⁴ obtained in the reaction using TFA (30% v/v) in place of TFSA.

These results suggest that the diarylamines are produced *via* aromatic *N*-substitution by the phenylnitrenium ion in the presence of TFSA as well as TFA (Scheme 1). The preferential *C*-substitution by the naphthyl nitrenium ion probably results from the favourable population of its positive charge at the 4-position of the ring rather than the nitrogen atom.⁶



Reagents: i, TFSA or TFA; ii, TFSA (10% v/v); iii, TFSA (5% v/v) or TFA (45% v/v); iv, TFSA (4% v/v) or TFA (30% v/v). All reactions at room temperature.

Table 2. Reactivities of biphenyl and naphthalene relative to benzene in *N*-substitution by the phenylnitrenium ion from phenyl azide (0.19–0.33 M) in the presence of TFSA or TFA at room temperature.

f_p for biphenyl ^a		f for 1-position of naphthalene ^b	
TFSA (5% v/v)	TFA (30% v/v)	TFSA (3% v/v)	TFA (45% v/v)
54	13	20	12

^a Concentrations of biphenyl were 0.91 and 0.67 M in benzene-TFSA and benzene-TFA, respectively. ^b Naphthalene (1.1 M) in benzene (5.8 M)-CH₂Cl₂-TFSA and naphthalene (0.64 M) in benzene (3.3 M)-CH₂Cl₂-TFA were used.

[‡] 4-Nitrophenyl azide did not decompose in the presence of TFA, but decomposed in the presence of TFSA (10% v/v) in 1 day.

With biphenyl and naphthalene as the aromatic component, the yield of diarylamines was as high in the presence of TFSA as that with TFA (see Table 1). Further, the f_p values for biphenyl and the f value for the 1-position of naphthalene were much larger in the presence of TFSA rather than TFA (Table 2). The transition state for the *N*-substitution, which is somewhat similar to a σ -complex because of the large negative value of ρ , would have as a near neighbour the trifluoromethanesulphonate or the trifluoroacetate anion in the presence of TFSA or TFA, respectively. The former anion is softer than the latter on the Pearson classification,⁷ so that the positive charge of the transition state may be delocalized throughout the two-ring system of biphenyl or naphthalene in the presence of TFSA. On the other hand, the harder trifluoroacetate anion presumably permits the positive charge to be delocalized over only the one-ring system. Thus, the greater delocalization assisted by the soft trifluoromethane-

§ $\log f_p$ correlated well with σ^+ to give a linear plot ($\rho = -4.5$) in the presence of TFA, but the value was much higher than that expected from the plot in the presence of TFSA.

sulphonate anion might lower the activation energy to favour the *N*-substitution of polynuclear aromatic compounds.

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