

N- and *C*-Attacks of Phenylnitrenium Ions Generated from Phenyl Azides in the Presence of Trifluoroacetic Acid and/or Trifluoromethanesulphonic Acid†

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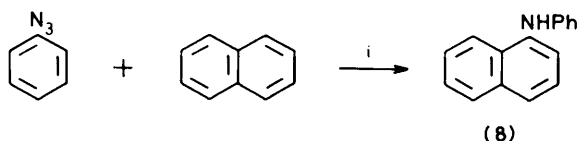
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Phenylnitrenium ions were generated from phenyl azides in the presence of trifluoroacetic acid (TFA) and/or trifluoromethanesulphonic acid (TFSA). Unsubstituted phenylnitrenium ions and those with an electron-withdrawing group such as NO₂ or CN undergo aromatic *N*-substitution, whereas those with an electron-donating group such as Me, OMe, CH₂Ph, or Ph undergo *C*-substitution, hydrogen abstraction, and tar formation. The special character of TFA and TFSA as compared with other acids is discussed.

Nitrenium ions containing divalent nitrogen with a positive charge have been extensively investigated in recent years. Arylnitrenium ions generated from *N*-hydroxy- and *N*-chloroanilines under neutral conditions¹ and from aryl azides in acidic media² are known to be reactive with nucleophiles at the ring-positions. According to MNDO molecular orbital calculations,³ a phenylnitrenium ion has a canonical resonance form in which the positive charge preferentially populates the *para*- and *ortho*-positions rather than the nitrogen atom; nevertheless we here describe a preferential attack on the nitrogen position of the phenylnitrenium ion generated from phenyl azide in the presence of TFA or TFSA. We further examine the effect of substituents on *N*- and *C*-attacks of phenylnitrenium ions formed from phenyl azides in the presence of TFA and/or TFSA, and discuss both the differing character of TFA from TFSA and the special behaviour of TFA or TFSA as compared with hydrogen halides and sulphuric acid.

Results and Discussion

Reactions of Phenyl Azide with Aromatics in the Presence of TFSA or TFA.—Reactions of phenyl azide (**1a**) with benzene, toluene, cumene, chlorobenzene, bromobenzene, or biphenyl in the presence of TFSA (5%, v/v) or TFA (30%, v/v) at room temperature for a few min or for 1 day, respectively, yielded 2- and 4-substituted diarylamines [(**2a**) and (**2j–n**), and (**3j–n**)] as *N*-substitution products after work-up with aqueous Na₂CO₃ (Table 1 and Scheme 1). Azobenzene and aniline (**4a**) were not identified by g.l.c. in the reaction with benzene. Products of *C*-attack, 2- and 4-aminobiphenyls (**5a**) and (**6a**), and trifluoromethanesulphonate (**7a**), and 4-amino-4'-phenylbiphenyl (**6n**), were isolated from the reactions with benzene and biphenyl, respectively (Table 1 and Scheme 1). The reaction with naphthalene afforded *N*-1-naphthylaniline (**8**) after work-up with aqueous Na₂CO₃ [Table 1 and equation (1)]. The yields are based on the azide used, and determined by g.l.c. analysis.



Reagents: i, TFSA (4%, v/v) or TFA (30%, v/v).

† Preliminary report, H. Takeuchi and K. Takano, *J. Chem. Soc., Chem. Commun.*, 1983, 447; H. Takeuchi, K. Takano, and K. Koyama, *ibid.*, 1982, 1254.

Table 1. Reactions of phenyl azide with aromatics PhX in the presence of TFSA (5% v/v) or TFA (30% v/v) at room temperature

[Azide]/M	X in PhX	Yield ^a (%)	
		(2)	(3)
0.25	a ; H	73 (66) ^b	
0.25	j ; Me	15 (35)	22 (47)
0.25	k ; Pr ⁱ	31 (33)	44 (44)
0.25	l ; Cl	19 (16)	55 (65)
0.25	m ; Br	16 (9)	46 (20)
0.28	n ; Ph ^c	24 (18) ^d	68 (43) ^d
0.36	Naphthalene ^e		^f

^a Yields which are based on azide used, in parentheses or otherwise refer to the reaction in the presence of TFA or TFSA, respectively. ^b Plus 8(7)% of compound (**5a**), 8(7)% of compound (**6a**), and 11% of compound (**7a**). ^c Concentrations of biphenyl: 2.6M in CH₂Cl₂-TFSA (2%, v/v) and 1.1M in CH₂Cl₂-TFA. ^d Plus 3(6)% of compound (**6n**). ^e Concentration of naphthalene: 1.5M in CH₂Cl₂-TFA. ^f 78(42)% of compound (**8**).

(a) *Decomposition via a Conjugate Acid of Phenyl Azide.*—Phenyl azide completely decomposed in TFA at 25 °C in ca. 20 min or in the presence of TFSA (1–5% v/v) at 25 °C in a few min, although the azide usually decomposes in aromatic solvents at temperatures >130 °C. Products derived from a triplet phenylnitrene,⁴ azobenzene, and aniline were not isolated; aniline was converted into trifluoroacetanilide in the presence of TFA under the reaction conditions, but trifluoroacetanilide was not obtained before work-up with aqueous Na₂CO₃ in the reaction with benzene. These indicate that the azide decomposes in the presence of TFA or TFSA *via* the conjugate acid of azide, not *via* the phenylnitrene.

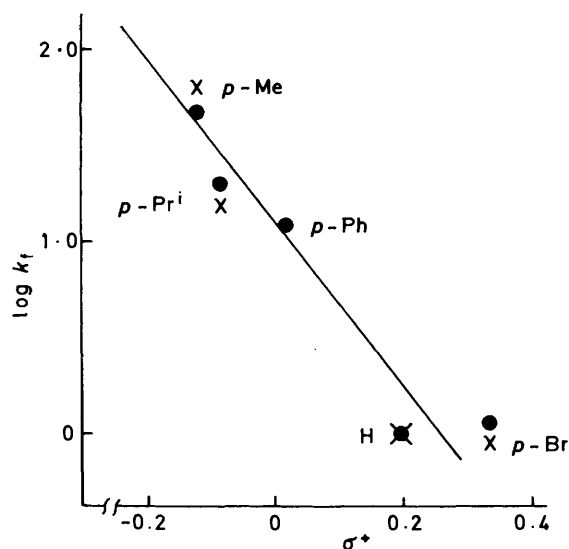
The decomposition of the azide in benzene (70%, v/v)-TFA(30%, v/v) was complete in ca. 10 h at 25 °C, but that in 1,4-dioxane (70%, v/v)-TFA (30%, v/v) did not proceed even after 1 day at 25 °C (see Table 2). This indicates that the hydrogen bonding between the oxygen atom of 1,4-dioxane and the hydrogen atom of TFA diminishes the formation of the conjugate acid of the azide. The decomposition of the azide in the presence of TFA is actually retarded in solvents containing oxygen or sulphur atoms such as ethers, alcohols, sulphides, thiols, etc. Thus, the effect of hydrogen bonding supports the decomposition *via* the conjugate acid.

(b) *Formation of a Phenylnitrenium Ion as an Intermediate.*—The substitution ratio *N*:*ortho*:*para* [i.e. (**2a**):(**5a**):(**6a**)] was 1.0:0.11:0.11 for the reaction with benzene both in the presence

Table 2. Rate constants for decomposition of phenyl azide (0.25 M) in the presence of TFA (30% v/v) at room temperature

Solvent	$k \times 10^5/s^{-1}$
Benzene	4.4 ^a
Toluene	2.6
<i>m</i> -Xylene	2.4
<i>p</i> -Xylene	2.3
1,4-Dioxane	~0 ^b

^a The decomposition of azide went to completion in *ca.* 10 h. ^b The decomposition did not proceed even after 1 day.

**Figure 1.** Plot of k_f against σ^+ for the formation of diarylamines in the reaction of phenyl azide with substituted benzenes in the presence of TFA (●) or TFSA (X).

of TFSA and TFA. The ratio is nearly the same as that for a reaction⁵ of *N*-phenylhydroxylamine with benzene in the presence of TFA; the reaction using a solution containing *N*-phenylhydroxylamine, benzene, and TFA in the molar ratio of 1:9:10 at 5 °C is reported to give a substitution ratio of 1.0:0.14:0.16.⁵ The slight difference from our substitution ratio may be due to the different reaction conditions. The result suggests that the two reactions using different precursors proceed *via* a common intermediate, the phenylnitrenium ion (see Scheme 1).

The *para*-attacking partial rate factors (k_f) for toluene, cumene, bromobenzene, and biphenyl were determined for the formation of diarylamines in the reaction between phenyl azide and aromatic compounds in the presence of TFA (30%, v/v) or of TFSA (5%, v/v) (1:10 molar ratio of phenyl azide to aromatic component). The correlation between $\log k_f$ and σ^+ gives a linear plot with $\rho = -4.5$ (Figure 1). If the formation of diarylamines results from an S_N2 mechanism involving an attack of the aromatic compound on the conjugate acid of azide, the decomposition of the azide should be greatly accelerated in an alkylbenzene (70%, v/v)-TFA (30%, v/v) system rather than in benzene (70% v/v)-TFA (30%, v/v); the decomposition should be increased by a factor of *ca.* 20* in the presence of toluene compared with benzene. However, the pseudo-first order rate constant ($k_{obs.}$) at 25 °C for the decomposition of the azide (*i.e.* decreasing concentration of azide) was slightly less in the presence of the alkylbenzene compared with benzene

Table 3. Reactions of phenyl azides ($p\text{-XC}_6\text{H}_4\text{N}_3$) with aromatic compounds in the presence of TFSA (18% v/v)-TFA (82% v/v) at room temperature^a

X of $p\text{-XC}_6\text{H}_4\text{N}_3$ (1)	[Azide]/M	Aromatic compd.	Acid (% v/v)	Yield ^b (%)		
				(3)	(4)	(5)
b ; Me	0.25	Benzene	16	0	2	37
c ; OMe	0.27	Benzene	16	0	4	0
d ; No ₂	0.24	Benzene	16	91	0	9
d ; No ₂	0.24	Toluene	16	<i>c</i>	0	0
e ; CN	0.28	Benzene	22	95	0	0

^a The decomposition of (1b) and (1c) was complete in a few min, but that of (1d) and (1e) in *ca.* 3 h. ^b Yields are based on the azide used. ^c 34% of (2d') and 38% of (3d').

(Table 2). The result therefore rules out the S_N2 mechanism, so that the conjugate acid of azide must spontaneously lose a nitrogen molecule in a rate-determining step to give the phenylnitrenium ion (Scheme 1). Thus, an electrophilic substitution of the aromatic compound by the nitrenium ion proceeds in the usual way (Scheme 1). This provides further support for the preferential *ortho*- and *para*-substitution and the large negative ρ value.

Sundberg and Sloan⁶ have reported that the reaction of aryl azides with mesitylene, anisole, *p*-xylene, and toluene in the presence of TFA (*ca.* 7.5% v/v) at 85 °C gives diarylamines by the S_N2 mechanism, but that no tractable products are found after reaction in 50:4 benzene-TFA after 24 h at reflux, although azide decomposition was complete. Their results mean that the S_N2 mechanism only occurs in the reaction with electron-rich aromatic compounds such as alkylbenzenes and anisole in the presence of low concentrations of TFA (*ca.* 7.5%) at high temperatures (*ca.* 80 °C).

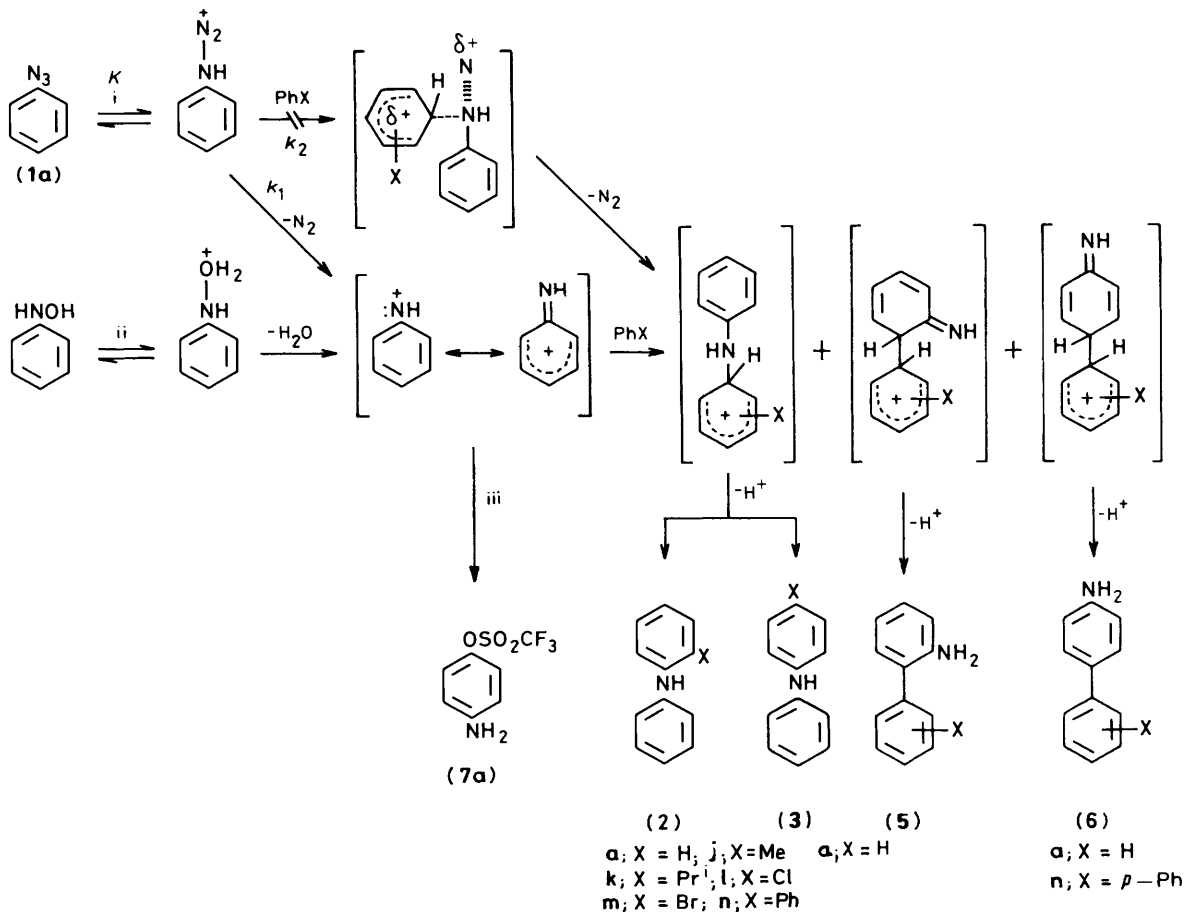
Regarding the S_N1 mechanism (see Scheme 1), $k_{obs.}$ is equal to $k_1 K [\text{TFA}]$; $k_{obs.}$ is proportional to K in the same concentration of TFA. As seen in Table 2, the decomposition in the presence of an alkylbenzene may be slightly retarded as compared with that in the presence of benzene. This can be explained by assuming that the K value is slightly smaller in the former case because of a decrease in the formation of the conjugate acid of the azide by a charge-transfer interaction of TFA with the aromatic solvent (*i.e.* the formation is decreased to a larger extent by the stronger TFA-alkylbenzene interaction).

The acid-independence of both the substitution ratio N :*ortho*:*para* and the ρ value excludes the possibility that the diarylamines are formed by an attack of the aromatic compound on a hydrogen bonded complex of the azide with TFA or TFSA.

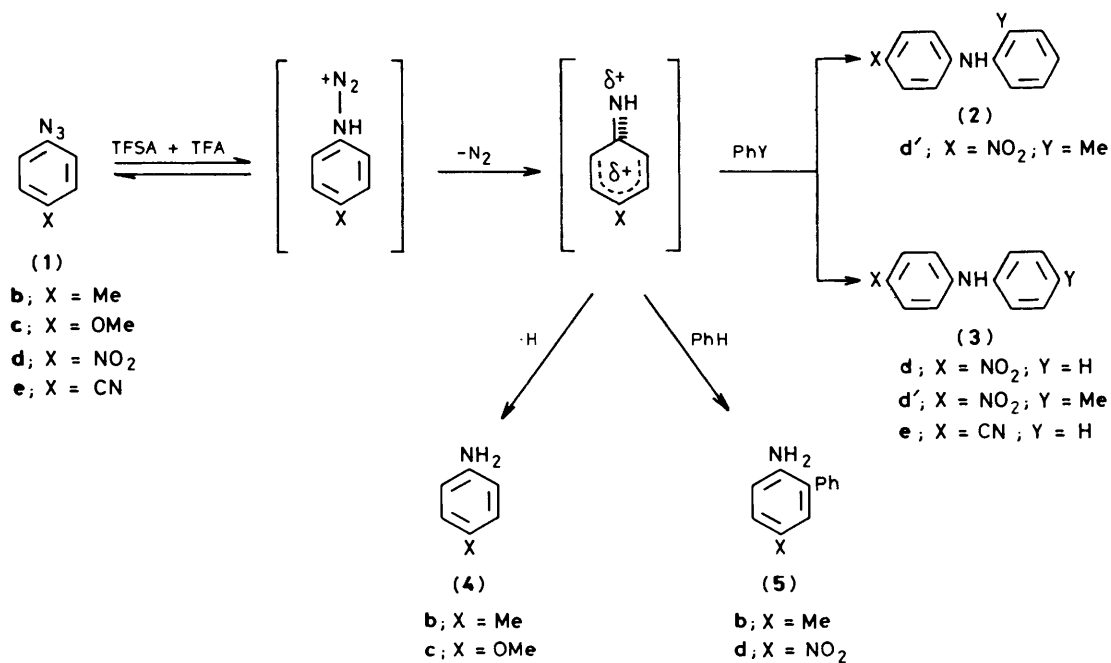
We considered the possibility that in aromatic solvents protonation⁷ (the formation of benzenium ions) occurs on the aromatic nucleus which in turn attacks the azide. However, this possibility could be eliminated since the decomposition of phenyl azide is much slower⁸ in benzene than in the presence of alkenes which give tertiary alkyl and benzylic cations by protonation (*i.e.* the induced decomposition by benzenium ion did not take place in benzene).

Reaction of Substituted Phenyl Azides with Aromatic Compounds in the Presence of TFSA and/or TFA.—Reactions of

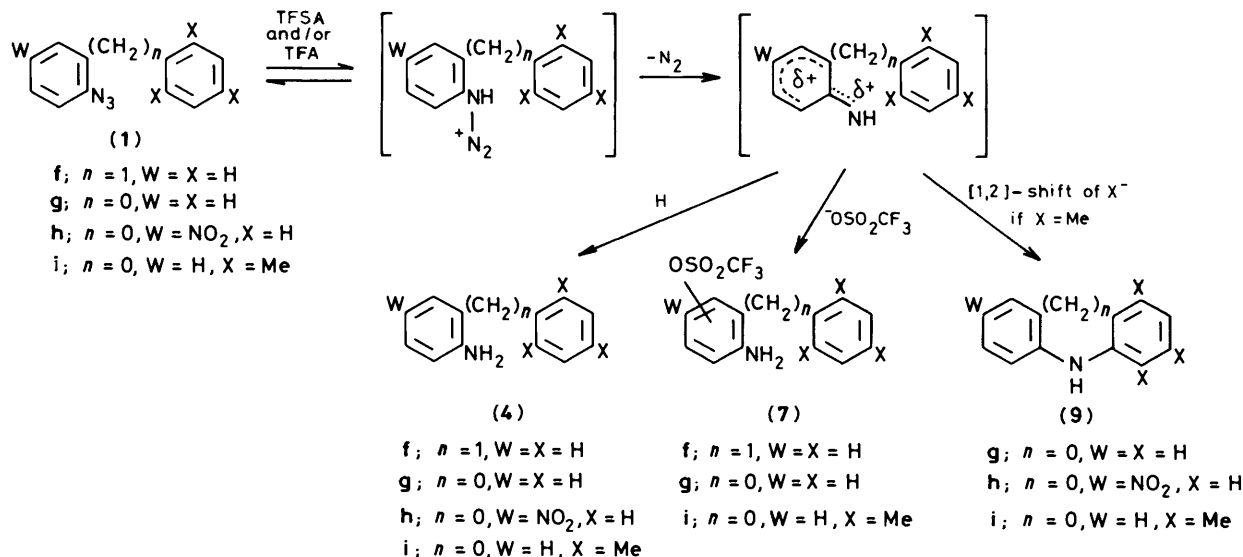
* In the S_N2 mechanism, $k_{obs.} = k_2 K [\text{TFA}] [\text{ArH}]$ where k_2 and K are shown in Scheme 1. The relative ratio of $k_{obs.}$ in toluene to that in benzene is equal to $(k_{Me}/k_H) \cdot \{[\text{toluene}]/[\text{benzene}]\} \approx 20$, where k_{Me}/k_H is the relative rate constant for the formation of *N*-phenyl-*o*- and -*p*-toluidines (2j) and (3j) with respect to diphenylamine (2a), since K and $[\text{TFA}]$ in toluene are nearly the same as those in benzene, respectively.



Scheme 1. Reagents: i, TFSA or TFA; ii, TFA; iii, ⁻OSO₂CF₃



Scheme 2



Scheme 3

p-tolyl azide (**1b**) and *p*-methoxyphenyl azide (**1c**) with benzene in the presence of both TFSA and TFA yielded no *N*-substitution products, *N*-phenyl-*p*-toluidine (**3b**) and *N*-*p*-methoxyphenylaniline (**3c**), respectively, but instead the *C*-substitution products, 2-phenyl-*p*-toluidine (**5b**) (37%) and tar, respectively, together with a small quantity of *p*-toluidine (**4b**) and *p*-anisidine (**4c**) (Table 3 and Scheme 2). The other product in the reaction of (**1b**) or (**1c**) was tar. Reactions of *p*-nitrophenyl azide (**1d**) and *p*-cyanophenyl azide (**1e**) with benzene in the presence of both TFSA and TFA afforded the *N*-substituted products, *N*-*p*-nitrophenylaniline (**3d**) and *N*-*p*-cyanophenylaniline (**3e**) respectively in good yields, (Table 3 and Scheme 2). A small amount of a *C*-substitution product, 2-amino-5-nitrobiphenyl (**5d**) was isolated in the reaction of (**1d**).

TFSA catalysed decomposition of *o*-azidophenyl(phenyl)methane (**1f**) or 2-azidobiphenyl (**1g**) failed to give 9,10-dihydroacridine (**9f**) or carbazole (**9g**) by intramolecular *N*-substitution, whereas 2-azido-5-nitrobiphenyl (**1h**) or 2-azido-2',4',6'-trimethylbiphenyl (**1i**) under similar conditions produced 3-nitrocarbazole (**9h**) or 1,2,4-trimethylcarbazole (**9i**) in 84–93 or 38% yields respectively (Table 4 and Scheme 3). Small quantities of the 2,4-disubstituted anilines (**4f**–**i**) were formed from (**1f**–**i**) (Table 3). Trifluoromethanesulphonates as *C*-attack products, (**7f**) (26–42%), (**7g**) (26%), and (**7i**) (17%), were formed from compounds (**1f**), (**1g**), and (**1i**), respectively; no such compound was produced by compound (**1h**) (Table 4 and Scheme 3).

TFA catalysed reactions of the azides (**1f**), (**1g**), and (**1i**) gave the 2,4-disubstituted anilines (**4f**) and (**4g**) as the sole isolated products; in the case of (**1i**), (**9i**) (7%) was also produced. All these reactions also gave tar formation (Table 4). The azide (**1h**) failed to decompose in the presence of TFA alone.

(a) *Formation of substituted phenylnitrenium ions.* There is no doubt as to the formation of a phenylnitrenium ion possessing an electron-donating group (*i.e.* Me, OMe, CH₂Ph, or Ms) from the corresponding azides since the *C*-attack^{1,2} [leading to compounds (**5**) and (**7**)] of nucleophiles on the nitrenium ion occurs along with the formation of tar and hydrogen abstraction products (**4**) as shown in Tables 3 and 4 [the tar and compound (**4**) are derived from triplet nitrenium ions as indicated below].

As previously mentioned, the reactions of the azides (**1d**), (**1e**),

Table 4. Reactions of aryl azides in CH₂Cl₂ in the presence of TFSA and/or TFA at room temperature^a

Azide	[Azide]/M	Acid	Acid (% v/v)	Yield ^b (%)		
				(4)	(7)	(9)
(1f)	0.23	TFA	46	6	—	0
(1f)	0.20	TFSA	5.2	Trace	42	0
(1f)	0.45	TFSA(87) + TFA(4.4) ^c		10	26	0
(1g)	0.22	TFA	43	20	—	0
(1g)	0.26	TFSA	5.1	12	26	6
(1h)	0.19	TFSA	4.6	15	0	84
(1h)	0.20	TFSA(47) + TFA(1.9) ^c		5	0	93
(1i)	0.38	TFA ^d	18	15	—	7
(1i)	0.33	TFSA ^e	8.4	5	17	38

^a The decomposition was completed in *ca.* 2 h in the presence of TFA, but in a few min in the presence of TFSA. ^b Yields are based on the azide used. ^c The mixed acids were used, and concentration (% v/v) was shown in the parenthesis. ^d The reaction was performed in the presence of TFA under reflux (*ca.* 40 °C) for 3 h. ^e In this reaction in the presence of TFSA, a brown oil was eluted with CH₂Cl₂-EtOH, but could not be purified by further column chromatography.

and (**1h**), afforded (**3d**), (**3e**), and (**9h**), respectively, in high yields by inter- and intra-molecular *N*-substitutions. The formation of a phenylnitrenium ion substituted by an electron-withdrawing group (*i.e.* NO₂ or CN) from the corresponding azide is established as follows. Both *para*- and *ortho*-attacking partial rate factors (p_f and o_f) for toluene and a ratio ($p:o$) of an *N*-attack at the *para*- to *ortho*-positions in toluene were lower in the reaction of the azide (**1d**) than in the reaction of the azide (**1a**), respectively; $p_f = 2.0$, $o_f = 0.9$, and $p:o = 1.1$ [*i.e.* a relative yield of the *p*- and *o*-toluidines (**3d'**):(**2d'**)] in the former reaction, and $p_f = 58$, $o_f = 20$, and $p:o = 1.5$ [*i.e.* a relative yield of *N*-phenyl-*o*- to *p*-toluidines (**3j**):(**2j**)] in the latter. The low substrate and positional selectivities indicate that an intermediate for the former reaction is more reactive than that (unsubstituted phenylnitrenium ion) for the latter. Thus, we can regard the intermediate for the former as *p*-nitrophenylnitrenium ion, not the conjugate acid of *p*-nitrophenyl azide, because the very high reactivity for the 4-nitrophenylnitrenium ion is the result of a large degree of localization of the positive

Table 5. Reactivities (k_f) of biphenyl and naphthalene relative to benzene in *N*-substitution by phenylnitrenium ion from phenyl azide in the presence of TFSA or TFA at room temperature

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

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

charge on the nitrogen atom due to an electron-withdrawing nitro group (this is discussed below).

(b) *The effect of substituents on N- and C-substitution of phenylnitrenium ions.* The above described reactivity dependence upon substituents permits us to postulate the following. The nitrenium ions possessing an electron-withdrawing group have their positive charge on the nitrogen atom rather than the ring-positions since the substituent cannot stabilize the positive charge, the nitrenium ions being perhaps in the singlet state^{8,9} by analogy with the phenylnitrenium ion.* Conversely, the positive charge of the nitrenium ions having an electron-releasing group is delocalised over the ring positions rather than the nitrogen atom as the result of the electron-donating resonance effect of the substituent. The prolongation of the lifetime by such a resonance-effect might allow the coexistence of the triplet with the singlet state which would give rise to the observed hydrogen abstraction (this is usually caused by triplet nitrenium ions¹⁰) and tar formation.

The formation of the carbazole (9i) from the azide (1i) appears to be *via* an *S_Ni* reaction which is an induced decomposition of the conjugate acid of the azide by an electron-rich 2,4,6-trimethylphenyl group. But, in the presence of TFA (30%, v/v) at 25 °C, the azide decomposed more slowly than (1g). This apparently excludes the *S_Ni* reaction. A lowering of the resonance between the two phenyl ring systems of the nitrenium ion from (1i) by the two *ortho*-substituents perhaps induces in the nitrenium ion behaviour intermediate between that of phenylnitrenium ions with an electron-donating group and those with an electron-withdrawing group. Thus, the nitrenium ion as well as the unsubstituted phenylnitrenium ion would be susceptible to both *N*- and *C*-attack.

Special Behaviour of TFA and TFSA.—(a) *The difference between TFA and TFSA.* In the reaction of biphenyl, log k_f correlated well with σ^+ to give the linear plot in the presence of TFA, but the value in the presence of TFSA was much higher than that expected from the plot (see Table 5). The reactivity (k_f) of the 1-position of naphthalene relative to benzene was much greater in the presence of TFSA rather than TFA (Table 5). Further, when biphenyl and naphthalene were used as the aromatic substrate, the yield of the diarylamines (2n), (3n), and (8) was higher in the presence of TFSA than with TFA (Table 1). These results were readily explained by the soft/hard concept. The transition state for the *N*-substitution, which because of the large negative value of ρ resembles a σ -complex, would have a

* Since the unsubstituted phenylnitrenium ion is ground-state singlet as described in refs. 8 and 9, the phenylnitrenium ions with electron-withdrawing group, which do the *N*-substitution like the unsubstituted phenylnitrenium ion, are presumably in the singlet states.

trifluoroacetate or trifluoromethanesulphonate anion as a near neighbour in the presence of TFA or TFSA, respectively. The latter anion is softer than the former on the Pearson classification,¹¹ so that delocalization of the positive charge of the transition state can occur throughout the two-ring system of biphenyl and naphthalene in the presence of TFSA. In contrast, the harder trifluoroacetate anion probably permits the positive charge to be delocalized over only the one-ring system. Therefore, the greater delocalization assisted by the softer trifluoromethanesulphonate anion would lower the activation energy to favour the *N*-substitution of polynuclear aromatic compounds.

The trifluoromethanesulphonates (7a), (7f), (7g), and (7i) were formed in the presence of TFSA, but not the corresponding trifluoroacetates or phenols in the presence of TFA (before or after work-up with aqueous Na₂CO₃). This suggests that the trifluoromethanesulphonate anion is more reactive than the trifluoroacetate anion. As for the reactions in which an intramolecular cyclization is impossible at the *C*-position [in the reactions of (1f–i)], the yield of hydrogen abstraction products (4f–i) is high in the presence of TFA compared with TFSA. The favourable formation of compound (4) is perhaps attributable to the absence of attack of trifluoroacetate anion on phenylnitrenium ions.

(b) *The effect of TFA or TFSA compared with sulphonic acid and hydrogen halides.* It has been found that attack at either the activated *ortho*- or *para*-positions of the phenylnitrenium ion generated from the azide (1a) in the presence of H₂SO₄ or HX leads eventually to the ring substituted amine.² 4-Nitro-2-phenyl(phenyl)nitrenium ion which is formed from the azide (1h) in the presence of hydrogen halides is known to be mainly attacked at the ring-position by halide ion.¹² These nitrenium ions generated in the presence of TFA and/or TFSA, however, undergo *N*-attack as indicated in this paper. The charge distribution in phenylnitrenium ions is dramatically altered by substituting trifluoroacetate or trifluoromethanesulphonate anion for halide or sulphate anions. We account for this phenomenon by the following assumption. In the presence of TFA or TFSA, the conjugate acid of the azide has the trifluoroacetate or trifluoromethanesulphonate anion at the position adjacent to the positively charged nitrogen, so that the nitrenium ions which are generated by a rapid loss of molecular nitrogen ensure distribution of the positive charge at the nitrogen atom by the assistance of the adjacent trifluoroacetate or trifluoromethanesulphonate anion. Such an adjacency is mentioned in the above mentioned soft/hard concept. The nitrenium ions generated in the presence of hydrogen halides or sulphonic acid are, however, free nitrenium ions, and are inert to the perturbation by the gegenion. This is perhaps based on the special character of the less solvated trifluoroacetate or trifluoromethanesulphonate anion which has high stability and low nucleophilicity.¹³ However, the phenylnitrenium ions having electron-donating substituents cannot be affected by this special character since the substituent greatly stabilizes the positive charge on the ring positions.

Experimental

I.r. spectra were obtained on a Hitachi model EPI-G3 spectrometer. ¹H and ¹³C N.m.r. spectra were taken with a Nippondenshi JNM-FX-60Q instrument. Analytical g.l.c. was performed on a Shimadzu GC-6A chromatograph using a glass column (1 m × 3 mm) [column A, 10% polyethylene glycol (20M) 60–80 Uniport KS; column B, 10% silicone SE-30 on 80–100 Chromosorb W; column C, 10% silicone OV-330 on 60–80 Uniport KS]. The analyses of products agreed within <3% on two runs. Preparative g.l.c. was carried out with a

Hitachi model 063-0012 unit using a column (2 m × 3 mm) packed with 10% silicone SE-30 on 60–80 Uniport KS.

Benzene, toluene, cumene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene, dichloromethane, 1,4-dioxane, biphenyl, and naphthalene were purified by standard methods before use. Trifluoroacetic acid (TFA), trifluoromethanesulphonic acid (TFSA), diphenylamine (**2a**), carbazole (**9g**), aniline (**4a**), *p*-toluidine (**4b**), *p*-anisidine (**4c**), *p*-nitroaniline (**4d**), *p*-cyanoaniline (**4e**), 2-aminobiphenyl (**5a**), azobenzene, and *N*-1-naphthylaniline (**8**) were reagent grade (Wako), and used without further purification. The following compounds were prepared by the methods described in the literature. Phenyl azide (**1a**),¹⁴ *p*-tolyl azide (**1b**),¹⁵ *p*-methoxyphenyl azide (**1c**),¹⁶ *p*-nitrophenyl azide (**1d**),¹⁷ *p*-cyanophenyl azide (**1e**),¹⁸ *o*-azidophenyl(phenyl)methane (**1f**),¹⁹ 2-azidobiphenyl (**1g**),¹² 2-azido-5-nitrobiphenyl (**1h**),¹² 2-azido-2',4',6'-trimethylbiphenyl (**1i**),²⁰ 9,10-dihydroacridine (**9f**),²¹ *N*-phenyl-*o*- and *p*-toluidines (**2j**) and (**3j**),²² 4-*N*-*p*-methoxyphenylaniline (**3c**),²³ *N*-chlorophenylaniline (**2l**),²⁴ *N*-*o*-bromophenylaniline (**2m**),²⁵ *o*-aminophenyl(phenyl)methane (**4f**),¹⁹ 2-amino-5-nitrobiphenyl (**4h**),¹² 4-aminobiphenyl (**6a**),²⁶ and trifluoroacetanilide.²⁷

Reactions of Phenyl Azide with Aromatic Compounds in the Presence of TFA or TFSA.—A solution (10 ml) containing phenyl azide, the aromatic compounds, and the acid was allowed to stand at room temperature; the reaction conditions and the results are shown in Table 1. In the experiment using naphthalene, dichloromethane was added as a solvent (see Table 1). After the reaction, TFA and volatile aromatic compounds were evaporated from the reaction mixture, and aqueous Na₂CO₃ was added until the solution reached pH > 7. The organic layer was extracted with benzene, and the products were isolated by preparative g.l.c., and identified by comparison with the i.r. and ¹H n.m.r. spectra of authentic specimens. The yields of the products were determined by g.l.c. using column A. In the reaction with benzene in the presence of TFA, azobenzene and trifluoroacetanilide were not detected by the g.l.c. analysis before treatment with aqueous Na₂CO₃. The following compounds were not prepared by the methods described in the literature and the structures were confirmed by their spectroscopic data.

N-*o*-Isopropylaniline (**2k**).²⁸ This compound was a liquid, *v*_{max} (neat) 3 370 (NH), 3 030 and 2 950 (CH), 1 595 and 1 495 (aromatic C=C), 1 450 (CH), 1 305 (C–N), 750 (*o*-substituted benzene ring), and 745 and 690 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 1.2 (6 H, d, Me), 2.8 (1 H, septet, CH), 4.2–4.6 (1 H, br, NH), and 6.5–7.5 (9 H, m, ArH); δ_C (CCl₄–CDCl₃) 23.2 (Me), 27.6 (CH), and 116.8, 120.0, 122.4, 123.2, 126.4, 126.8, and 129.6 (2', 4', 5-, 3-, 6-, 4-, and 3'-ArC).

2-Anilinobiphenyl (**2n**).²⁹ This was a liquid, *v*_{max} (neat) 3 390 (NH), 3 030 (aromatic CH), 1 590, 1 510, and 1 495 (aromatic C=C), 1 310 (C–N), 760 (*o*-substituted benzene ring), and 745 and 695 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 5.3–5.7 (1 H, br, NH) and 6.4–6.8 (14 H, m, ArH); δ_C (CCl₄–CDCl₃) 120.0, 122.8, and 132.4 (C-2, -4, and -3 of aniline group) and 119.2, 122.8, 128.8, 129.6, 130.4, and 131.2 (C-3, -5, -4', -4, -2', -3 and -6 of biphenyl group).

N-*p*-Isopropylphenylaniline (**3k**). This was a white crystalline product (m.p. 71–72 °C),³⁰ *v*_{max} (Nujol) 3 390 (NH), 1 600, and 1 510 (aromatic C=C), 1 310 (C–N), 820 (*p*-substituted benzene ring), and 750 and 690 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 1.2 (6 H, d, Me), 2.8 (1 H, septet, CH), 4.2–4.6 (1 H, br, NH), and 6.5–7.5 (9 H, m, ArH); δ_C (CCl₄–CDCl₃) 24.0 (Me), 33.2 (CH), and 116.8, 118.8, 120.4, 127.2, and 129.2 (C-2', -2, -4', -3, and -3' of phenyl group).

N-*p*-Chlorophenylaniline (**3l**). This had m.p. 74 °C,³¹ *v*_{max} (Nujol) 3 400 (NH), 1 590 and 1 500 (aromatic C=C), 1 320 (C–N), 820 (*p*-substituted benzene ring), and 750 and 695 cm⁻¹

(mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 4.0–5.1 (1 H, br, NH) and 6.7–7.8 (9 H, m, ArH); δ_C (CCl₄–CDCl₃) 117.6, 118.2, 121.1, 128.6, and 128.7 (C-2', -2, -4', -3', and -3 of phenyl group).

N-*p*-Bromophenylaniline (**3m**). This had m.p. 88 °C,³² *v*_{max} (Nujol) 3 380 (NH), 1 580 and 1 495 (aromatic C=C), 1 310 (C–N), 800 (*p*-substituted benzene ring), and 745 and 690 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 5.2–5.9 (1 H, br, NH) and 6.7–8.0 (9 H, m, Ph); δ_C (CCl₄–CDCl₃) 118.1, 118.8, 121.4, 129.1, and 131.9 (C-2', -2, -4', -3', and -3 of phenyl group).

p-Anilinobiphenyl (**3n**). This had m.p. 112 °C,³³ *v*_{max} (Nujol) 3 370 (NH), 1 595 and 1 520 (aromatic C=C), 1 320 (C–N), 840 (*p*-substituted benzene ring), and 750 and 690 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 5.2–6.0 (1 H, br, NH) and 6.5–8.0 (14 H, m, ArH); δ_C (CCl₄–CDCl₃) 119.2, 122.0, and 130.8 (C-2, -4, and -3 of aniline group) and 120.4, 128.0, 129.6, and 130.4 (C-3, -2' and -4', -2, and -3' of biphenyl group).

p-Aminophenyl trifluoromethanesulphonate (**7a**). This compound was a liquid which was purified by column chromatography using Wakogel C-300, eluting with CH₂Cl₂, *v*_{max} (neat) 3 480, 3 390, and 3 200 (NH₂), 3 030 (CH), 1 625 (NH₂), 1 600 and 1 500 (aromatic C=C), 1 415, 1 210, and 610 (OSO₂), 1 135 and 880 (CF₃), and 830 cm⁻¹ (*p*-substituted benzene ring); δ_H (CCl₄–CDCl₃) 2.5–3.2 (2 H, br, NH₂), 6.3–7.2 (4 H, ABq, ArH); δ_C (CCl₄–CDCl₃) 115.1, 122.1, 141.5, and 146.3 (C-3, -2, -1, and -4 of phenyl group). This compound became brown with time at room temperature, consequently the structure was characterized only by its i.r. and ¹H and ¹³C n.m.r. spectra.

Reactions of Substituted Phenyl Azides with Aromatic Compounds in the Presence of TFSA and/or TFA.—The reaction of *p*-tolyl azide (**1b**), *p*-methoxyphenyl azide (**1c**), *p*-nitrophenyl azide (**1d**), or *p*-cyanophenyl azide (**1e**) (500 mg), with benzene (10 ml) was carried out in the presence of a mixture (2.0 ml) of both TFSA and TFA at room temperature. The reactions of the azides (**1f**–**i**) were also performed in dichloromethane in the presence of TFSA and/or TFA at room temperature. The detailed reaction conditions and the results are indicated in Tables 3 and 4. After work-up with aqueous Na₂CO₃, the products were isolated by column chromatography over silica gel using benzene as the eluant, with the exception of compounds (**3d**), (**3e**), and (**9h**) which were isolated by recrystallization from the below-mentioned solvent. The yields of the products were determined by g.l.c. employing column C for compounds (**2d'**) and (**3d'**) and column B for the remainder. The new compounds, 2-amino-5-(trifluoromethylsulphonyloxy)phenylphenylmethane (**7f**), 2-amino-5-(trifluoromethylsulphonyloxy)biphenyl (**7g**), and 2-amino-5-(trifluoromethylsulphonyloxy)-2',4',6'-trimethylbiphenyl (**7i**), were unstable at room temperature, so that the structures were characterized by only their i.r. and ¹H and ¹³C n.m.r. spectra. The following products were not synthesized by the authentic methods, and the structures confirmed:

2-Amino-5-methylbiphenyl (**5b**). This was a liquid, *v*_{max} (neat) 3 440, 3 350, and 3 180 (NH₂), 3 130, 3 000, 2 900, and 2 840 (CH), 1 620 (NH₂), and 1 500 (aromatic C=C), 1 490 and 1 440 (CH), 1 295 and 1 280 (C–N), 880 and 815 (1,2,4-trisubstituted benzene ring), and 760 and 700 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄–CDCl₃) 2.3 (3 H, s, Me), 2.8–3.7 (2 H, br, NH₂), and 6.4–7.8 (8 H, m, ArH); δ_C (CCl₄–CDCl₃) 20.3 (Me) and 115.3, 126.6, 128.3, 128.7, 128.8, and 130.6 (C-3, -4', -2', -4, -3', and -6 of biphenyl group). The ¹H n.m.r. spectrum is almost in agreement with one reported of this compound.

N-*p*-Nitrophenylaniline (**3d**). This had m.p. 132–134 °C (from benzene) (lit.,³⁴ 131–133 °C), *v*_{max} (Nujol) 3 330 (NH),

1 600 and 1 520 (aromatic C=C), 1 580 and 1 300 (NO₂), 1 180 and 1 100 (C-N), 840 (*p*-substituted benzene ring), and 750 and 690 cm⁻¹ (mono-substituted benzene ring); δ_H (CDCl₃) 4.0—4.8 (1 H, br, NH), and 6.5—8.4 (9 H, m, ArH); δ_C (CDCl₃) 113.6, 121.9, 124.6, 126.1, 128.2, 129.6, 139.4, and 150.2 (C-2, -2', -4', -3, -4, -3', -1', and -1' of phenyl group).

N-p-Nitrophenyl-o-toluidine (**2d'**). This had m.p. 113—116 °C (lit.,³⁵ 115 °C), *v*_{max.} (Nujol) 3 300 (NH), 1 600 and 1 525 (aromatic C=C), 1 590 and 1 290 (NO₂), 1 175 and 1 195 (C-N), 830 (*p*-substituted benzene ring), and 745 cm⁻¹ (*o*-substituted benzene ring); δ_H (CDCl₃) 2.25 (3 H, s, Me), 5.8—6.3 (1 H, br, NH), and 6.6—8.4 (8 H, m, ArH); δ_C (CDCl₃) 17.8 (Me) and 111.3, 124.7, 126.2, 127.1, 128.2, 131.4, 133.1, 137.4, and 151.2 (C-2', -6, -4 and -3', -5, -2, -3, -4', -1, and -1' of phenyl group).

N-p-Nitrophenyl-p-toluidine (**3d'**). This had m.p. 131—135 °C (lit.,³⁵ 136 °C), *v*_{max.} (Nujol) 3 300 (NH), 1 610 and 1 530 (aromatic C=C of), 1 590 and 1 300 (NO₂), 1 180, and 1 110 (C-N), and 830 and 800 cm⁻¹ (*p*-substituted benzene ring); δ_H (CDCl₃) 2.4 (3 H, s, Me), 6.0—6.5 (1 H, br, NH), and 6.7—8.4 (8 H, m, ArH); δ_C (CDCl₃) 20.9 (Me) and 113.1, 122.7, 126.2, 130.2, 131.4, 134.7, 136.7, and 150.8 (C-2', -2, -3', -3, -4, -4', -1, and -1' of phenyl group).

N-p-Cyanophenylaniline (**3e**). This had m.p. 99—100 °C (from CHCl₃-CCl₄) (lit.,³⁶ 101—102 °C), *v*_{max.} (Nujol) 3 310 (NH), 2 200 (CN), 1 590 and 1 510 (aromatic C=C), 1 330 and 1 170 (C-N), 815 and 830 (*p*-substituted benzene ring), and 760 and 690 cm⁻¹ (mono-substituted benzene ring); δ_H (CDCl₃) 6.2—6.8 (1 H, br, NH) and 6.8—8.0 (9 H, m, ArH); δ_C (CDCl₃) 119.9 (CN) and 101.2, 114.8, 121.1, 123.8, 129.5, 133.6, 140.0, and 148.0 (C-4, -2', -2, -4', -3', -3, -1', and -1' of phenyl group) (Found: C, 80.35; H, 5.0; N, 14.7. Calc. for C₁₃H₁₀N₂: C, 80.4; H, 5.2; N, 14.4%). The melting point and i.r. and ¹H n.m.r. spectra were nearly the same as those described in the literature.³⁶

3-Nitrocarbazole (**9h**). This had m.p. 219—220 °C (from benzene) (lit.,³⁷ 212—213 °C), *v*_{max.} (Nujol) 3 320 (NH), 1 605 and 1 500 (aromatic C=C), 1 580 and 1 310 (NO₂), 1 240, 1 190, and 1 085 (C-N), and 815, 750, and 725 cm⁻¹ (aromatic rings); δ_H (CDCl₃) 7.2—9.2 (7 H, m, ArH) and 8.0—8.8 (1 H, br, NH); δ_C [CDCl₃-(CD₃)₂CO] 111.2, 112.3, 117.4, 121.0, 121.4, 121.6, and 127.8 (C-1, -8, -4, -2, -5 or -6, -5 or -6, and -7).

1,2,4-Trimethylcarbazole (**9i**). These pale yellow crystals had m.p. 101.5—102 °C (from light petroleum) *v*_{max.} (Nujol) 3 410 (NH), 1 615, 1 515, and 1 505 (aromatic C=C), 1 320 and 1 290 (C-N), 750 and 730 cm⁻¹ (aromatic rings); δ_H (CCl₄-CDCl₃) 2.3 (3 H, s, 1- or 2-Me), 2.2 (3 H, s, 1- or 2-Me), 2.8 (3 H, s, 4-Me), 6.7—8.3 (5 H, m, ArH), and 7.5—7.9 (1 H, br, NH); δ_C (CCl₄-CDCl₃) 12.7 (1-Me), 19.4 (2- or 4-Me), 20.1 (2- or 4-Me), 109.8, 114.1, 119.0, 121.9, 123.3, 124.2, 129.5, and 132.6 (C-8, -1, -6, -5, -3, -7, -4, and -2) (Found: C, 86.15; H, 7.1; N, 6.75. C₁₅H₁₅N requires C, 86.1; H, 7.2; N, 6.7%). The melting point of *1,2,4-trimethylcarbazole* is different from that of *1,2,3-trimethylcarbazole* (127.5—128.5 °C)³⁸ or that of *1,3,4-trimethylcarbazole* (146—146.5 °C).³⁹ Had the product been *1,3,4-* or *2,3,4-trimethylcarbazole*, a strong peak should have appeared in the ¹³C n.m.r. spectrum at ca. 131 or 108 p.p.m. corresponding to C-2 or C-1 respectively, owing to the substituent effect of methyl groups. That this peak was not observed confirmed this product to be *1,2,4-trimethylcarbazole*.

2-Amino-5-trifluoromethylsulphonyloxyphenyl(methyl)methane (**7f**). This was a liquid, *v*_{max.} (neat) 3 470, 3 380, and 3 200 (NH₂), 3 050, 3 010, and 2 900 (CH), 1 625 (NH₂), 1 600 and 1 495 (aromatic C=C), 1 415, 1 250, 1 210, and 610 (OSO₂), 1 140 and 950 (CF₃), 860 and 820 (1,2,4-tri-substituted benzene ring), and 730 and 700 cm⁻¹ (monosubstituted benzene ring); δ_H (CCl₄-CDCl₃) 3.0—3.9 (2 H, br, NH₂), 3.85 (2 H, s, CH₂), and 6.4—7.6 (8 H, m, ArH); δ_C (CCl₄-CDCl₃) 37.8 (CH₂) and 115.6, 120.1, 123.1, 125.7, 126.6, 128.0, 128.6, 137.3, 141.2, and 144.3 (C-3, -4, -6, -1, -4', -2', -3', -1', -5, and -2 of phenyl groups).

2-Amino-5-trifluoromethylsulphonyloxybiphenyl (**7g**). This was a liquid, *v*_{max.} (neat) 3 470, 3 380, and 3 200 (NH₂), 3 040 and 3 010 (CH), 1 620 (NH₂), 1 600, 1 500, and 1 480 (aromatic C=C), 1 415, 1 240, 1 210, 600, and 630 (OSO₂), 1 140 and 905 (CF₃), 850 and 815 (1,2,4-trisubstituted benzene ring), and 750 and 700 cm⁻¹ (mono-substituted benzene ring); δ_H (CCl₄-CDCl₃) 3.0—4.2 (2 H, br, NH₂) and 6.4—7.8 (8 H, m, ArH); δ_C (CCl₄-CDCl₃) 115.4, 120.9, 122.8, 127.7, 127.9, 128.6, 128.7, 137.3, 141.3, and 143.0 (C-3, -6, -4, -4', -1, -2', or -3', -2' or -3', -1', -5, and -2 of biphenyl group).

2-Amino-5-trifluoromethylsulphonyloxy-2',4',6'-trimethylbiphenyl (**7i**). This was a liquid, *v*_{max.} (neat) 3 450, 3 370, and 3 170 (NH₂), 3 000, 2 900, and 2 840 (CH), 1 610 (NH₂), 1 580, 1 500, and 1 480 (aromatic C=C), 1 415, 1 240, 1 210, and 610 (OSO₂), 1 140 and 900 (CF₃), 850 and 815 (1,2,4-trisubstituted benzene ring), and 780 and 760 cm⁻¹ (Ph); δ_H (CCl₄-CDCl₃) 2.0 (6 H, s, 2'- and 6'-Me), 2.25 (3 H, s, 4'-Me), 3.0—3.7 (2 H, br, NH₂), and 6.6—7.6 (5 H, m, ArH); δ_C (CCl₄-CDCl₃) 18.8 (2'- and 6'-Me), 20.0 (4'-Me), and 113.7, 119.7, 121.7, 125.7, 127.5, 131.6, 135.4, 136.3, 140.1, and 142.4 (C-3, -6, -4, -1, -3' and -5', -4', -2', and -6', -1', -5, and -2).

Rates of Decomposition of Phenyl Azide.—Phenyl azide (2.5 mmol) was dissolved in 1,4-dioxane, benzene, toluene, *m*-xylene, or *p*-xylene in the presence of TFA (30% v/v) to give a total volume of 10 ml. The rates of decomposition of the azide were determined at 25 °C by measurement of the volume of nitrogen gas evolved as a function of time. The results are summarized in Table 2.

Hammett Plot.—A solution (10 ml) containing phenyl azide (2.5 mmol) and an aromatic substrate (benzene and toluene, benzene and cumene, benzene and bromobenzene, or benzene and biphenyl) in the presence of TFA (30% v/v) or TFSA (5% v/v) was allowed to stand at room temperature for 1 day or a few minutes, respectively. The molar ratio of phenyl azide to aromatic substrate was less than 1:10. After the reaction mixture had been treated as described above, the ratios (**2a**):(**2j**), (**2a**):(**2k**), (**2a**):(**2m**), and (**2a**):(**2n**), were determined by g.l.c. using column A. The *para*-attacking partial rate factors (*k_p*) for toluene, cumene, bromobenzene, and biphenyl were calculated on the basis of the above product ratios, initial concentration of the aromatic compound, the number of C-H bonds of benzene, and of *para*-CH bonds of the substituted aromatics. The product ratios did not vary by the treatment of a mixture of (**2a**), (**2j**), (**2k**), (**2m**), and (**2n**) under the reaction conditions in benzene.

Relative Reactivity (k_r) of the 1-Position of Naphthalene to One C-H Bond of Benzene.—TFA (5.5 ml) was added to a solution of phenyl azide (0.28 g), naphthalene (1.0 g), benzene (3.5 ml), and dichloromethane (2.0 ml), and the mixture was allowed to react at 20 °C for 1 day. The reaction of phenyl azide (0.27 g) with naphthalene (1.0 g) in benzene (3.5 ml)-dichloromethane (2.0 ml) solution in the presence of TFSA (3%, v/v) was carried out 25 °C in a few minutes. These reaction mixtures were treated as described above and the ratio (**8**):(**2a**) was determined by g.l.c. using column A. The relative reactivity (*k_r*) was determined by employing the product ratio, the initial concentration of benzene and naphthalene, and the relative number of 1-positions of naphthalene with respect to one C-H bond from among the 6 C-H bonds of the benzene molecule.

ortho- and para-Attacking Partial Rate Factors (o_f and p_f) for Toluene in the Reaction with p-Nitrophenylnitrenium Ion.—A mixture of TFA (1.65 ml) and TFSA (0.35 ml) was added to *p*-nitrophenyl azide (0.5 g) dissolved in a mixture of benzene (6.7 ml) and toluene (3.3 ml) and the reaction mixture set aside at

room temperature for 4 h. The mixture was then diluted with benzene (10 ml) and basified with aqueous Na_2CO_3 . G.l.c. analysis of the organic layer using column C gave the relative yields of *N*-phenyl-*o*- and *p*-toluidines (**2d'**) and (**3d'**) with respect to (**3d**). The values of o_f and p_f were calculated by the methods similar to those described in the Hammett plot.

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