Aromatic N-Substitution by Phenylnitrenium Ion. Reactions of Phenyl Azide with Aromatics in the Presence of Trifluoroacetic Acid

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Reactions of phenyl azide with aromatics in the presence of trifluoroacetic acid gave diarylamines by an electrophilic N-substitution of the phenylnitrenium ion onto aromatics.

The phenylnitrenium ion (1) has a canonical resonance-form in which the positive charge preferentially populates the *para*- and *ortho*-positions rather than the nitrogen atom, according to MNDO molecular orbital calculations.[1] Thus, nucleophiles

Scheme 1
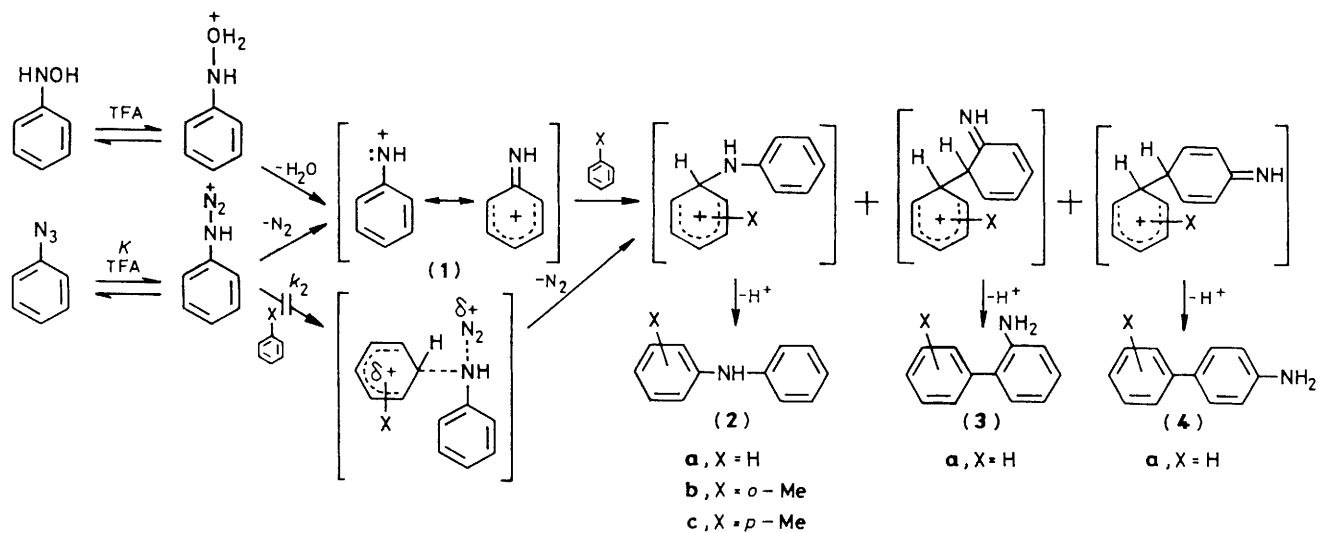
Table 1. Reactions of phenyl azide with aromatics in the presence of TFA.

| Substrate | TFA/ % v/v | [Azide] /M | T/ °C | t/h | % of azide decomposed | Yield,[a] % | | | | | | |
						(2a)	(2b)	(2c)	N-phenyl-1-naphthylamine	N-phenyl-2-napthylamine	(3a)	(4a)
Benzene	60	0.23	30	1	92	55					11	12
Toluene	30	0.45	25	24	100		30	31				
Naphthalene[b]	100	0.5	70	1	100				41	8.2		

[a] Yield based on azide decomposed. [b] A solution containing naphthalene (1.0 M) in TFA was refluxed.

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attack these ring positions when the phenylnitrenium ion is formed (in the decomposition of phenyl azide in strongly acidic media[2] or in acetic acid[3]). The reaction of phenyl azide[4] or N-phenylhydroxylamine[5] with aromatics in the presence of aluminium chloride or trifluoroacetic acid (TFA), respectively, has been reported to yield diarylamines however; the reasons for this N-substitution have not been established. We here report the first elucidation of the mechanism of an aromatic N-substitution by the phenylnitrenium ion.

The reaction of phenyl azide with benzene, toluene, and naphthalene in the presence of TFA gave diphenylamine (2a), 2- and 4-methyldiphenylamines (2b) and (2c), and N-phenyl-1- and -2-naphthylamines, respectively and the yields, determined by g.l.c., are summarized in Table 1. In the reaction with benzene, phenylnitrene-derived products,[6] azobenzene and trifluoroacetanilide,† were not detected but C-substitution products, 2- and 4-aminobiphenyls (3a) and (4a), were isolated in 11% and 12% yields, respectively. The substitution ratios N:C and ortho:para for the reaction were 2.4 and 0.92, respectively. These ratios are nearly equal to those‡ for the reaction of N-phenylhydroxylamine with benzene in the

presence of TFA,[5] suggesting that the two reactions proceed via a common intermediate, the phenylnitrenium ion (Scheme 1).

Partial rate factors, f_p, for the para-position of toluene, cumene, chlorobenzene, and bromobenzene were determined for the formation of diarylamines in solutions of TFA (30% v/v)–aromatic substrates (70% v/v) containing the azide (molar ratio of azide to aromatics $= <1:10$). The correlation between $\log f_p$ and σ_p^+ gives a linear plot with $\rho = -4.5$. The large negative value of ρ indicates that the diarylamines are afforded via N-substitution of the phenylnitrenium ion onto the aromatics (Scheme 1).

Phenyl azide decomposed almost completely in TFA at 25 °C in ca. 20 min, but was quite stable in benzene at 25 °C for 1 day.§ This result and the lack of formation of nitrene products suggest that azide decomposition in the presence of TFA does not occur via the phenylnitrene but via an azide conjugate acid instead. Decomposition in benzene (70% v/v)–TFA (30% v/v) solution went to completion at 25 °C in ca. 10 h but phenylazide in 1,4-dioxan (70% v/v)–TFA (30% v/v) solution at 25 °C had not decomposed after 1 day, owing to hydrogen bonding between the oxygen atoms of the 1,4-dioxan and the hydrogen atom of TFA which diminishes the formation of the conjugate acid. This also strongly supports decomposition via an azide conjugate acid.

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† Trifluoroacetanilide was obtained from the reaction of TFA with aniline. The aniline is formed from triplet nitrene (ref. 6) in the thermolysis of phenyl azide in benzene.

‡ An experiment using a solution of N-phenylhydroxylamine, benzene, and TFA in the molar ratio 1:22:20 at 5 °C has been reported to give ratios N:C and ortho:para as 2.0 and 0.92, respectively. The slight difference of the N:C ratio from our value may be due to the different reaction conditions.

§ Phenyl azide usually decomposes in aromatic solvent at $T > 130$ °C.

If the above substitution effect and large negative ρ value come from an acid-catalysed S_N2-type reaction involving attack of aromatics on an azide conjugate acid (see Scheme 1), decomposition of the azide (*i.e.* decreasing concentration of azide) in the presence of alkylbenzenes rather than benzene should be greatly accelerated. The first-order rate constant (k_1)¶ for the decomposition in benzene (70% v/v)–TFA (30% v/v) solution at 25 °C, however is slightly greater than that using 70% v/v of toluene, ethylbenzene, *m*-xylene, or *p*-xylene in the presence of TFA (30% v/v) at 25 °C. The observation rules out the S_N2 reaction, so instead the conjugate acid of azide must spontaneously lose a nitrogen molecule in a rate-determining step to give the phenylnitrenium ion providing further support for the idea that the substitution effect and large negative ρ value come from the reaction of a phenylnitrenium ion with the aromatics. The formation of

a nitrenium ion possessing a positive charge on the nitrogen atom is perhaps assisted by a neighbouring trifluoroacetate anion which has high stability and low nucleophilicity.

References

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¶ Regarding the S_N2 mechanism, $k_1 = k_2K[\text{TFA}][\text{ArH}]$ where k_2 and K are shown in Scheme 1, and k_1 is nearly proportional to k_2 in the experiments if the K values of these systems are almost equal. The result shown for k_1 presumably means that K in the presence of alkylbenzenes is slightly smaller than that in the presence of benzene owing to suppression of formation of the azide conjugate acid by the charge-transfer interaction between TFA and aromatics.