Efficient Direct Aromatic Amination by Hydrazoic Acid in the Presence of Both Trifluoromethanesulphonic Acid and Trifluoroacetic Acid

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Reactions of hydrazoic acid with aromatic compounds in the presence of both trifluoromethanesulphonic acid and trifluoroacetic acid efficiently gave primary arylamines by a concerted process involving nucleophilic attack of the aromatic compound on the conjugate acid of the azide and elimination of N_2 from the conjugate acid.

Direct aromatic amination is of great interest in mechanistic and synthetic fields. We have reported the direct aromatic amination by ethoxycarbonylnitrenium ion,[1] arylnitrenium ion,[2] arylnitrenium–$AlCl_3$ complexes[3] and parent nitrenium ion.[4] The formation of primary arylamines by the parent nitrenium ion is contaminated by a side reaction *via* the triplet nitrenium ion especially when the arene is a good H-atom donor. However, we have now found that the title amination provides primary arylamines from a variety of arenes without side reactions. Hydrazoic acid **1** has also been used for direct aromatic amination in the presence of $AlCl_3$ or H_2SO_4,[5,6] but the yield is not high because of side reactions resulting in the formation of tar or sulphonic acid and in the conversion[7] of **1** to hydrazine.

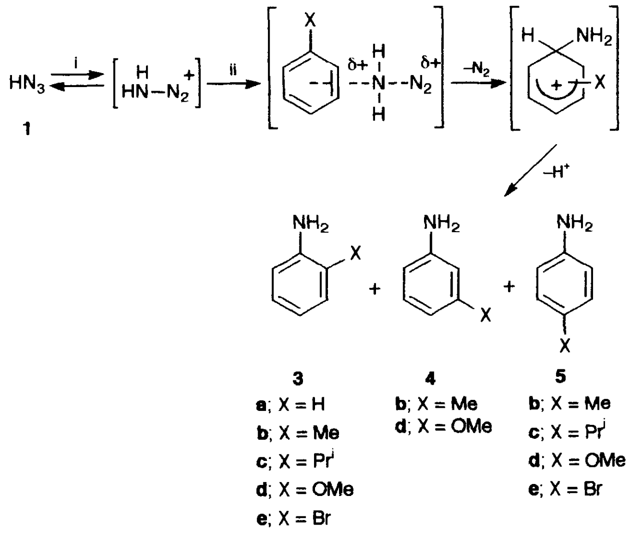
The reaction of **1** with benzene **2a** or toluene **2b** in the presence of both trifluoromethanesulphonic acid (TFSA) and trifluoroacetic acid (TFA) gave quantitatively aniline **3a** or 2-, 3- and 4-toluidines **3b**, **4b** and **5b** after treatment with aqueous Na_2CO_3 (Table 1). The reaction of **1** with cumene, anisole, bromobenzene, mesitylene or isodurene **2c–g** also afforded 2- and 4-isopropylaniline **3c** and **5c**, 2-, 3- and 4-anisidines **3d**, **4d** and **5d**, 2- and 4-bromoanilines **3e** and **5e**, 2,4,6-trimethylaniline **3f** or 2,3,4,6-tetramethylaniline **3g**, respectively, in good yields (Table 1).

The reaction of **1** with nitrobenzene did not lead to decomposition of the azide at 60 °C, and thus gave none of the corresponding amines (Table 1). The denitrogenation occurred at a relatively high temperature (60 °C) in the reactions with benzene, toluene or bromobenzene, but

Table 1 Reactions of hydrazoic acid **1**[a] with the arenes **2** in the presence of acid

			TFSA	TFA	Yield[b] (%)			
Arene **2**	T/°C	t/h	(%), v/v	(%), v/v	**3**	**4**	**5**	S_f
a; Benzene	60	12	10	34	100	—	—	
a; Benzene[c]	60	12	0	38	0	—	—	
b; Toluene	60	12	10	34	57	8	35	0.94
c; Cumene	25	7	10	34	52	0	44	
d; Anisole	60	12	10	34	34	2	43	1.6
e; Bromobenzene	60	12	10	34	42	0	47	
f; Mesitylene	25	1	10	34	99	—	—	
g; Isodurene	25	1	10	34	73	—	—	
g; Isodurene[c]	25	12	0	38	0	—	—	
h; Nitrobenzene[d]	60	12	10	34	0	0	0	

[a] A solution containing **1** (1.7 mol dm^{-3}) in $CHCl_3$ (3.0 cm^3) was added to a mixture of TFA (5.0 cm^3), TFSA (1.5 cm^3) and the arene (5.0 cm^3). [b] The yields are based on **1** used. [c] On using TFA instead of both TFSA and TFA, **1** did not decompose. [d] On using nitrobenzene as the arene, the denitrogenation did not take place.



Scheme 1 *Reagents*: i, TFSA and TFA; ii, PhX **2**; on using mesitylene or isodurene as PhX, 2,4,6-trimethylaniline **3f** or 2,3,4,6-tetramethylaniline **3g** was formed, respectively

smoothly took place at a lower temperature (25 °C) in the reactions with cumeme, mesitylene or isodurene (Table 1). The results suggest that nucleophilic attack of the arene is involved in the denitrogenation (Scheme 1).

On using TFA without TFSA, **1** did not decompose in the presence of benzene or isodurene (Table 1). The selectivity factor, $S_f = \log [2 \times (\%para)/(\%meta)]$, for the formation of toluidines did not depend on the acid participating in the reaction; the reaction of **1** with toluene at 20 °C in the presence of both TFA and fluorosulphonic acid (FSA) provided the same S_f value as that for the reaction using TFSA instead of FSA. These results indicate that the reaction requires an acid such as TFSA or FSA which is stronger than TFA, and proceeds *via* an intermediate which is independent of this acid. Thus, the intermediate should be the conjugate acid of **1**, not a hydrogen-bonding complex between **1** and the acid (Scheme 1).

Therefore, the reaction may proceed *via* a concerted process involving both nucleophilic attack of the arene on the conjugate acid of **1** and elimination of N_2 from the conjugate acid (Scheme 1).

The high S_f values (*i.e.* the low *meta*-selectivity) for the aromatic amination (Table 1) also support the concerted process; if the free $^+HN_2$ fragment[6] were the actual electrophile, one would expect much lower S_f values since a relatively high *meta*-content suggests that the attacking species are highly active.[7] Both Schmidt[8] and Bertho[9] postulated the nitrene route for the amination by **1** in the presence of H_2SO_4. The route can be ruled out since the rate of denitrogenation depends upon the nucleophilic character of the arene; if the reaction proceeded *via* the nitrene, the rate should be independent of the arene nucleophilic nature. The reaction of aminyl radicals with benzene or toluene gives a mixture of amines which are decomposed to NH_4, biphenyl and arylamine (low yield) on distillation,[10,11] and so a route *via* aminyl radicals can be ruled out.

The strong acidity of TFSA and the high solubility of TFSA in TFA play an important role in the aromatic amination. The efficient amination of readily oxidised alkylbenzenes such as cumene, mesitylene or isodurene results from the favourable concerted process and from the non-oxidising nature of TFSA and TFA. Contamination by diamination did not occur because the product is a salt before treatment with Na_2CO_3 and is less nucleophilic than the starting arene.

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