

ALIPHATIC C-H, N-INSERTION VERSUS AROMATIC N-SUBSTITUTION  
IN THE REACTION OF ARYLNITRENIUM-BORON TRIFLUORIDE COMPLEXES  
WITH METHYLATED BENZENES

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**Abstract** - The boron trifluoride promoted decomposition of a number of substituted phenyl azides in toluene, para-xylene, meta-xylene or mesitylene at 60°C, leads preferentially to N-benzylamines or diarylamines depending on both ring substituent effect and nucleophilic character of the solvent.

Recently considerable attention has been devoted to the generation of arylnitrenium ions which have been proved to be of great synthetic, mechanistic and biological interest.<sup>1</sup>

Like arylnitrenes, arylnitrenium ions can exist in singlet and triplet states as supported by MNDO molecular orbital prediction.<sup>2</sup> Singlet arylnitrenium ions have been shown to undergo nucleophilic aromatic N- and/or C-attack, depending on the arylnitrenium ion substituent and/or reaction conditions.<sup>3</sup> On the other hand triplet arylnitrenium ions have been so far reported to afford arylamines, generally as by product, as the exclusive recognizable products arising from hydrogen abstraction reaction.<sup>4</sup> In previous papers<sup>5</sup> we have pointed out that boron halides promote a facile decomposition of aryl azides, likely leading to intermediate arylnitrenium-BX<sub>3</sub> complexes, capable of undergoing intramolecular aromatic N-cyclization.

Now we report preliminary results from a study of the reactions of boron trifluoride etherate with the substituted phenyl azides (**1a-g**) in methylated benzenes. These reactions provide the first evidence that triplet arylnitrenium ions can undergo aliphatic C-H insertion.

In fact these reactions afforded aromatic N-substitution products i.e. the diarylamines (**6a**)-(10a)(**6c-g**) in addition to the N-benzylamines (**2a**)-(4a), (**2b**)-(2d), and the anilines (**11a-g**) to an extent very dependent upon the phenyl azide substituent and the nucleophilicity of the aromatic solvent.

To a degassed solution of 4-methylphenyl azide (**1a**) (2.5 mmol) in toluene (10 ml) ca. 47% BF<sub>3</sub>Et<sub>2</sub>O (2.5 mmol) was added and the resulting mixture was allowed to react at 60°C for 12 h. After hydrolysis and column chromatography, N-benzyl-4-

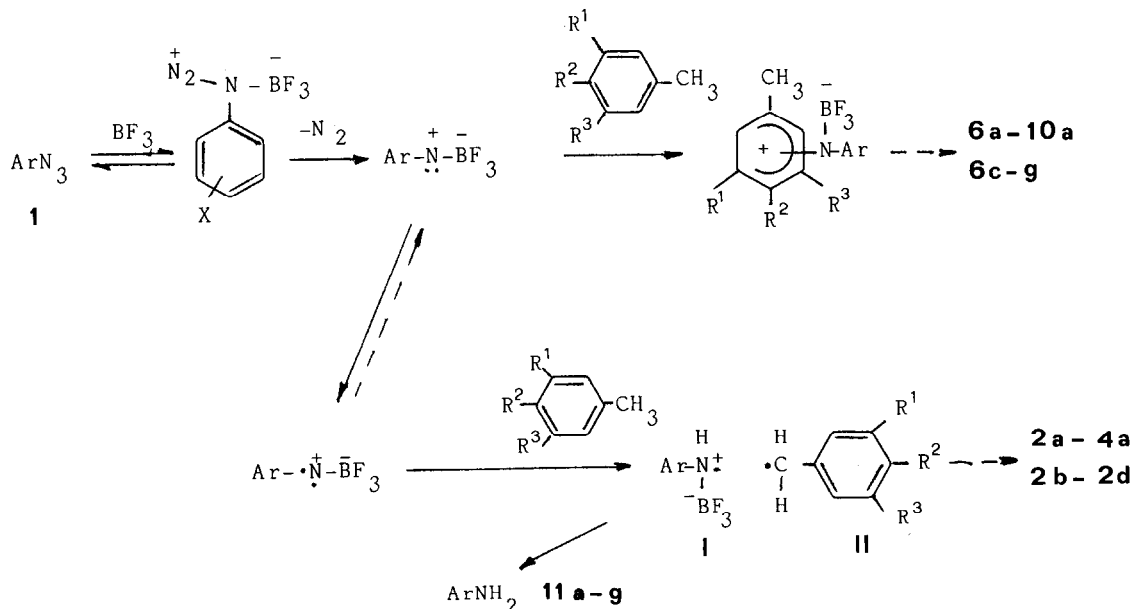
toluidine (**2a**) (43%) and p-toluidine (**11a**) (7%), were isolated in addition to trace amounts of a mixture of the para-(**6a**) and ortho-diarylamines (**7a**). The same reaction carried out in p-xylene, m-xylene or mesitylene showed that a progressive increase in the yield of aromatic N-substitution at the expense of C-H aliphatic N-insertion and hydrogen abstraction occurs with increasing the nucleophilic character of the aromatic ring (Table 1).

**Table 1.** Reaction of 4-methylphenylazide (**1a**) in methylated benzenes in the presence of  $\text{BF}_3\text{Et}_2\text{O}$  at  $60^\circ\text{C}$ .

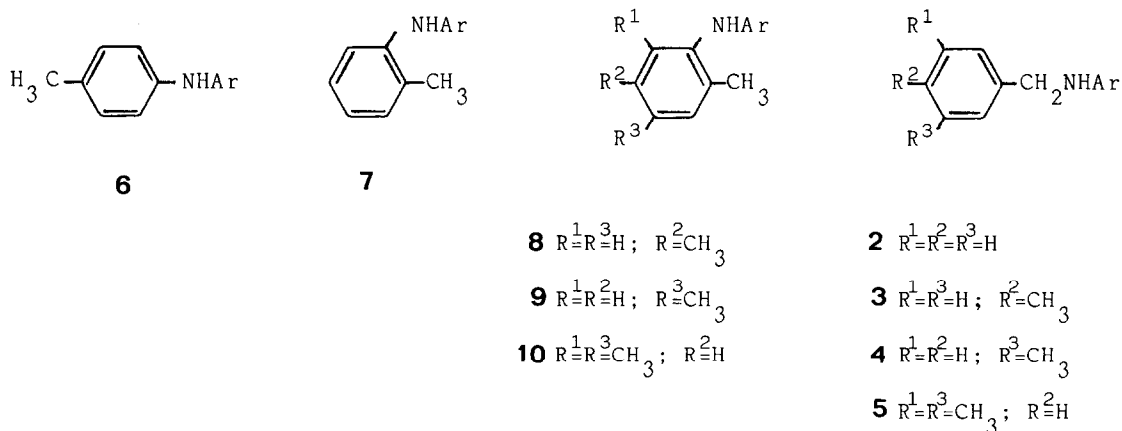
Substrate	Products (%)		
Toluene	<b>2a</b> (43)	<b>6a+7a</b> (Traces) <sup>a</sup>	<b>11a</b> (7)
p-xylene	<b>3a</b> (36)	<b>8a</b> (9)	<b>11a</b> (5)
m-xylene	<b>4a</b> (7,5)	<b>9a</b> (67.5)	<b>11a</b> (5)
mesitylene	<b>5a</b> (0)	<b>10a</b> (55)	<b>11a</b> (1)

a) Isomer ratio not determined

Moreover, kinetic studies suggest that the 4-tolylnitrenium  $-\text{BF}_3$  complex, arising from the azide **1a- $\text{BF}_3$  complex by loss of nitrogen, should be involved in these reactions. The rate of decomposition of the azide (**1a**) was found to be independent of the methylated benzene employed.<sup>6</sup> In the light of these results, it might be inferred that the occurrence of the N-benzyl-4-toluidines (**2a**)-(4a) is ascribable to a radical route involving hydrogen abstraction from the solvent by a possible triplet nitrenium-ions to give benzyl radicals (II) and anilino radical-ions (I), from which (**2a**)-(4a) would be ultimately formed by coupling.**



$\text{Ar}=\text{C}_6\text{H}_4\text{X}$ ;  $\text{X}=\text{a}=\text{p}-\text{CH}_3$ ;  $\text{b}=\text{o}-\text{CH}_3$ ;  $\text{c}=\text{m}-\text{CH}_3$ ;  $\text{d}=\text{p}-\text{Cl}$ ;  $\text{e}=\text{m}-\text{Cl}$ ;  $\text{f}=\text{H}$ ;  $\text{g}=\text{p}-\text{NO}_2$



Hydrogen abstraction by anilino radical-ion would be also responsible for the little amounts of 4-toluidine (**11a**). The above conclusion was carefully provided by the occurrence of 1,2-diphenylmethane, which would arise from dimerization of benzyl radical, determined by G.L.C. in very low yield from the decomposition of (**1a**) in toluene.

As might have been expected, the extent of aromatic N-substitution increases at the expense of radical insertion (and hydrogen abstraction) with increasing the nucleophilicity of the solvent which would favour the trapping of the singlet nitrenium- $BF_3$  complex initially formed. The findings obtained from the  $BF_3$  promoted decomposition of azides (**1b-g**) in toluene, under the same conditions, seem to support the above conclusion (Table 2).

**Table 2.** Reaction of substituted phenyl azides (**1a-g**) in toluene in the presence of  $BF_3 \cdot Et_2O$  at 60°C.

Phenyl azide	Products (%)			
4-methylphenylazide <b>1a</b>	<b>2a</b> (43)	<b>6a+7a</b> (traces) <sup>a</sup>	<b>11a</b> (7)	
2-methylphenylazide <b>1b</b>	<b>2b</b> (42)	<b>6b+7b</b> (0)	<b>11b</b> (3)	
3-methylphenylazide <b>1c</b>	<b>2c</b> (14)	<b>6c+7c</b> (32) <sup>a</sup>	<b>11c</b> (5)	
4-chlorophenylazide <b>1d</b>	<b>2d</b> (38)	<b>6d+7d</b> (12) <sup>a</sup>	<b>11d</b> (3)	
3-chlorophenylazide <b>1e</b>	<b>2e</b> (0)	<b>6e+7e</b> (49) <sup>a</sup>	<b>11e</b> (2)	
phenylazide <b>1f</b>	<b>2f</b> (0)	<b>6f+7f</b> (52) <sup>a</sup>	<b>11f</b> (4)	
4-nitrophenylazide <b>1g</b>	<b>2g</b> (0)	<b>6g+7g</b> (72) <sup>a</sup>	<b>11g</b> (3)	

<sup>a</sup> Isomeric mixture (Isomer ratio not determined)

The extent of C-H insertion increases at the expense of N-substitution with increasing the electron-donating power of the substituent on the phenylazide ring, which would lower the reactivity of the resulting singlet arylnitrenium- $BF_3$  complex, thus prolonging its life-time, and favouring its intersystem crossing to the triplet state. On this basis, the effect of the 4-Cl-substituent can be explained in terms of a significant stabilization to the singlet arylnitrenium- $BF_3$  complex resulting from direct resonance interaction with the positive nitrogen.

Finally we point out that the absence of any product arising from aromatic C-substitution, in all cases examined suggest that the arylnitrenium-BF<sub>3</sub> complexes, irrespective of the substituent present in the aryl ring, essentially bear the positive charge on the nitrogen atom. This trend, which appears to be analogous to that apparently exhibited by phenylnitrenium. AlCl<sub>3</sub> complex,<sup>3c</sup> is not consistent with that observed with arylnitrenium ions bearing electron-releasing substituents which have been shown to undergo preferentially C-substitution and hydrogen abstraction. We believe that this point deserves further attention.

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#### References and notes

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