

Triflic Acid Catalyzed Phenylamination of Aromatics with Phenyl Azide¹

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Diarylamines are of substantial synthetic and industrial importance.² They have been used as intermediates for synthesis of carbazole derivatives, carbamazepine, acridine, phenazines, and spiroacridins, etc.³ AlCl₃-catalyzed amination of arenes with phenyl azide in the presence of a proton source has been reported⁴ by Nakamura *et al.* The yields of arylphenylamines were in the range of 62–91%. Ullmann-type reactions⁵ are applicable only to electron-deficient substrates. Friedel–Crafts amination reactions are known⁶ but yields are generally not high. The majority of literature procedures for the preparation of diarylamines and diphenylamines involve amination of anilines with phenols or arenesulfonates at elevated temperature in the presence of acid catalysts.⁷ Shudo and Okamoto have reported⁸ the acid-catalyzed reactions of *N*-arylhydroxylamines with trifluoroacetic and triflic acids. Aminobiphenyls are formed as the major products in the reaction of *N*-arylhydroxylamines and triflic acid. Other methods are also available for the preparation of diarylamines.⁹ Takeuchi *et al.* have found¹⁰ that phenyl azide reacts with aromatics in the presence of trifluoroacetic acid to give diarylamines in moderate to good yields (40–60%). A mechanism involving¹⁰ phenylnitrenium ion as intermediate was proposed.

We have previously studied¹¹ the aminodiazonium ion prepared by protonation of hydrazoic acid in superacids.

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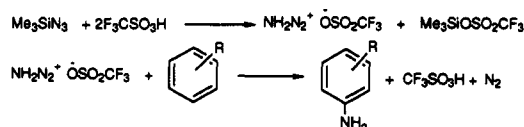
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Table I. Phenylamination of Aromatics with C₆H₅N₃/CF₃SO₃H

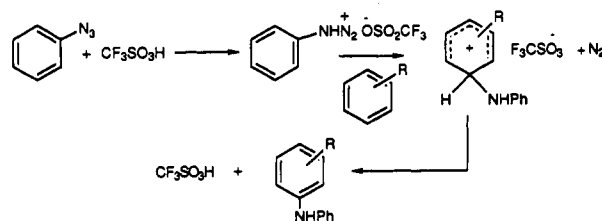
| ArH substrate | reacn time (h) | temp (°C) | solvent ^d | yield ^a (%) | C ₆ H ₅ NHAr ^b isomer distribution (%) | | |
|------------------|----------------|-----------|----------------------------------|------------------------|---|----------|----------|
| | | | | | <i>o</i> | <i>m</i> | <i>p</i> |
| benzene | 1 | 55 | C ₆ H ₆ | 82 | | | |
| toluene | 1 | 60 | C ₇ H ₈ | 94 | | | |
| <i>o</i> -xylene | 1 | 50 | C ₈ H ₁₀ | 90 | 37.5 | – | 62.5 |
| chlorobenzene | 2 | 65 | C ₆ H ₅ Cl | 82 | 20 | 3 | 77 |
| bromobenzene | 2 | 60 | C ₆ H ₄ Br | 88 | 14.6 | 0.8 | 84.6 |
| naphthalene | 2 | 50 | CH ₂ Cl ₂ | 84 ^c | | | |
| anisole | 2 | 42 | CH ₂ Cl ₂ | 75 | 35 | – | 65 |
| adamantane | 2 | 50 | CH ₂ Cl ₂ | <i>e</i> | | | |
| benzotrile | 2 | 42 | CH ₂ Cl ₂ | trace | | | |
| nitrobenzene | 2 | 42 | CH ₂ Cl ₂ | <i>e</i> | | | |

^a Isolated yield based on phenyl azide used. ^b All the amines reported in this study are known literature compounds^{4,8} and gave satisfactory spectroscopic and mass spectral data. ^c The major 1-isomer was obtained in >95% yield. ^d Reactant was used as solvent unless otherwise indicated. ^e No reaction.

We have also reported¹² that trimethylsilyl azide gives the aminodiazonium ion by protonation in triflic acid. The aminodiazonium ion was found to react with aromatic hydrocarbons to give the corresponding arylamines in good yields.



In continuation of our studies, we report that phenyl azide/triflic acid is a highly efficient reagent for the high yield electrophilic phenylamination of aromatics.



The aromatic substrate and triflic acid were premixed. Phenyl azide dissolved in the same aromatic or appropriate solvent is then slowly added to the premixed solution at 42–65 °C. The reaction takes place with brisk evolution of nitrogen. The results are summarized in the Table I. The yields of the aminated products are good to excellent (75–94%). The reaction allows fast, convenient, and high-yield phenylamination of alkyl- and haloaromatics. The high *ortho/para* selectivity observed, with only a small amount of *meta* product, indicates the involvement of a reactive phenylaminodiazonium ion intermediate.¹³ We have carried out competitive phenylamination between benzene and toluene. The observed ratio of *K_T/K_B* = 11 further indicates the intermediacy of a substantially electron-deficient intermediate. It is possible that excess triflic acid protosolvates¹⁴ the phenylaminodiazonium ion, thus enhancing its electrophilic nature. We cannot rule

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(13) Attempted protonation of phenyl azide to characterize the phenylaminodiazonium ion intermediate in FSO₃H/SO₂ClF at –78 °C was, however, unsuccessful and gave only decomposition products.

(14) For a review, see: Olah, G. A. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 767.

out the intermediacy of the alternative, highly reactive phenylnitrenium ion in the reaction. However, attempted preparation of *N*-(1-adamantyl)aniline by phenylamination of adamantane using similar conditions was not successful. Nitrenium ions are known to react with adamantane.

In conclusion, our studies show that phenyl azide/triflic acid is a powerful phenylaminating agent and gives the corresponding diarylamines in good to excellent yields.

Experimental Section

Materials. All solvents and aromatics were high purity (>99%) commercial products and distilled before use. Triflic acid was purchased from the 3M Co. Phenyl azide (99%) was prepared according to the literature procedure¹⁵ and freshly distilled before use.

General Procedure for the Phenylamination of Aromatics. The aromatic substrate and solvent (75 mL) were added to an oven-dried three-necked flask under a dry nitrogen atmosphere and fitted with a magnetic stirrer, thermometer, a reflux condenser, and a dropping funnel. The vessel was then charged with freshly distilled triflic acid (20 mL). The solution was

allowed to stir at ambient temperature for 10 min. The reaction mixture was then warmed in an oil bath to the reaction temperature indicated in Table I. To the stirred solution was then added slowly (exothermic reaction), over a period of 1 h, phenyl azide (5 g, 42 mmol) dissolved in the same solvent (20 mL). After the addition, the reaction mixture was stirred further at the same temperature until completion of the reaction (followed by GC-MS analysis of the quenched aliquot, see Table I). The reaction mixture was then cooled, poured into ice water (200 mL), and extracted with ether (2 × 50 mL). The organic and aqueous layers were separated. The aqueous layer was reextracted with ether (50 mL). The combined ether extracts were washed with cold 5% sodium bicarbonate solution (3 × 25 mL) and water and dried over anhydrous K₂CO₃. Diarylamine products were isolated after evaporation of the solvent. The reported yields are based on the amount phenyl azide used (Table I). The products and isomer distributions were analyzed by GC-MS (using a Finnigan INCOS-50 mass spectrometer used in combination with a Varian 3400 gas chromatograph with a DB-5 column). The crude products were chromatographed on silica gel to give pure compounds. The products were identified by ¹H NMR and ¹³C NMR and compared with authentic samples (GC and spectroscopic Comparisons).

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