−3 to 5 °C, 230 mL (4.9 mol) of 50% NaOH was added to neutralize the HCl and decompose the remaining aluminum salts. The conversion of 4-chlorobenzyl chloride was 100% containing 66% of the 4,4′-isomer and 7% dialkylation products. The contents of the flask were transferred to a 1-L steel bomb equipped with a magnetically driven efficient stirring rod with baffles and gas dispersion capability, an oxygen inlet, pressure gauge, rpm meter, heating unit with external and internal thermocouples, and a sampling port. To the mixture was added 15.8 g (0.039 mol) of Aliquat 336. The bomb was sealed and charged with 210 psig of oxygen at 25 °C. The vessel was heated, and the reaction mixture was maintained at 46–50 °C and 150–210 psig for 92 h (83% conversion at 92 h and 70% conversion of the 4,4′-dichlorodiphenylmethane at 26.2 h). The product was treated with methylene chloride and water, and the organic phase solvent was evaporated to yield 135 g of crude product. Of this crude product, 106 g were triturated with 100 mL of hexane and washed with an additional 100 mL of hexane to yield 48 g of material after filtration. This material was 85% 4,4′-dichlorobenzophenone by GC analysis.

Trimethylsilyl Azide/Triflic Acid, a Highly Efficient Electrophilic Aromatic Amination Reagent[1]

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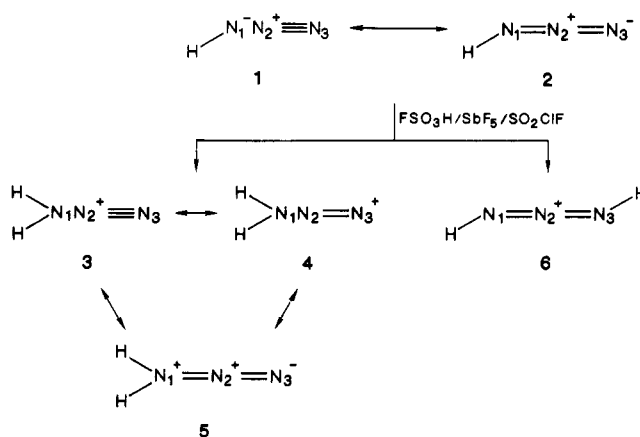
Introduction

Aromatic amines are important synthetic intermediates. Usually they are prepared by nitration of the aromatics followed by the reduction of the corresponding nitro compounds.[2] Direct one-step aminations of aromatics are known but so far give only moderate yields (≤75%).[2,3]

The direct electrophilic amination of aromatics has its origin in Graebe and Jaubert's work of 1901.[4] They discovered the amination of aromatic hydrocarbons with hydroxylammonium chloride in the presence of Friedel–Crafts catalysts. Kovacic and co-workers systematically investigated aminations with different reagents such as hydroxylamine and its salts,[5] alkylhydroxylamines,[6] hydroxylamine-*O*-sulfonic acid,[7] and hydrazoic acid.[8] Usu-

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(2) Schroter, R.; Müller, E. *Houben Weyl, Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, 1957; Vol. XI/1, pp 341–488.

(3) (a) Kovacic, P. *Friedel–Crafts and Related Reactions*, Interscience Publishers: New York, 1964; Vol. III/2, p 1493. (b) Sheradsky, T. *The chemistry of amino, nitroso and nitro compounds and their derivatives*; John Wiley: New York, 1982; Part 1, pp 395–416.

(4) (a) Graebe, C. *Ber. Dtsch. Chem. Ges.* 1901, *34*, 1778. (b) Jaubert, G. F. *C. R. Hebd. Seances Acad. Sci.* 1901, *132*, 841.

(5) Kovacic, P.; Bennet, R. P.; Foote, J. L. *J. Am. Chem. Soc.* 1962, *84*, 759.

(6) Kovacic, P.; Foote, J. L. *J. Am. Chem. Soc.* 1961, *83*, 743.

(7) Kovacic, P.; Bennet, R. P. *J. Am. Chem. Soc.* 1961, *83*, 221.

(8) Kovacic, P.; Russell, R. L.; Bennett, R. B. *J. Am. Chem. Soc.* 1964, *86*, 1588.

Scheme I. Protonation of Hydrazoic Acid

ally a 2-fold molar excess of a Friedel–Crafts halide was necessary to provide sufficient reactivity. The catalysts coordinate with the reagent and increase the polarization of the nitrogen–oxygen bond and thus increase the electrophilic nature of the nitrogen.[5-8] The yields of these reactions vary between 5 and 70%.[5-8] The reported isomer distributions confirm the electrophilic nature of the reactions, but an involvement of the free nitrenium ion NH$_2^+$ seems unlikely.

Olah and co-workers investigated the structure and properties of the aminodiazonium ion prepared by protonation of hydrazoic acid in superacids.[9] In contrast to the stable aromatic diazonium ions, aliphatic diazonium ions generally can only be obtained in highly acidic media due to elimination of nitrogen. Olah was able to show by NMR spectroscopy that hydrazoic acid, as well as methyl or ethyl azides, was protonated under superacidic stable ion conditions. Regarding the mesomeric structures of azides (1 ⇌ 2), the protonation could take place either on N-1 or on N-2. The former would lead to the mesomeric aminodiazonium ion (3–5) and the latter to the iminodiazenium ion (6) (Scheme I). ^{15}N NMR spectroscopy showed evidence only for the formation of the aminodiazonium ion.

A convenient in situ preparation of the aminodiazonium ion allowing its use for the amination of aromatics was also reported.[9] For this purpose sodium azide (or trimethylsilyl azide) was reacted with anhydrous aluminum chloride and subsequently with dry hydrogen chloride gas to form the aminodiazonium tetrachloroaluminate. This intermediate reacts with aromatic hydrocarbons and leads to the corresponding aminoarenes in relatively good yields (e.g. toluene ∼73%, chlorobenzene ∼25°). The observed isomer distributions are typical for electrophilic aromatic substitutions.

In continuation of our studies we now have found in trimethylsilyl azide/triflic acid a highly efficient improved reagent system that allows simple and nearly quantitative amination of aromatics.

Results and Discussion

On the basis of our earlier work,[9] trimethylsilyl azide is a suitable and improved synthon for aromatic amination, because it is a well-known source of azide, soluble in most organic solvents, and should not form cumbersome insoluble salts after cleavage of the silicon–nitrogen bond. In order to improve the homogeneity of the system and to provide stable ion conditions, a protic superacid should

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(9) Mertens, A.; Lammertsma, K.; Arvanaghi, M.; Olah, G. A. *J. Am. Chem. Soc.* 1983, *105*, 5657.

Table I. Amination of Aromatics with (Me₃)SiN₃/CF₃SO₃H

substrate	reaction time, min	T, °C	yield,[a] %	ortho	meta	para
benzene	50	55	95			
toluene	50	50	96	54	9	37
o-xylene	50	40	93			
mesitylene	50	50	95			
chlorobenzene	90	70	93	45	7	48
bromobenzene	90	65	73	52	6	42

(column group header: isomer distribution over ortho/meta/para)

[a] Isolated yield based on azide used.

be more convenient as catalyst than a Lewis acid such as AlCl₃. Triflic acid (trifluoromethanesulfonic acid) combines several advantageous features such as high acidity ($H_0 \sim -14^{10}$), nonoxidizing nature,[10] stability, and ready availability. Therefore, an investigation of trimethylsilyl azide/triflic acid as an amination system was undertaken.

The aromatic substrate and triflic acid are mixed and trimethylsilyl azide slowly added to the solution at 30–90 °C, depending on the reactivity of the aromatic substrate. The reaction can be easily followed by the evolution of nitrogen. The results are summarized in Table I. They show that the system allows a fast, convenient, and almost quantitative electrophilic one-step amination of alkylbenzenes and halobenzenes (bromobenzene was also reactive under these reaction conditions). Highly deactivated aromatics reacted only sluggishly and generally in low yield. In the case of p-dichlorobenzene, a temperature of 85 °C was necessary to observe reaction. At such elevated temperatures, however, the decomposition of the silyl azide reagent was significant in comparison to electrophilic amination of the deactivated aromatic ring. The yield of 1,4-dichloro-2-aminobenzene was less than 5% and nitrobenzene and trifluorotoluene showed only very low reactivity. In the case of α,α,α-trifluorotoluene, the yield of amination product was ~10%. With nitrobenzene the yield of nitroanilines was less than 3% due to further deactivation of the ring by the protonation of nitro group in the triflic acid medium (nitrobenzene, pK_{BH^+} -12^{10}). Therefore, this amination procedure is only suitable for substrates that are not protonated by triflic acid and are not strongly deactivated by electron-withdrawing groups.

It was also possible to carry out the amination reaction in hydrocarbon solvents. In the case of toluene in hexane solution, 79% isolated yield of toluidines was obtained, despite the low solubility of triflic acid in alkanes. 1,2-Dichloroethane as a solvent led to considerable chlorination of the substrates.

The suggested reaction pathway is shown in Scheme II. Aminodiazonium triflate acts as a synthon for "NH₂⁺" and is the reactive species in the amination reactions.

The relative $k_{toluene}/k_{benzene}$ rate at 55 °C was 3, indicative of low substrate selectivity, although a fast encounter controlled initial reaction cannot be excluded.

In conclusion we have shown that direct, nearly quantitative amination of aromatics, such as benzene, alkylbenzenes, and monohalobenzenes, is possible with the trimethylsilyl azide/triflic acid reagent system. This method should significantly extended the synthetic potential of direct aromatic amination methods in organic synthesis.

Experimental Section

Materials. All solvents and aromatics were high purity (≥99%) commercial products or distilled before use. Triflic acid was

(10) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley: New York, 1985.

Scheme II[a]
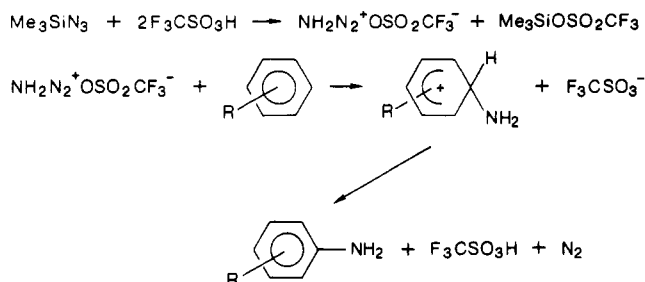
obtained from the 3M Company and trimethylsilyl azide from Aldrich.

General Procedure for the Amination of Aromatics. The aromatic substrate (75 mL) was placed into a three-necked, 200-mL round-bottomed flask, equipped with magnetic stirrer, thermometer, and dropping funnel, which was kept under nitrogen. Triflic acid (20 mL, 0.22 mol) was added and the solution was warmed up to the reaction temperature indicated in Table I. Then 4.4 g of trimethylsilyl azide (0.037 mol) in 20 mL of the same aromatic was added slowly through the dropping funnel. Reaction generally starts immediately as indicated by evolution of N₂. After the azide addition was completed the mixture was stirred until no more N₂ gas was evolved (see Table I for total reaction time). The solution was then cooled to room temperature and poured onto ice. Excess aromatics were extracted with dichloromethane (3×). The aqueous layer was neutralized with 30% sodium hydroxide solution until a pH of about 13 was reached. The arylamines were then extracted with dichloromethane and dried over magnesium sulfate. Product arylamines were isolated after evaporating the solvent. They were analyzed by GC analysis in comparison with authentic samples and by GC-MS (s Finnigan INCOS-50 mass spectrometer used in combination with a Varian 3400 gas chromatograph). Isomeric mixtures were determined by GC analysis on a Varian 3700 gas chromatograph equipped with a DB-1 column maintained at 120 °C.

Registry No. Benzene, 71-43-2; phenylamine, 62-53-3; toluene, 108-88-3; o-methylphenylamine, 95-53-4; m-methylphenylamine, 108-44-1; p-methylphenylamine, 106-49-0; o-xylene, 95-47-6; methyl-o-xylene, 118420-91-0; mesitylene, 108-67-8; methylmesitylene, 88-05-1; chlorobenzene, 108-90-7; o-chlorophenylamine, 95-51-2; m-chlorophenylamine, 108-42-9; p-chlorophenylamine, 106-47-8; bromobenzene, 108-86-1; o-bromophenylamine, 615-36-1; m-bromophenylamine, 591-19-5; p-bromophenylamine, 106-40-1; triflic acid, 1493-13-6; trimethylsilyl azide, 4648-54-8.

**Oxyfunctionalization of Hydrocarbons. 14.
Electrophilic Hydroxylation of Aromatics with
Bis(trimethylsilyl) Peroxide/Triflic Acid**[1]

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Introduction

Acid-catalyzed electrophilic hydroxylation of aromatics has received considerable attention during the last 20 years. Before 1970 there were only scanty reports of such hydroxylations using peroxy acids or *tert*-butyl hydro-

(1) For 13 in this series, see: Olah, G. A.; Ernst, T. D. *New J. Chem.*, submitted.

(2) March, J. *Advanced Organic Chemistry*; John Wiley: New York, 1985; p 498.