Table I. Amination of Aromatics with $(Me_3)SiN_3/CF_3SO_3H$

substrate	reaction time, min	T, °C	yield,[a] %	isomer distribution 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

[a] Isolated yield based on azide used.

be more convenient as catalyst than a Lewis acid such as $AlCl_3$. 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 "NH_2^+" and is the reactive species in the amination reactions.

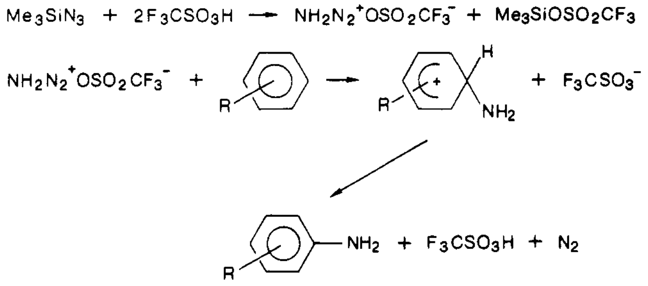
The relative $k_{toluene}/k_{benzene}$ rate at 55 °C was 3, indicative of low substrate selectivity, although a fast encounter controlled initial reaction cannot be excluded.

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 obtained from the 3M Company and trimethylsilyl azide from Aldrich.

Scheme II[a]



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 N_2. After the azide addition was completed the mixture was stirred until no more N_2 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.

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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.

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

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-

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[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.

peroxide.[2] In general, the obtained results were poor because the introduction of a hydroxyl group activates the ring for further reaction and oxidation. In 1970 Vesely and Schmerling[3] found that liquid hydrogen fluoride is an effective catalyst for the hydroxylation of aromatics with aqueous hydrogen peroxide. A year later Kurz and Johnson[4] reported the hydroxylation of aromatics by the use of hydrogen peroxide in the presence of aluminum chloride. The yields were low to moderate (70% for anisole, 40% for toluene and 14% for chlorobenzene),[4] but very little further oxidation products were formed. In 1978 Olah et al.[5] reported results of hydroxylation with 90% hydrogen peroxide in superacidic media. Phenols formed in such systems are protonated by the superacid and deactivated against further electrophilic attack or secondary oxidation, resulting in yields of around 50%. Two years later Olah[6] found 30% aqueous hydrogen peroxide to be a suitable reagent for the hydroxylation of alkylbenzenes in pyridinium polyhydrogen fluoride solution, which gave comparable yields. Olah et al.[7] subsequently found the use of aqueous hydrogen peroxide with hydrogen fluoride/boron trifluoride to be advantageous, because HF/BF_3 is inexpensive and recoverable. Jacquesy et al.[8-10] have also shown that electrophilic hydroxylations of phenols and arylamines can occur through the protonated form of the substrate at high acidity.

Whereas hydrogen peroxide can be an effective hydroxylating agent, its use is not always convenient. Such is also the case with HF and BF, not in small part due to their volatility and corrosive nature.

$AlCl_3$-catalyzed hydroxylation of xylenes with bis(trimethylsilyl) peroxide was reported[11] in the context of studying the ipso attack in aromatic hydroxylation, but yields were poor. Nevertheless, bis(trimethylsilyl) peroxide looked to us as a promising reagent, particularly in conjunction with a more suitable acid catalyst system. Triflic acid seemed to be well suited because of its high acidity and its nonoxidizing nature.[12] We have consequently embarked on a study of aromatic hydroxylation with bis(trimethylsilyl) peroxide/triflic acid and report herein our results.

Results and Discussion

Bis(trimethylsilyl) peroxide was prepared according to Ricci's procedure,[13] who used it for the hydroxylation of organolithium compounds. It is conveniently prepared from a dried complex of hydrogen peroxide and 1,4-diazabicyclo[2.2.2]octane (DABCO) and chlorotrimethylsilane in 40 to 50% yield.

$$\mathrm{DABCO} + 30\%\ \mathrm{H_2O_2} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{DABCO{\bullet}2H_2O_2} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{CH_2Cl_2},\ \mathrm{Me_3SiCl}} \mathrm{Me_3SiOOSiMe_3}$$

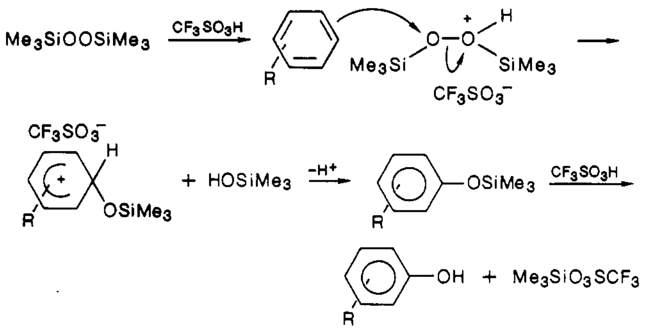
Table I. Hydroxylation of Aromatics with Bis(trimethylsilyl) Peroxide/Triflic Acid

substrate	T, °C	yield,[a] %	isomer distribution, % ortho	meta	para
benzene	0	77[b]			
toluene	0	88[c]	63	10	27
mesitylene	0	94[d]			
o-xylene	−50	63[e]	(2,3-) 48	(2,6-) 22	(3,4-) 30
naphthalene	−50	92[f]	(α-) 67		(β-) 33
chlorobenzene	0	76	63		37
	0	71	34	10	56

[a] Preparative, isolated yield based on peroxide. [b] In addition 3% (trimethylsiloxy)benzene was obtained. [c] Also traces of (trimethylsiloxy)toluenes. [d] Also 2% (trimethylsiloxy)mesitylene was obtained. [e] 21% of the dimer of 6,6-dimethyl-2,4-cyclohexadien-1-one was also isolated and found identical with the compound reported by Mazur et al.[14] [f] 7% (trimethylsiloxy)naphthalenes were also formed.

For hydroxylation the aromatic substrate (40 mL) and triflic acid (10 mL) were mixed and bis(trimethylsilyl) peroxide (1.5 g, 7.6 mmol) diluted in the same aromatic (15 mL) was slowly added to the solution t −20 to +25 °C. By the use of bis(trimethylsilyl) peroxide and triflic acid, it is possible to obtain a practically homogeneous system. Further, there is only little heat evolved and the acidity of triflic acid is not much affected. In case of the hydroxylation of naphthalene the reaction was carried out in dichloromethane solution.

The described system allows fast and convenient one-step hydroxylation of aromatics in high yield (Table I). The de facto hydroxylation yields are even somewhat higher, because some yet uncleaved (trimethylsiloxy)arenes were also found as byproducts in the workup, which can be further cleaved to phenolic products. They also support the probable mechanistic path of the reaction.



$$\mathrm{Me_3SiO_3SCF_3} + \mathrm{HOSiMe_3} \longrightarrow \mathrm{Me_3SiOSiMe_3} + \mathrm{CF_3SO_3H}$$

The found isomer distributions are in accord with the electrophilic nature of the reaction. Although no detailed study of selectivity was carried out, a $k_{\mathrm{toluene}}/k_{\mathrm{benzene}}$ ratio of 20 was found in competitive hydroxylation of toluene and benzene at −40 °C, indicating moderate substrate selectivity. The observed ortho/para ratio in the case of toluene agrees with the expected trends.[7]

Naphthalene is not entirely inert in triflic acid at 0 °C (the mixture darkens), but at −50 °C no color change was observed. A substantial excess of triflic acid is necessary for the success of the hydroxylation reaction (in case of naphthalene, a 10- to 14-fold excess over the peroxide was used). The ratio of 1- and 2-naphthols was not much influenced by changing temperatures. The conversion of the intermediate (trimethylsiloxy)naphthalenes into the naphthols is somewhat slower than in the case of toluene.

The reaction of o-xylene at −50 °C showed an additional effect of the used medium. Dimethylphenols were obtained in about 63% yield. The isomer distribution (48%

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(13) Taddei, M.; Ricci, A. *Synthesis* **1986**, 633.
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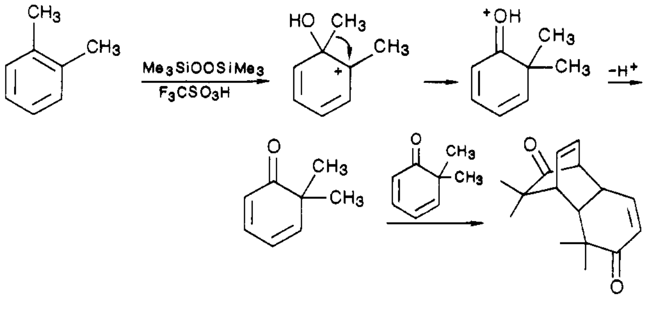
2,3; 22% 2,6 30% 3,4) clearly reveals the occurrence of methyl shifts. Similar observations were reported earlier in related superacid-catalyzed hydroxylations using H_2O_2.[5,7,11] Furthermore, we succeeded in isolating from the reaction mixture 21% of a nonphenolic additional oxygen-containing compound (based on the peroxide). The compound was identified by its analytical and spectral properties as the dimer of 6,6-dimethyl-2,4-cyclohexadien-1-one and was found in all regard identical with the earlier reported compound by Mazur et al.[14] obtained in the reaction of dimethylbenzenes with O(^{3}P) atoms on adsorbed phases. Taking this into account, the yield of the hydroxylation of o-xylene thus is also very high.



A reasonable mechanistic path for the formation of this dimethyl ketone involves ipso attack followed by a methyl shift and cycloadditive dimerization of the intermediate 6,6-dimethyl-2,4-cyclohexadien-1-one catalyzed by the acid.

In conclusion, bis(trimethylsilyl) peroxide/triflic acid is a highly effective hydroxylating reagent for aromatics, providing the corresponding phenols in high yields. The method is safe and more effective than the previously developed ones and should find general use for electrophilic hydroxylation of aromatic substrates.

Experimental Section

Materials. All solvents and aromatic substrates were high purity (⩾99%) commercial products or distilled before use. Hydrogen peroxide (31%) was purchased from Mallinckrodt. DABCO (~97%) and chlorotrimethylsilane (98%) were Aldrich products. NMR spectroscopy: spectra were obtained on a Varian VXR-200 spectrometer. GC analysis: Isomeric distributions were determined after silylation by *N,O*-bis(trimethylsilyl)trifluoroacetamide (Pierce) on a Varian 3700 gas chromatograph equipped with a DB-1 column (column temperature, 100 °C). GC-MS: a Finnigan INCOS-50 mass spectrometer was used in combination with a Varian 3400 gas chromatograph.

Preparation of Bis(trimethylsilyl) Peroxide. The preparation was carried out according to Ricca's procedure.[13] The purity of the peroxide was determined by GC analysis and ^{1}H NMR. The peroxide generally had a purity of 90%. The main impurity was hexamethylsiloxane.

General Procedure for the Hydroxylation of Aromatics. The aromatic substrate (40 mL) was added into a three-necked, 100-mL round-bottomed flask, equipped with magnetic stirrer, thermometer, and dropping funnel, which was kept under nitrogen. Triflic acid (10 mL, 0.11 mol) was then added while the solution was cooled to the adequate reaction temperature (see Table I). Subsequently 1.5 g (~90%, 7.6 mmol) of bis(trimethylsilyl) peroxide in 15 mL of the aromatic substrate was slowly introduced through the dropping funnel. The solution was usually stirred for 30 min after the addition and then quenched with ice water (25 mL). The organic material was extracted with dichloromethane (3 × 100 mL). It was washed with 10% sodium bicarbonate solution to remove any acid and then extracted with 10% sodium hydroxide solution. This solution was neutralized with 37% hydrochloric acid until a pH of about 1 was reached. Phenolic products were then extracted with dichloromethane, dried, and filtered. After evaporation of the solvent they were characterized by GC and GC-MS analyses and thin layer chromatography (silica gel, dichloromethane eluent).

In case of solid aromatics, such as naphthalene, 0.1 mol of the aromatic substrate was dissolved in 35 mL of dichloromethane and the peroxide was diluted in 15 mL dichloromethane. Otherwise, the above procedure was unchanged. All yields are based on the amount of peroxide used.

Identification of 6,6-dimethyl-2,4-cyclohexadien-1-one dimer in accord with Mazur[14] showed the following: IR (neat) ν 2968, 2926, 2870, 1723, 1666, 1633, 1561, 1471, 1385, 1293, 1253, 1129, 1098 cm^{-1}; GC-MS, *m/e* 122 ($C_8H_{10}O$, $M^{\bullet+}$ monomer, 50), 107 (8), 94 (9), 93 (12), 91 (13), 79 (100), 77 (45).

Acknowledgment. This work was generously supported by the National Science Foundation. Thomas D. Ernst is grateful for a fellowship of the Swiss National Science Foundation.

Registry No. Benzene, 71-43-2; phenol, 108-95-2; toluene, 108-88-3; *o*-methylphenol, 95-48-7; *m*-methylphenol, 108-39-4; *p*-methylphenol, 106-44-5; mesitylene, 108-67-8; 2,4,6-trimethylphenol, 527-60-6; *o*-xylene, 95-47-6; 2,3-dimethylphenol, 526-75-0; 2,6-dimethylphenol, 576-26-1; 3,4-dimethylphenol, 95-65-8; naphthalene, 91-20-3; α-naphthalenol, 90-15-3; β-naphthalenol, 135-19-3; chlorobenzene, 108-90-7; *o*-chlorophenol, 95-57-8; *m*-chlorophenol, 108-43-0; *p*-chlorophenol, 106-48-9; (trimethylsiloxy)benzene, 1529-17-5; (trimethylsiloxy)mesitylene, 18052-51-2; 6,6-dimethyl-2,4-cyclohexadien-1-one, 21428-63-7; α-(trimethylsiloxy)naphthalene, 6202-48-8; β-(trimethylsiloxy)naphthalene, 18081-08-8; bis(trimethylsilyl) peroxide, 5796-98-5; triflic acid, 1493-13-6.

Electrophilic Aromatic Substitution. 11.[1] A Kinetic Study of the BF_3-Catalyzed Benzylation Reaction in Nonpolar Solvents. Kinetic Evidence for BF_3 Catalytic Activity Involving a Fluorine-Bridged BF_3 Dimer

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In aromatic substitution of toluene and benzene the statistically limiting rate ratio is governed by the number of possible substitution positions, i.e., k_T/k_B should be 5/6 or 0.83 at a minimum. However, values less than this have been reported. In an earlier study[2] we suggested Nakane's k_T/k_B of ~0.6 for ethylation in nonpolar solvents[3] was caused by side reactions, particularly disproportionation, which became important after phase separation had occurred. More recently Nakane carried out a series of competitively determined benzylations of toluene and benzene catalyzed by boron trifluoride hydrate in hexane where k_T/k_B values for chlorobenzyl chlorides and benzyl chloride were found again to be below 0.83, this time 0.7.[4] Interestingly, similar k_T/k_B ratios (and product toluene isomer percentages) were determined for reactions in *solvent* boron trifluoride hydrate. However when boron

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