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Supported Tetramethylammonium Nitrate/ Silicasulfuric Acid as a Useful Reagent for Nitration Aromatic Compounds Under Solvent-Free Conditions

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Abstract: A variety of aromatic compounds are nitrated to the parent nitro aromatic compounds under solvent-free conditions using supported tetramethylammonium nitrate/silicasulfuric acid as a useful reagent. This methodology is useful for nitration of activated and deactivated aromatic rings.

Keywords: Nitration, silicasulfuric acid, solvent-free

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INTRODUCTION

Conventional methods for the nitration of aromatic rings utilize a mixture of nitric and sulphuric acids or nitronium tetrafluoroborate.^[1] In the case of borane/nitronium salt, HF and BF₃ are liberated.^[1] We have been engaged in the synthesis of azido aromatic compounds as photoaffinity ligands.^[2] The nitro compounds required for the synthesis of these derivatives were prepared by the conventional nitric sulfuric acid or nitronium tetraborate methods.^[3] Reaction under solvent-free conditions have recently attracted attention.^[4–6] The advantage of these methods over the conventional classical method is that they show cleaner reactions, decreased reaction time, and easier workup.

RESULTS AND DISCUSSION

In continuation of our ongoing program to develop environmentally benign methods under solvent-free conditions,^[7] we report here a convenient method for nitration of aromatic compounds with supported tetramethylammonium nitrate/silicasulfuric acid under solvent-free conditions.

Supported nitration reagent (tetramethylammonium nitrate/silicasulfuric acid) is prepared by grinding 2.4 mmol (0.66 g) of silicasulfuric acid^[8] with 1.2 mmol of tetramethylammonium nitrate (0.16 g) in a mortar with a pestle to produce a homogenous mixture. The process in its entirety involves grinding a mixture of 1 molar ratio of aromatic compounds, and 1.2 molar ratio of nitration reagent in a mortar. The resulting mixture was left at room temperature for the time specified in Table 1. This reaction proceeds rapidly and purification of product is straightforward (Scheme 1).

Aromatic compounds with oxidizable functional groups such as thiophenol, benzaldehyde, and anthracene are converted to diphenyldisulfide, benzoic acid, and anthraquinone respectively. The site of the electrophilic attack by this reagent was found to be identical to the conventional methods (Table 1).^[1–3]

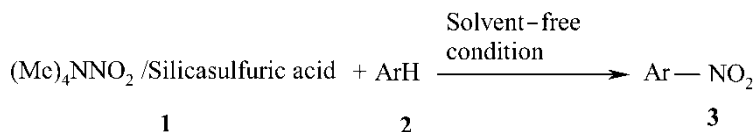
To evaluate the efficiency of this reaction under solvent-free conditions in comparison with the reaction in solution, several experiments were performed. We performed the reaction of naphthalene in several solvents, such as acetonitrile, diethylether and dichloromethane. We determined that dichloromethane is the best solvent for this reaction. When naphthalene was treated with 1.2 molar ratio of this reagent, only 80% of naphthalene was converted to 1-nitro naphthalene after 5 h of stirring at room temperature. In acetonitrile only 55% of naphthalene was converted to 1-nitro naphthalene after 5 h and in diethyl ether the yield of the product was obtained trace.

In summary, we report here a novel method for nitration of aromatic compounds under solvent-free conditions. This procedure is an efficient, mild, and green method for nitration of activated and deactivated aromatic

Table 1. Nitration of aromatic compounds **2** with reagent **1** to nitroarens **3** under solvent-free conditions at room temperature

Entry	ArH (2)	ArNO ₂ (3) (o : m : p ratio)	Time (min)	Yield ^c (%) ^{a,b}	M ^{a,b} (°C) (lit) ^[1–3,9]
1	Benzene	Nitrobenzene	1	90	Oil
2	Toluene	Nitrotoluene (15 : 0 : 85)	1	92	49–51 (54.5)
3	1,4-Dimethylbenzene	2,5-Dimethyl-1-nitrobenzene	1	92	Oil
4	Mesitylene	Nitromesitylene	2	85	41–43 (44)
5	Naphthalene	1-Nitronaphthalene	2	90	57–59 (61.5)
6	Nitrobenzene	1,3-Dinitrobenzene	10	60	90 (89.5)
7	Bromobenzene	Bromo-nitrobenzene (5 : 0 : 95)	2	92	122–125 (127)
8	Chlorobenzene	Chloro-nitrobenzene (20 : 0 : 80)	2	90	79–81 (83)
9	Benzyl bromide	4-Nitrobenzyl bromide	2	97	99–101 (98–100)
10	Benzyl chloride	4-Nitrobenzyl chloride	2	95	70–72 (71)
11	Biphenyl	4-Nitrobiphenyl	10	51	113–115 (114)
12	Benzoic acid	3-Nitobenzoic acid	10	72	137–140 (139–142)
13	2,6-Dimethylepyridine N-oxide	1-Nitro 2,6-dimethylepyridine N-oxide	3	86	146–147 (—)
14	Anthracene	Anthraquinone	3	80	283–285 (286)
15	Thiophenol	Diphenyldisulfide	1	95	59–61 (58–60)
16	Benzaldehyde	Benzoic acid	5	82	121–123 (122)

^aConfirmed by comparison with authentic samples (IR, TLC, and NMR).^bMolar ratio of 1 : 2 (1 : 1).^cYield of isolated pure product after purification.

*Scheme 1.*

compounds to the corresponding nitro aromatic compounds under solvent-free conditions.

EXPERIMENTAL

All of the yields refer to isolated products after purification. All of the products were characterized by comparison of their spectral (IR, ^1H NMR, and TLC) and physical data (melting) with those of authentic samples.^[1–3,9] All ^1H NMR spectra were recorded at 300 MHz in CDCl_3 relative to TMS as an internal standard. All of the reactions were carried out in the absence of solvent at room temperature under a hood with strong ventilation.

Preparation of Silicasulfuric Acid

A 500-mL suction was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (46.6 g, 0.4 mol) and gas inlet tube for conducting HCl gas over an adsorbing solution (i.e., water) and charged 60.0 g of silica gel. Chlorosulfonic acid was added dropwise over a period of 40 min at rt. The HCl gas evolved from the reaction vessel immediately after the addition was completed and the mixture was shaken for 30 min at room temperature. A white solid (silicasulfuric acid; 92.0 g) was obtained.^[8]

Typical Experimental Procedure: Nitration of Naphthalene with Tetramethylammonium Nitrate Silicasulfuric Acid

The reagent (tetramethylammonium nitrate/silicasulfuric acid) was prepared by mixing silica sulfuric acid (2.4 mmol, 0.66 g) with tetramethylammonium nitrate (1.2 mmol, 0.16 g) using a pestle and mortar for 5 s. Then, naphthalene (1 mmol, 0.13 g) was added and ground with a pestle in a mortar for 2 min. The progress of the reaction was followed by TLC or GC. Then, diethylether ($2 \times 10\text{ mL}$) was added to the reaction mixture. After vigorous stirring it was filtered through a sintered glass funnel and the solvent was evaporated under vacuum. The crude product was purified by column chromatography on silica gel using a mixture of cyclohexane and

ethyl acetate as eluent (80:20) to give 1-nitro naphthalene in 90% yield (0.155 g, mp: 57–59).

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