

Supported Bismuth(III) Nitrate on Silica Sulfuric Acid as Useful Reagent for Nitration of Aromatic Compounds under Solvent-Free Conditions*

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Abstract—A number of aromatic compounds were nitrated to the corresponding nitroaromatic derivatives with the use of supported bismuth(III) nitrate on silica sulfuric acid under solvent-free conditions.

Conventional methods for the nitration of aromatic compounds utilize a mixture of nitric and sulfuric acids or nitronium tetrafluoroborate [1]. In the latter case, the nitration is accompanied by liberation of HF and BF₄ [1]. Nitro derivatives necessary for the preparation of azido-substituted aromatic compounds as photo-affinity ligands [2] were obtained by usual nitric-sulfuric acid and nitronium tetrafluoroborate methods [3]. In the recent time, reactions occurring under solvent-free conditions attract much attention [4–6]. The main advantages of such methods, as compared to classical procedures, are cleaner reactions, reduced reaction time, and easy isolation of the products.

In continuation of our studies on the development of ecologically friendly procedures for carrying out chemical reactions in the absence of a solvent [7], the present communication describes an extremely convenient method for nitration of aromatic compounds with supported bismuth(III) nitrate on silica sulfuric acid under solvent-free conditions. The nitrating agent was prepared by grinding 2 mmol (0.8 g) of silica sulfuric acid [8] with 0.33 mmol (0.13 g) of anhydrous bismuth(III) nitrate in a mortar until a homogeneous mixture was obtained. Appropriate aromatic substrate was added to the reagent prepared in such a way so that the substrate-to-reagent molar ratio was 1:(1.2–1.5), and the mixture was thoroughly ground in a mortar and was left to stand at room temperature or

heated for a time indicated in table. The reaction was fast, and the product was readily isolated by extraction and purified by chromatography.

Activated aromatic compounds were converted into the corresponding nitro derivatives in excellent yields by the action of 1.2 equiv of the reagent in 1–4 min at room temperature. Reactions with less active substrates were carried out with 1.5 equiv of the reagent under stirring at 50–70°C; in these cases, the reaction time was 120–180 min, and the products were isolated in good yields (see table). The nitration of aromatic compounds containing readily oxidizable groups, e.g., benzenethiol and benzaldehyde, was accompanied by oxidation to afford diphenyl disulfide and benzoic acid, respectively. The regioselectivity in the nitration with supported Bi(III) nitrate on silica sulfuric acid was the same as in the conventional procedures [1–3].

In order to estimate the efficiency of nitration under solvent-free conditions in comparison to the reaction in solution, we performed nitration of toluene in several solvents: methanol, acetone, diethyl ether, methylene chloride, tetrahydrofuran, and 1,4-dioxane. Tetrahydrofuran turned out to be the best among the above solvents. When toluene was treated with silica sulfuric acid-supported Bi(NO₃)₃ at a ratio of 1:1.2, the conversion was only 40% in 24 h under reflux. The yield of the product did not increase in the presence of 2 equiv of the reagent.

We can conclude that the proposed procedure for the nitration of aromatic compounds with supported

* The text was submitted by the authors in English.

Nitration of aromatic compounds with silica sulfuric acid-supported bismuth(III) nitrate^a in the absence of a solvent

Initial compound	Product ^b (<i>ortho:meta:para</i> ratio)	Temperature, °C	Reaction time, min	Yield, ^c %
Benzene	Nitrobenzene	25	3	90
Toluene	Nitrotoluene (25:0:75)	25	3	90
1,4-Dimethylbenzene	2,5-Dimethyl-1-nitrobenzene	25	3	90
1,3-Dimethylbenzene	2,4-Dimethyl-1-nitrobenzene	25	4	90
Bromobenzene	1-Bromo-4-nitrobenzene	25	4	90
Chlorobenzene	Chloronitrobenzene (20:0:80)	25	4	80
<i>N,N</i> -Dimethylaniline	4-Nitro- <i>N,N</i> -dimethylaniline	25	2	100
<i>N,N</i> -Diethylaniline	4-Nitro- <i>N,N</i> -diethylaniline	25	4	90
Benzenethiol	Diphenyl disulfide	25	3	95
Anisole	Nitroanisole (15:0:85)	25	2	90
4-Bromoanisole	4-Bromo-2-nitroanisole	25	7	80
4-Methoxybenzaldehyde	4-Methoxy-3-nitrobenzaldehyde	25	10	80
Phenol	Nitrophenol (15:0:85)	25	8	85
3-Chlorophenol	5-Chloro-2-nitrophenol	25	10	80
Hydroquinone	Nitrohydroquinone	25	10	80
2,6-Dimethylpyridine <i>N</i> -oxide	2,6-Dimethyl-4-nitropyridine <i>N</i> -oxide	25	10	90
Naphthalene	1-Nitronaphthalene	50	10	95
Biphenyl	4-Nitrobiphenyl	65	120	80
2-Naphthol	1-Nitro-2-naphthol	70	120	60
Benzoic acid	3-Nitrobenzoic acid	70	180	80
Benzaldehyde	Benzoic acid	65	40	90

^a Reactant molar ratio 1:2 (1:1).

^b The products were identified by comparing their IR and ¹H NMR spectra and TLC data with those of authentic samples.

^c Isolated product after purification.

bismuth(III) nitrate on silica sulfuric acid under solvent-free conditions is effective for both activated and deactivated substrates.

EXPERIMENTAL

The products were identified by comparing their spectral (IR and ¹H NMR), chromatographic (TLC), and physical parameters (melting and boiling points) with those of authentic samples [1–3]. The ¹H NMR spectra (300 MHz) were recorded from solutions in chloroform-*d* relative to tetramethylsilane as internal reference. All reactions were carried out in the absence of a solvent in a hood with strong ventilation.

Silica sulfuric acid. A 500-ml flask equipped with a constant-pressure dropping funnel and a gas-outlet tube (which was connected to a gas-washing bottle filled with water to absorb liberated hydrogen chloride) was charged with 60.0 g of silica gel. Chlorosulfonic acid, 23.3 g (0.2 mol), was added dropwise

over a period of 40 min at room temperature. Gaseous hydrogen chloride immediately began to evolve. When the addition of chlorosulfonic acid was complete, the mixture was shaken for 30 min at room temperature to obtain 76.0 g of silica sulfuric acid as a white solid [8].

General procedure for nitration of aromatic compounds with supported bismuth(III) nitrate on silica sulfuric acid. *Nitration of anisole.* The nitrating agent was prepared by mixing 0.16 g (0.36 mmol) of bismuth(III) nitrate with 0.8 g (2.4 mmol) of silica sulfuric acid in a mortar. The mixture was ground until a fine homogeneous white powder was obtained. A mixture of 1.16 g (1.2 mmol) of the reagent and 0.11 g (1 mmol) of anisole was ground in a mortar until the initial compound disappeared (2–3 min, according to the TLC data; see table). The mixture was treated with methylene chloride (2×15 ml, each time under vigorous stirring) and filtered through a sintered glass funnel, and the solvent was removed under reduced pressure. The crude product was purified by column

chromatography on silica gel using cyclohexane–ethyl acetate (8:2) as eluent. The yield of 4-nitroanisole was 0.13 g (85%).

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