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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/lsyc20

Nitration of Some Aromatic Compounds by Sodium Nitrate in the Presence of Benzyltriphenylphosphonium Peroxodisulfate

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To cite this article: Hassan Tajik , Mohammad Ali Zolfigol , Jalal Albadi & Ramin Eslami (2007) Nitration of Some Aromatic Compounds by Sodium Nitrate in the Presence of Benzyltriphenylphosphonium Peroxodisulfate, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:16, 2771-2776, DOI: <u>10.1080/00397910701481179</u>

To link to this article: http://dx.doi.org/10.1080/00397910701481179

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Synthetic Communications[®], 37: 2771–2776, 2007 Copyright © Taylor & Francis Group, LLC ISSN 0039-7911 print/1532-2432 online DOI: 10.1080/00397910701481179



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Abstract: A simple, mild, and regioselective method for the nitration of some aromatic compounds using sodium nitrate in the presence of benzyltriphenylphosphonium peroxodisulfate in acetonitrile as solvent is reported. Mild reaction conditions and good to excellent yields of the products are the noteworthy advantages of the method.

Keywords: aromatic compounds, benzyltriphenylphosphonium peroxodisulfate, nitration, phenols, sodium nitrate

The nitration of aromatic compounds has received considerable attention in organic synthesis and industrial processes.^[1] Nitration typically requires the use of a mixture of concentrated or fuming sulfuric acid with nitric acid, leading to an excessive waste stream. Therefore, many methods have been

Received in the U.K. August 4, 2006

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Yield^b Time (h) Entry Substrate Product(s) 1 1.5 100 -он MeO ·ОН MeO ΝO2 OMe OMe 2 2.5 100 ΟН O_2N ΟН 3 100 5.5 -ОН ΟН O_2N ĊI 4 2 95 ЮΗ -ОН O_2N MeÓ MeÓ QН OН 5 2 90 | NO₂ NO₂ ОН 6 3 90 ОН 7 3.5 80° OH ΟН 0,N O_2N_2 3 80 8 CO₂H HO CO₂H но юн он O_2N 9 65 70° CO₂H ·CO₂H юΗ юн 9 10 100 OMe 0₂N OMe

Table 1. Nitration of some aromatic compounds with $NaNO_3^a$ in the presence of benzyltriphenylphosphonium peroxodisulfate in acetonitrile

(continued)

Entry	Substrate	Product(s)	Time (h)	Yield ^b
11			8.5	100
12	MeO	MeO OMe	4	100
13	MeO-OMe OMe		2.5	100
14	MeO OMe	O2N-OMe MeO OMe	3	100
15	CI OMe		10	80
16	OMe	OMe NO ₂	5	95
17	OMe	NO ₂ OMe	6	75 ^c

Table 1. Continued

^{*a*}Molar ratio of substrate/BTPPPDS/NaNO₃, 1:1:1.2. ^{*b*}Conversion.

^cIoslated yield.

reported in which regioselectivity, overnitration, and competitive oxidation of substrates have been the subject of investigation.^[2-9]

In the previous research, we have used peroxodisulfate ion as an oxidant in the iodination and bromination of aromatic compounds, which showed excellent regioselectivity.^[10,11] We performed the nitration reaction in the presence of this oxidant and hoped to obtain good results. Therefore, we have used sodium nitrate as the source of nitrate and benzyl-triphenylphosphonium peroxodisulfate as an oxidant^[12] for the nitration of

some activated aromatic compounds in acetonitrile as solvent. The progress of the reactions was monitored by thin-layer chromatography (TLC) or gas chrometography (GC). According to the obtained results, this method can be used as a useful addition to the present methodologies for the mild and regioselective nitration of phenols and methoxyarenes (Table 1, Scheme 1).

All the reactions were performed under reflux conditions. According to the obtained results, *p*-methoxyphenol, *o*-methoxyphenol, and *o*-chlorophenol were converted quantitatively to the corresponding nitro products (Table 1, entries 1–3), Phenol, 3-methoxyphenol, 1-naphthol, 2-naphthol, 2,4-dihydroxybenzoic acid, and salicylic acid were also reacted, and the corresponding products were obtained in good yields (Table 1, entries 4 and 9). Anisole, 2-methylanisole, 3-methylanisole, 1,2,4-trimethoxybenzene, and 1,2,3-trimethoxybenzene were quantitatively converted to their corresponding mononitrated products (Table 1, entries 10–14). 3-Chloroanisole, 1-methoxynaphthaline, and 2-methoxynaphthalene gave the corresponding nitrated products in 80, 90, and 70% yields respectively. Cleavage of ether linkage in methoxy moiety of described substrates was not observed. Resorcinol and cathechol gave side products. Therefore, this system is not suitable for the mononitration of these substrates.





Scheme 1.

Nitration of Aromatic Compounds

In conclusion, the easy procedure, simple workup, and excellent to good yields of the products will make this method a useful addition to the available methodologies.

EXPERIMENTAL

All of the products were characterized by comparison of their physical and spectral data with those of known samples^[13] or analyzed using GC or mass spectroscopy. All chemicals were purchased from Merck or Fluka chemical companies. Benzyltriphenylphosphonium peroxodisulfate was prepared according to the previously reported procedure.^[14]

Nitration of Aromatic Compounds with NaNO₃ in the Presence of Benzyltriphenylphosphonium Peroxodisulfate in Acetonitrile as Solvent: General Procedure

To a mixture of aromatic compounds (1 mmol) and NaNO₃ (1.2 mmol) in acetonitrile (5 mL), benzyltriphenylphosphonium peroxodisulfate (1 mmol) was added, and the resulting mixture was stirred at reflux conditions for 1.5 to 10 h. The progress of reaction was monitored by TLC (eluent: ether/CCl₄, 3:7) or GC (capillary column). After completion of the reaction, the mixture was filtered, and the filtrate was separated and diluted with *n*-hexane (5.0 mL). The resulting solution was transferred to a separatory funnel and washed with aqueous solution of Na₂S₂O₃ (0.1 M, 10 mL) and then H₂O (10 mL). The organic layer was separated and dried over anhydrous Na₂SO₄ (5 g). Evaporation of the solvent under reduced pressure gave the pure product.

ACKNOWLEDGMENT

We are thankful to Guilan University and University of Persian Gulf Research Council for the partial support of this work.

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