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Environmentally benign synthesis of aromatic nitro compounds using silica supported inorganic nitrates#

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Simple, rapid, clean and environmentally benign synthesis of aromatic nitro compounds by using inorganic nitrates as nitrating agents adsorbed on silica gel as a solid support has been reported.

Keywords: Inorganic nitrates, Nitration, Nitro compounds, Silica gel, Solid support

Introduction

Nitration reactions and synthesis of nitro compounds have an immense importance in the synthetic organic chemistry[1]. Nitro compounds are widely used and act as chemical feedstock and also for synthesis of medicines, dyes, perfumes, anticancerous drugs, fertilizers, plastics and explosives[2,3]. Therefore, nitration of aromatic compounds has received great attention of late, due to unsolved problems such as regioselectivity, over nitration and competitive oxidation of substrates. Explosions may occur in many of the procedures in the preparation of aromatic nitro compounds, and it is therefore necessary to adopt safer methodologies, which involve low cost, eco friendly[4] and easily available reagents while preparing nitro compounds.

Traditional nitration with a mixture of nitric acid and sulfuric acid is notoriously unselective for nitration of substituted compounds and disposal of spent liquors presents a serious environmental concern. Although this process is still in use in industries, nitrations are generally notorious processes, generating nitrogen oxide (NOx) fumes and large quantities of waste acids. Nitration of aromatic compounds using supported reagents[5,6] has less attention. The use of solid acid catalyst is potentially attractive because of the ease of removal and recycling of the catalyst and the possibility that solid support might influence the selectivity. Inorganic solids offer significant benefits by providing effective catalysis and in some cases, enhance selectivity. Application of inorganic nitrates such as bismuth nitrate[7,8] [$Bi(NiO_3)_3$], cerium ammonium nitrate[9] (CAN), sodium nitrite[10] ($NaNO_2$) and potassium nitrate (KNO_3) as nitrating agent were found to be more useful for nitration of aromatic compounds using silica gel as a solid support.

This study presents designing and development of a new eco-friendly nitration methodology, which has avoidance of excess acids to minimize waste.

Experimental Procedure

All chemicals were of LR grade. The completion of reaction and purity of products were checked by silica gel TLC. Products were characterized by comparing their physical constants and spectral data with authentic samples. Melting points were determined by open capillary method and are uncorrected.

Proposed Nitration Method

Aromatic substrate (1 mmol) was added to suspension of silica gel (10 g) and inorganic nitrates (1 mmol) [$Bi(NiO_3)_3$, CAN, $NaNO_2$ and KNO_3] in THF (10-15 ml). Reaction mixture was then irradiated under microwave oven (power level 40 %) until the completion of reaction. That was monitored by silica gel TLC technique (hexane: ethyl acetate, 1:3). Reaction mixture was then poured into methanol to afford a crude product, which was then filtered to give fine crystals of desired product (Table 1). All synthesized nitro compounds were characterized by

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Table—1 Aromatic nitro compounds

S No.	Substrates	Products	Inorganic nitrates (yield, %)				mp/bp (°C) [Lit mp/bp (°C)][8-10]
			$Bi(NiO_3)_3$	CAN	$NaNO_2$	KNO_3	
1	Anisole	4-nitro anisole	92	88	90	76	272[273] *
2	Aniline	2-nitro aniline	90	78	87	88	76[73-76]
3	Anthracene	9-nitro anthracene	89	84	86	78	142[142-143]
4	Benzene	nitro benzene	88	88	81	83	210[210]*
5	Benzoic acid	3-nitro benzoic acid	87	77	74	78	140[140-142]
6	Bromobenzene	4-nitro bromobenzene	82	78	82	68	126[126]
7	Naphthalene	1-nitro naphthalene	88	87	80	76	59[59]
8	Nitrobenzene	di- nitrobenzene	89	84	75	82	210[210]
9	Phenol	4-nitro phenol	60	50	55	64	113[113-114]
		2-nitro phenol	25	30	24	30	
10	Toulene	4-nitro toulene	88	76	73	74	52[52-54]
11	Resorcinol	2-nitro resorcinol	78	72	81	73	81[81]
12	Benzaldehyde	3-nitro benzaldehyde	92	80	87	81	58[57-59]
13	Phthalic anhydride	3-nitro phthalic anhydride	87	82	88	78	163[163-165]

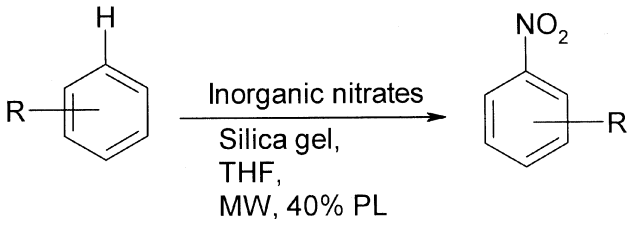

Fig.1— Nitration using silica supported inorganic nitrates

TLC, physical constants (mp/bp) in comparison with their literature data[8-10].

Conclusions

Application of inorganic nitrates [$Bi(NiO_3)_3$, CAN, $NaNO_2$ and KNO_3] were found to be more useful nitrating agents than conventional methods for nitration of aromatic compounds using silica gel as solid support with comparable yields of products under environmentally benign approach. $Bi(NiO_3)_3$ was found to be better nitrating agent followed by CAN, $NaNO_2$ and KNO_3.

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References

1 Olah G A, Malhotra R & Narang S C, *Nitration Methods and Mechanism* (VCH; New York) 1989.

2 Zollinger H, *Color Chemistry; Properties and Applications of Dyes*, **2nd edn** (John Willey, New York) 1991.

3 Meyer R, Kholar J & Homburg A, *Explosives*, **5th edn** (John Willey, New York) 2002**.**

4 Samajdar S, Frederick F B & Bimal K B, Montmorrilonite impregnated with bismuth nitrate: A versatile reagent for the synthesis of nitro compounds of biological significance, *ARKIVOC*, **8** (2000) 27-33.

5 Zolfigol M A, Mirjalili B F, Bamoniri A, Ali M, Zarchi K, Zarei A, Khadooz L & Noei J, Nitration of aromatic compounds on silica sulfuric acid, *Bull Korean Chem Soc*, **25** (2004) 1414-1416.

6 Laszlo P, *Preparative Chemistry using Supported Reagents*, **2nd edn** (Academic Press, London) 1987.

7 Samajdar S, Becker F F & Banik B K, Surface mediated highly efficient regioselective nitration of aromatic compounds by bismuth nitrate, *Tetrahedron Lett*, **41** (2000) 8017-8020.

8 Muathen H A, Selective nitration of aromatic compounds with bismuth subnitrate and thionyl chloride, *Molecules*, **8** (2003) 593-958.

9 Baciocchi E & Ruzziconi R, *Free Radicals in Synthesis and Biology* (Kluwer Acdemic, Dordrecht) 1989.

10 Zolfigol M A, Madrakin E & Ghaemi E, Silica sulfuric acid /$NaNO_2$ as novel heterogeneous system for the nitration of phenols under mild conditions, *Molecules*, **7** (2002) 734-742.