Eco-Friendly Nitration of Aromatic Compounds Using Different Solid Supports

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Abstract

Eco-friendly method for nitration of aromatic compounds using different solid supports has been successfully reported.

Key words: eco-friendly nitration, nitro compounds, solid supports, microwave irradiation

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].

Traditional nitration with a mixture of nitric acid and sulphuric acid is notoriously unselective for nitration of substituted compounds and disposal of the spent liquors presents a serious environmental concern. Although this process is still in use in industries, nitration are generally notorious processes, generating nitrogen oxide (NO_x) fumes and large quantities of waste acids. An alternative approach has been developed *i.e.* eco-friendly nitration methodology for the synthesis of aromatic compounds using microwave irradiation as a part of green chemistry.

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 the solid might influence the selectivity had also been reported [7]. In the last few years, supported reagents [6] have been increasingly used in organic synthesis, mainly because the reactions are carried out under mild conditions and the organic products are easily isolated. Claycop, a reagent consisting of acidic montmorillonite clay impregnated with anhydrous cupric nitrate has been reported for both mono and dinitration of various types of aromatic compounds including phenol [7]. Nasser *et al.* [8] reported the synthesis of aromatic nitro compounds using $Zn(NO_3)_2 \cdot 2N_2O_4$ supported on charcoal as solid support. The nitration of certain aromatic compounds could be achieved by reaction for several hours with $Cu(NO_3)_2$ or $Fe(NO_3)_2$ deposited on montmorillonite clay, acetic anhydride and a chlorinated solvent as reported by Laszlo [6]. The 'Clay zinc' [$Zn(NO_3)_2$ deposited on clay] could also be used for mono nitration of phenols in a few minutes under microwave irradiation in an unmodified microwave oven [9].

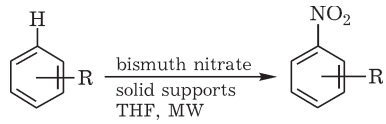
Choudhary *et al.* [10] have effectively used Fe^+-exchanged montmorillonite catalyst for the

selective nitration of chlorobenzene. The solid-state nitration of 6-hydroxycoumarins on montmorillonite K-10 clay support under microwave irradiation has been achieved by Nemai *et al.* [11]. Vassena *et al.* [12] have used solid acids such as silica impregnated sulphuric acid, H-β, mordenite, ZSM-5 and ZSM-12 under vapour phase conditions. Varma *et al.* [13] have developed a solid state synthesis of β-nitrostyrene from readily available styrene and its substituted derivatives using inexpensive clay supported nitrate salts, clayfen and clayan.

Propelled by environmental protection awareness, we have developed a new eco-friendly nitration methodology using bismuth nitrate supported on different solid supports for synthesis of various aromatic nitro compounds. The comparative study for the synthesis of aromatic nitro compounds using different solid supports has been successfully reported.

EXPERIMENTAL

All chemicals were of synthetic grade. The fly ash (a waste generated from thermal power stations) was collected from thermal power plant at Deepnagar, Bhusawal, Dist-Jalgaon, M. S. (India) and used as such for the reactions. A microwave oven (model OM 0018C, 2450 MHz, 900 W) with facility to change the power level was used to carry out the reactions. The completion of reaction and purity of products were checked by silica gel TLC. The microwave irradiation time was up to 4–10 min depending on the substrate (s). The products were characterized by comparing their physical constants with authentic samples and literature data. Physical constants (m. p./b. p*.) were determined by open capillary method and are uncorrected (Scheme 1).



Scheme 1. MW mediated nitration using solid supported bismuth nitrate.

GENERAL PROCEDURE FOR PREPARATION OF SOLID SUPPORTED BISMUTH NITRATE

The bismuth nitrate pentahydrate (0.01 mol) was dissolved in THF (10 ml) in evaporating flask. The mixture was stirred vigorously for 20 min until the complete dissolution of the crystals of bismuth nitrate pentahydrate. It forms the colourless suspension of bismuth nitrate pentahydrate. The solid supports such

TABLE 1

Synthesis of aromatic nitro compounds using different solid supports

No.	Substrates	Products	Yields, %			m.p./ b.p. (°C)
			A	B	C	[lit. m.p./ b.p. (°C)] [14]
1	Anisole	4-Nitroanisole	92	87	82	272 [273*]
2	Aniline	2-Nitroaniline	90	88	87	76 [73–76]
3	Anthracene	9-Nitroanthracene	89	85	83	142 [142–143]
4	Benzene	Nitrobenzene	88	85	84	210 [210]*
5	Benzoic acid	3-Nitrobenzoic acid	87	84	79	140 [140–142]
6	Bromobenzene	4-Nitrobromobenzene	82	80	81	126 [126]
7	Naphthalene	1-Nitronaphthalene	88	82	82	59 [59]
8	Nitrobenzene	1, 3-Dinitrobenzene	89	84	84	210 [210]
9	Phenol	4-Nitrophenol	60	58	54	113 [113–114]
		2-Nitrophenol	25	22	22	
10	Toluene	4-Nitrotoluene	88	84	84	52 [52–54]
11	Resorcinol	2-Nitroresorcinol	78	73	74	81 [81]
12	Benzaldehyde	3-Nitrobenzaldehyde	92	83	82	58 [57–59]
13	Phthalic anhydride	3-Nitrophthalic anhydride	87	85	78	163 [163–165]

Note. A – silica gel, B – montmorillonite clay, C – fly ash.

as silica gel, montmorillonite and fly ash (5 g each) were added separately and stirred for another 20 min. The solvent (THF) was removed under reduced pressure using rotary evaporator on water bath at 40 °C.

GENERAL PROCEDURE FOR NITRATION OF AROMATIC COMPOUNDS

The solid supported bismuth nitrate was added to aromatic substrate (s) dissolved in solvent. The resulting reaction mixture was then exposed to microwave irradiation at (30 power level) until completion of reaction, (monitored by using silica gel TLC). The reaction mixture was then repeatedly washed with ethanol (3×20 ml) and the filtrate was allowed to evaporate to afford the crude products. The crude products were recrystallised from ethanol. All synthesized compounds (Table 1) were characterized by comparing their physical constants with literature data [14].

CONCLUSION

Supported reagents have been widely used in organic synthesis and possess industrial applications and their importance is likely to increase as a result of new environmental demands and the drive towards clean technologies in the manufacture of pharmaceutical and fine chemical inter-mediates. Solid support increases its reactivity towards the aromatic compounds due to the effective surface area available for the reaction.

The solid support may possess different reactivity/selectivity depending on the substrate (bearing electron withdrawing or electron donating group). The nitration of phenol leads to the formation of *o*-phenol (25 %) and *p*-nitrophenol (60 %), while aniline and toluene give only *o*-nitroaniline (90 %) and *p*-nitrotoluene (88 %), respectively. The dinitration of benzene gives 1,3-dinitrobenzene in 89 % yield.

Application of bismuth nitrate $Bi(NiO_3)_3$ as nitrating agent was found to be more useful than conventional methods for nitration of aromatic compounds using different solid supports such as silica gel, montmorillonite clay and fly ash as solid supports with comparable yields of products, under the environmentally benign approach. In general, the yields of products were higher for silica gel followed by montmorillonite clay and fly ash as solid supports. This study presents designing and development of new eco-friendly nitration methodology, which has avoidance of excess acids to minimize waste as a part of green chemistry.

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