Catalysis Communications 42 (2013) 35–39

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Faujasite catalyzed nitrodeiodination of iodopyrazoles

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ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 11 July 2013
Accepted 17 July 2013
Available online 26 July 2013

Keywords:
Faujasite
Iodopyrazoles
Heterogeneous catalysis
Nitropyrazoles

ABSTRACT

Nitrodeiodination of iodopyrazoles using nitric acid/Faujasite has been investigated. The present procedure is simple, rapid and convenient and requires no sulfuric acid or oleum and may be applied for the synthesis of several nitropyrazoles in good yields in drug and pharmaceutical industries.

1. Introduction

Nitropyrazoles have been used as biologically active compounds including antibiotics or their analogues, agrochemicals, dyestuffs, phosphores, non-linear optical materials and recently as energetic materials [1]. The presence of nitro group in the pyrazole ring considerably enlarges the possibility of functionalization of various types of pyrazole derivatives [2]. The methods to synthesize nitropyrazoles are diverse and depend upon the nature of substituent groups in the pyrazole ring, the electron density distribution in it, nitration mixtures, nitration conditions, and so on. Pyrazoles are nitrated with fuming nitric acid, nitric-sulfuric acid, nitric acid-acetic anhydride, nitric acid-trifluoro acetic anhydride or nitromethane-nitronium tetrafluoroborate. In many cases, it is impossible to introduce NO_2 group into the desired position of the pyrazole ring and therefore indirect methods are used. Hüttel and Büchele [3] described the rearrangement of N-nitropyrazoles into 4-nitropyrazoles in cold sulfuric acid solution. Janssen et al. synthesized 3(5),4-dinitropyrazole from 3(5)-nitropyrazole under Morgan–Ackerman nitration conditions [4,5]. 1-Methyl-3(5)-nitropyrazole, 1-methyl-4-nitropyrazole and 1-methyl-3(5),4-dinitropyrazole were synthesized from 1-methylpyrazole refluxing in nitric–sulfuric acid mixture [6–8]. N-Nitropyrazoles in anisole, xylene, benzonitrile, chlorobenzene, nitrobenzene, n-decane, mesitylene, N-methylformamide, or propylene glycol at 120–190 °C for 3–7 h were rearranged into 3-nitropyrazole, 3(5),4-dinitropyrazole and 3,5-dinitropyrazole [6–8]. C-Nitropyrazoles were formed quantitatively and in some instances denitration of N-nitropyrazoles during thermal isomerization was observed. The oxidative iodination of pyrazoles prior to nitration is a desirable route to prepare C-polynitropyrazoles in higher yields. We have synthesized 3(5),4-dinitropyrazole and 3,4,5-trinitropyrazole in good yields from 3(5),4-diiodopyrazole and 3,4,5-triiodopyrazole respectively using fuming nitric acid and nitric–sulfuric acid mixture [9,10].

The traditional nitration methodologies usually suffer from low yields, starting material availability, harsh conditions, and/or difficulty to separate isomer formation prompted researchers to search for the alternative methodologies. The limitations and drawbacks of usual methods such as tedious work-up, strongly acidic media, oxidation ability of reagents (e.g., nitric acid), thermal isomerizations and safety problems can be avoided using metal nitrates impregnated on solid supports. The supported metal nitrates such as $Bi(NO_3)_3.5H_2O/SiO_2$ [11,12], $AgNO_3/BF_3$ [13], $Cu(NO_3)_2$/clay [14], $Ce(NH_4)_2(NO_3)_6/H_2SO_4/SiO_2$ [15], $Fe(NO_3)_3$/clay [16] and metal nitrates/clay activated by acetic anhydride [17] have been used for the nitration of aromatic compounds. We have used HNO_3/silica and HNO_3/silica-sulfuric acid for the nitrolysis of iodopyrazoles [10]. It was demonstrated that nitrogen (IV) oxide in the presence of Faujasite nitrates both pyrazole and N-nitropyrazole [18]. Faujasite is easier to handle because it holds the acidity internally, readily separable from the products by simple filtration, recyclable and requires milder reaction conditions. Unlike the more hazardous acid catalysts (e.g., sulfuric acid, hydrofluoric acid, solid phosphoric acid, etc.,) Faujasite is recyclable with greater ease and lower expense, leading to less waste and fewer byproducts. Furthermore more hazardous strong acids, many steps, low yields and much waste can be avoided and greater returns shall be achieved. To the best our knowledge synthesis of nitropyrazoles from iodopyrazoles using nitric acid over Faujasite catalyst (H-form) has not been reported elsewhere. We report herein the synthesis of nitropyrazoles in good to higher yields from iodopyrazoles using nitric acid/Faujasite at room temperature for the first time.

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1566-7367/$ – see front matter
http://dx.doi.org/10.1016/j.catcom.2013.07.032

2. Experimental section

2.1. General

All the reagents and solvents were obtained from Merck, Alfa-Aesar or Aldrich and used without further purification. Thin layer chromatography (silica gel GF-254 type) was routinely used to monitor the progress of reactions. Melting points were recorded by a capillary melting point apparatus and were uncorrected. IR spectra were recorded on Perkin Elmer FT-IR-1600 spectrophotometer in KBr matrix. The signals are reported in wave numbers (cm^{-1}). ^1H NMR and ^{13}C NMR spectra were recorded on 300 MHz Varian instrument with DMSO-d_6 and $CDCl_3$ solvents. The chemical shift values are reported in δ units (ppm) relative to TMS as an internal standard. GC-MS was carried out with glass columns packed with 3% OV-17 on Chromosorb W (100–120 mesh) treated with DMCS in a Varian 1400 instrument fitted with flame ionization detector, nitrogen being used as carrier gas. Faujasite (H-form, SiO_2/Al_2O_3 mole ratio of 80, surface area of 780 m^2/g) and nitric acid (d 1.52 g/cm^3) were used for the nitrolysis of iodopyrazoles.

2.1.1. General procedure for the synthesis of mononitropyrazoles

To iodopyrazole (1 mmol) dissolved in THF (10 mL), Fuajasite (250 mg) was added. Nitric acid (d 1.52 g/cm^3, 10 mL) was added slowly and the mixture was stirred at room temperature for required time. The catalyst was recovered by filtration and the filtrate was extracted repeatedly with dichloromethane. The solvent was removed under vacuum to obtain nitropyrazole.

2.1.2. General procedure for the synthesis of dinitropyrazoles

To iodopyrazole (1 mmol) dissolved in THF (10 mL), Fuajasite (500 mg) was added. Nitric acid (d 1.52 g/cm^3, 20 mL) was added slowly and the mixture was stirred at room temperature for required time. The catalyst was recovered by filtration and the filtrate was extracted with dichloromethane. The solvent was removed under reduced pressure to get dinitropyrazole.

2.1.2.1. 1-Methyl-3(5),4-dinitropyrazole (6). IR, υ (KBr) cm^{-1}: 1551, 1533, 1522, 1371 and 1342 (C–NO_2); 2994(C–H). ^1H NMR (300 MHz, $CDCl_3$, 300 K) δ (ppm) = 4.04(s, 3-H); 8.33 (s, 5-H). ^{13}C NMR (300 MHz, $CDCl_3$, 300 K) δ (ppm) = 38.3 (t, CH_3); 147 (C-3); 127 (C-4); 133 (C-5). EI-MS: m/z 172 ($M^{+\bullet}$). Anal. calcd for $C_4H_4N_4O_4$ C 27.91; H 2.30; N 32.52; found C 27.88; H 2.34; N 32.54.

2.1.3. General procedure for the synthesis of trinitropyrazoles

To iodopyrazole (1 mmol) dissolved in THF (10 mL), Fuajasite (500 mg) was added. Nitric acid (d 1.52 g/cm^3, 30 mL) was added slowly and the mixture was stirred at room temperature for required time. The catalyst was recovered by filtration and the filtrate was extracted with dichloromethane. The solvent was removed under vacuum to obtain trinitropyrazole.

2.1.3.1. 3,4,5-trinitropyrazole (10b). IR, υ (KBr) cm^{-1}: 1554, 1521, 1445, 1413, 1371, 1346 and 1284 (C–NO_2); 3145 (N–H). ^1H NMR (300 MHz, $CDCl_3$, 300 K) δ (ppm) = 12.1(s, 1H, NH). ^{13}C NMR (300 MHz, $CDCl_3$, 300 K) δ (ppm) = 123 (C-4); 144 (C-3); 347 (C-5). EI-MS: m/z 203 ($M^{+\bullet}$). Anal. calcd for $C_3HN_5O_6$ C 17.71; H 0.54; N 34.54; found C 17.72; H 0.46; N 34.44.

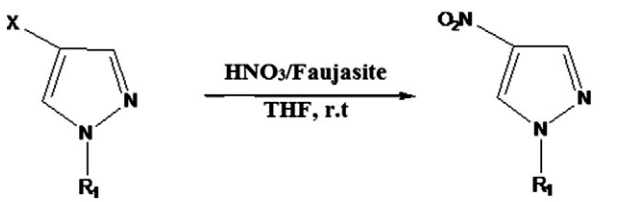
2.1.3.2. 1-Methyl-3,4,5-trinitropyrazole (11b). IR, υ (KBr) cm^{-1}: 1552, 1532, 1454, 1384, 1323(C–NO_2); 2994 (CH_3). ^1H NMR (300 MHz, $CDCl_3$, 300 K) δ (ppm) = 4.3 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$, 300 K) δ (ppm) = 43.5 (t, CH_3); 124 (t, C4); 136 (t, C3); 148 (t, C5). EI-MS: m/z 217 (M^+). Anal. calcd for $C_4H_3N_5O_6$ C 22.15; H 1.35; N 32.22; found C 22.5; H 1.3.

3. Results and discussion

Faujasites due to their high degree of hydration, high selectivity, exceptional stability and low density are extremely useful as catalysts in many organic reactions. The framework of Faujasite structure is open with complete sodalite-type cages and with very large cavities having 12-membered ring openings [19,20]. The reactions are known to take place within the pores of catalyst, which allows a greater degree of product control. The solid catalyst accommodates up to 260 molecules of H_2O per unit cell. We have chosen Faujasite (H-form) as catalyst for the nitrolysis (i.e., nitrodeiodination) of iodopyrazoles. Fuajasite was activated at 120 °C for 6 h before used in the nitrolysis. The iodopyrazole together with nitric acid/Fuajasite in THF have been stirred and the evaporation of solvent under vacuum comprises the reaction conditions for successful and regiospecific nitration. To establish the optimum conditions several reactions were performed on 4-iodopyrazole (**1a**) and 4-iodo-1-methypyrazole (**1b**) as the model substrates varying the amounts of Fuajasite at room temperature (Scheme 1). We found that there was no remarkable change in the yields of **2a** and **2b** when the reactions prolonged or increased the amount of catalyst. The replacement of iodine proceeded easily in nitric acid over Fuajasite. Table 1 summarizes the nitrodeiodination of series of iodopyrazoles and their corresponding nitropyrazoles.

Generally, pyrazoles are nitrated in the 4-position facilitated by electron-donating and retarded by electron-withdrawing groups. The substrates with electron-donating groups readily underwent nitration in excellent yields (72%) and the deactivated substrates underwent nitration in good yields (>60%). The free 3- and 5-positions of pyrazoles are strongly deactivated by the nitro group in the 4-position thus the yields are lower despite of harsh conditions and the nature of nitration mixture. On the other hand 1-phenylpyrazole and its analogues underwent substitution in the 4-position of the pyrazole ring [18]. 1-Phenyl-4-iodopyrazole (**7a**), 1-(*p*-nitrophenyl)-4-iodopyrazole (**8a**) and 1-benzyl-4-iodopyrazole (**9a**) nitrolysed into 1-phenyl-4-nitropyrazole (**7b**), 1-(*p*-nitrophenyl)-4-nitropyrazole (**8b**) and 1-benzyl-4-nitropyrazole (**9b**) respectively.

Diiodopyrazoles (**3c** and **5c**) and triiodopyrazoles (**10a** and **11a**) were also nitrolysed into dinitro pyrazoles (**4** and **6**) and trinitropyrazoles (**10b** and **11b**) respectively in good yields. Dinitropyrazoles are utterly deactivated by vicinal nitro groups thus hindering the substitution in the 5-position of pyrazole ring. The presence of vicinal nitro groups in **4** and **6** deactivated the 5-position and consequently the nitrolysis has not been observed rather quantitative iodopyrazoles were recovered. 3,4,5-Trinitropyrazole (**10b**) is neither hygroscopic nor highly acidic in nature [19]. It displays low sensitivity to external stimuli and outstanding thermal and chemical stability of nitrated aromatic compounds. The exceptional stability/or low sensitivity of **10b** is because of its low acidity (pKa 2.35). 1-Methyl-3,4,5-trinitropyrazole (**11b**) has been considered as the next generation melt-cast explosive [9]. The product obtained after the nitrolysis of 3,4,5-triiodo-1-



(1a) R_1= H, X = I
(1b) R_1= CH_3, X = I
(2a) R_1= H
(2b) R_1= CH_3

Scheme 1. Faujasite catalyzed nitrodeiodination of iodopyrazoles.