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Mild basic ionic liquids as catalyst for the multi-component synthesis of 7-amino-1,3-dioxo-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole and 6,6-dimethyl-2-phenyl-9-aryl-6,7-dihydro-[1,2,4]triazolo[*1,2-a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione derivatives

Hamid Reza Shaterian *, Kobra Azizi

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, PO Box 98135-674, Zahedan, Iran

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ABSTRACT

Synthesis of 7-amino-1,3-dioxo-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole derivatives by a three component reaction of aryl aldehydes, 4-phenylurazole and malononitrile or ethyl cyanoacetate in the presence of catalytic amount of weak basic ionic liquids such as *N*-butyl-*N*-methylpyrrolidinium acetate, 1-butyl-3-methylimidazolium imidazolide, and 1-ethyl-3-methylimidazolium acetate under solvent-free conditions is described. In addition, preparation of 6,6-dimethyl-2-phenyl-9-aryl-6,7-dihydro-[1,2,4]triazolo[*1,2-a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione derivatives from the reaction of aryl aldehydes, 4-phenylurazole and dimedone in the presence of mentioned catalysts under mild, ambient and solvent-free conditions at room temperature is reported. Reusability of catalysts, and easy isolation of products along with excellent yields are the advantages of these methods.

1. Introduction

Economical ionic liquids are important in the organic synthesis, which could effectively drive the development of green and chemical industries [1–3]. As is known to all, discovering a new ionic liquid is relatively easy, but determining its usefulness as a solvent and catalyst requires a much more substantial investment [1–5]. With the fast development of green chemistry and our tireless efforts, herein, we applied some weak basic ionic liquids such as *N*-butyl-*N*-methylpyrrolidinium acetate, 1-butyl-3-methylimidazolium imidazolide, and 1-ethyl-3-methylimidazolium acetate (Fig. 1) as catalysts in the synthesis of 7-amino-1,3-dioxo-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole and 6,6-dimethyl-2-phenyl-9-aryl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2*H*,5*H*,9*H*)-trione derivatives (Scheme 1).

2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. The weak basic ionic liquids such as *N*-butyl-*N*-methylpyrrolidinium acetate, 1-butyl-3-methylimidazolium imidazolide, and 1-ethyl-3-methylimidazolium acetate were prepared according to the reported procedure [6–8]. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The spectra were measured in DMSO-d_6 relative to TMS (0.00 ppm). Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. TLC was performed on silica-gel Poly Gram SIL G/UV 254 plates.

2.1. General procedure for the synthesis of 7-amino-1,3-dioxo-1,2,3,5-tetrahydropyrazolo[1,2-a][1,2,4]triazole derivatives under solvent-free conditions

The mixture of the aldehydes (10 mmol), malononitrile or ethyl cyanoacetate (10 mmol), 4-phenylurazole (10 mmol) and ionic liquids containing *N*-butyl-*N*-methylpyrrolidinium acetate (15 mol%), 1-butyl-3-methylimidazolium imidazolide (20 mol%), or 1-ethyl-3-methylimidazolium acetate (15 mol%) as weak basic catalyst was stirred at 80 °C for the specific time. After completion of the reaction, it was cooled to room temperature. Then, 5 mL of water was added to the mixture. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2 × 5 mL). The solid product was purified by

* Corresponding author. Tel.: +98 541 2446565; Fax: +98 541 2431067.
E-mail address: hrshaterian@chem.usb.ac.ir (H.R. Shaterian).

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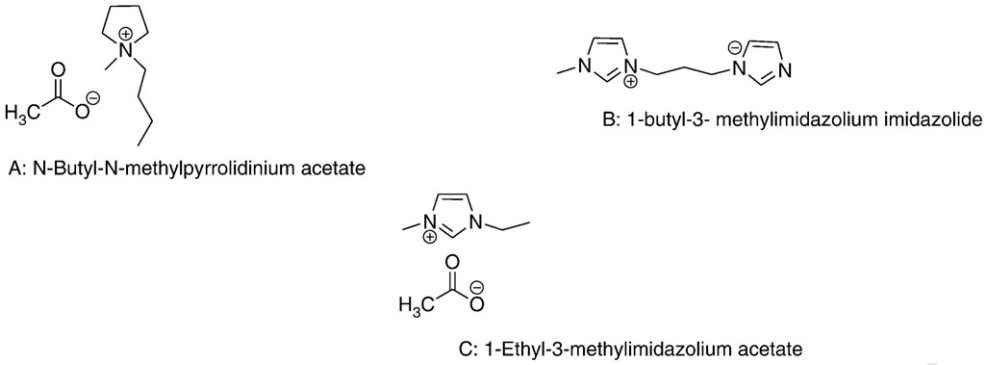


Fig. 1. The structure of mild basic ionic liquids: *N*-butyl-*N*-methylpyrrolidinium acetate, 1-butyl-3-methylimidazolium imidazolide, and 1-ethyl-3-methylimidazolium acetate.

recrystallization procedure in ethanol. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused. Select characterizations data for the new products are given below:

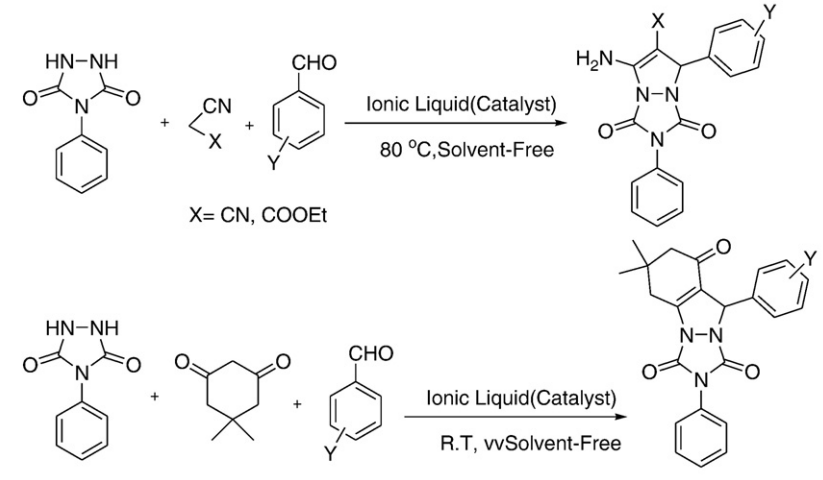
Ethyl 7-amino-5-(4-chlorophenyl)-1,3-dioxo-2-phenyl-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole-6-carboxylate (Table 1, entry 8): Yellow powder; m.p = 143 °C.; IR (KBr): ν_{max} = 3465, 3337, 1785, 1720, 1685 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.30 (3H, t, J = 6.8 Hz, CH_3), 3.96 (2H, q, J = 6.7 Hz, CH_2), 5.85 (1H, s, CH), 7.23–8.10 (11H, m, Ar, NH_2) ppm.; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.7, 58.8, 63.8, 83.3, 127.3, 128.5, 129.2, 129.3, 130.1, 131.4, 138.4, 140.3, 149.7, 151.5, 153.7, 164.8 ppm.; Anal. Calcd. for $C_{20}H_{17}ClN_4O_4$: C, 58.19; H, 4.15; N, 13.57%. Found: C, 58.10; H, 4.16; N, 13.60%.

Ethyl 7-amino-5-*p*-tolyl-1,3-dioxo-2-phenyl-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole-6-carboxylate (Table 1, entry 9): Yellow powder; m.p = 149 °C.; IR (KBr): ν_{max} = 3462, 3333, 1782, 1715, 1685 cm^{-1}.; ^1H NMR (300 MHz, DMSO-d_6): δ = 1.33 (3H, t, J = 5.9 Hz, CH_3), 2.03 (3H, s, Me), 3.92 (2H, q, J = 5.8 Hz, CH_2), 5.85 (1H, s, CH), 7.22–8.10 (11H, m, Ar, NH_2) ppm.; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.8, 20.1, 58.8, 63.7, 83.6, 126.8, 128.7, 129.1, 129.5, 130.5, 131.2, 138.2, 140.5, 149.8, 151.6, 152.8, 164.5 ppm.; Anal. Calcd. for $C_{21}H_{20}N_4O_4$: C, 64.28; H, 5.14; N, 14.28%. Found: C, 64.25; H, 5.10; N, 14.29%.

Ethyl 7-amino-5-(4-nitrophenyl)-1,3-dioxo-2-phenyl-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole-6-carboxylate (Table 1, entry 10): Yellow powder; m.p = 179 °C.; IR (KBr): ν_{max} = 3427, 3300, 1775, 1725, 1675 cm^{-1}.; ^1H NMR (300 MHz, DMSO-d_6): δ = 1.02 (3H, t, J = 7.02 Hz, CH_3), 3.96 (2H, q, J = 7.02 Hz, CH_2), 5.98 (1H, s, CH), 7.32–7.75 (11H, m, Ar, NH_2) ppm.; ^{13}C NMR(75 MHz, DMSO-d_6): δ = 14.8, 59.0, 63.8, 82.7, 124.0, 127.4, 129.2, 129.4, 129.5, 131.4, 137.9, 147.6, 148.4, 151.4,153.9, 164.5 ppm.; Anal. Calcd. for $C_{20}H_{17}N_5O_6$: C, 56.74; H, 4.05; N, 16.54%. Found: C, 56.70; H, 4.10; N, 16.55%.

2.2. Synthesis of 6,6-dimethyl-2-phenyl-9-aryl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione derivatives under ambient and solvent-free conditions

The mixture of the aldehydes (10 mmol), dimedone (10 mmol), 4-phenylurazole (10 mmol) and ionic liquids containing *N*-butyl-*N*-methylpyrrolidinium acetate (15 mol%), 1-butyl-3-methylimidazolium imidazolide (20 mol%), or 1-ethyl-3-methylimidazolium acetate (15 mol%) as weak basic catalyst was stirred under ambient and solvent-free conditions for the specific time. After completion of the reaction, 5 mL of water was added to the mixture. The ionic liquid was



Ionic Lquids = A: *N*-Butyl-*N*-methylpyrrolidinium acetate, B:1-Butyl-3- methylimidazolium imidazolide , and C: 1-Ethyl-3-methylimidazolium acetate

Scheme 1. Synthesis of 7-amino-1,3-dioxo-1,2,3,5-tetrahydropyrazolo[*1,2-a*][1,2,4]triazole and 6,6-dimethyl-2-phenyl-9-aryl-6,7-dihydro-[1,2,4]triazolo[*1,2-a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione derivatives.

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