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Research Article

IONIC LIQUID-MEDIATED, RAPID ADDITION REACTION BETWEEN NINHYDRIN AND HYDRAZIDES

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ABSTRACT
Ionic liquids such as 1, 3-dialkylimidazolium bromides and make excellent solvents for addition reaction between ninhydrin and hydrazides. The present method does not involve any hazardous organic solvent. Therefore, this procedure could be classified as green chemistry. very simple and rapid with excellent yields and easy work.

Keywords: *Ionic Liquids, Addition Reaction, Ninhydrin, Hydrazides*

INTRODUCTION
Ionic liquids (ILs) have attracted considerable attention in recent years due to their unique properties, such as lack of measurable vapor pressure, non-flammability and recyclability (Welton, 1999).Their high polarity and ability to dissolve both inorganic and organic materials can result in enhanced rates of chemical processes and can provide higher/different selectivity's compared to conventional solvents. Thus, as a result of their 'green' credentials and potential to enhance rate and selectivity (Wasserscheid and Welton, 1987; Dupont *et al.*, 2002), ILs has been used as solvents in chemical transformations. However, the ability of ILs to serve as catalysts (Harjani *et al.*, 2002) and reagents (Ranu *et al.*, 2002) has not been explored to any great extent (Ranu and Banerjee, 2005; Walborsky and Hornyak, 1955).
In continuation of our previous works on the reaction between hydrazides nucleophiles in the presence of acidic organic compounds (Hassanabadi, 2013; Hassanabadi *et al.*, 2011) we wish to report herein the results of our studies on the reaction between ninhydrin and hydrazides in the presence of Ionic liquids such as 1,3-dialkylimidazolium bromides and make excellent solvents.

MATERIALS AND METHODS
Melting points were determined with an Electro thermal 9100 apparatus. All melting points are uncorrected. Elemental analyses were performed using a Heraeus CHN–O–Rapid analyzer. Mass spectra were recorded on a Finnegan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H and ^{13}C spectra were recorded on Bruker DRX-400 Avance spectrometer in d_6-DMSO using TMS as the internal standard. Chemicals were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General Procedure

An equimolar mixture of ninhydrin and hydrazides was dissolved in ionic liquid (1 g), and the reaction content was allowded to stir at 100° C for 10 min. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled at room temperature and poured into ice water. The solid precipitated was filtered and dried. The purity of the products was confirmed by TLC.

Recovery of the Ionic Liquid

An attempt was made to recover the ionic liquid. After completion of the reaction, the reaction mixture was poured on ice water, and the product was filtered off. The filtrate was extracted with ethyl acetate to recover unreached reactants, and the aqueous layer was subjected to evaporation of water to get viscous liquid, which on cooling gave the ionic liquid. The recovered ionic liquid was reused for two more cycles of the same cyclocondensation and found to act satisfactorily.

***Ethyl N'-(2-Hydroxy-1,3-dioxoindan-2-yl)hydrazine carboxylate* (3a)**
White Powder, Yield: 90%; m.p. 140-142˚C. IR (KBr) (ν_{max}, cm^{-1}): 3320 ,3065 (OH, NH), 1711, 1620 (C=O). Calcd. for $C_{12}H_{12}N_2O_5$: C, 54.55; H, 4.58; N, 10.60%. Found: C, 54.48 H, 4.60; N, 10.46 %. MS (m/z, %): 264 (M, 6). ^{1}H NMR (400 MHz, DMSO): δ 1.11 (3H, t, $^3J_{HH}$ = 7Hz, CH_3), 3.92 (2H, q, $^3J_{HH}$ = 7Hz, OCH_2), 5.81 and 6.77 (2H, 2s, 2NH), 7.98-8.04 (4H, m, 4CH aromatic), 8.33 (1H, broad s, OH). ^{13}C NMR (100 MHz, DMSO): δ 15.35 (CH_3), 60.92 (OCH_2), 83.35 (C), 124.58, 137.67 and 139.84 (6C aromatic), 157.99 (C=O), 196.15 (2C=O).

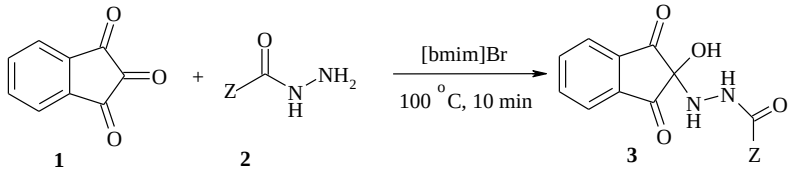
***Benzoic acid N'-(2-Hydroxy-1,3-dioxoindan-2-yl)hydrazide* (3b)**
White Powder, Yield: 91%; m.p. 162-164˚C. IR (KBr) (ν_{max}, cm^{-1}): 3350 ,3115 (OH, NH), 1710, 1623 (C=O). Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45%. Found: C, 64.70 H, 4.22; N, 9.38 %. MS (m/z, %): 296 (M, 10). ^{1}H NMR (400 MHz, DMSO): δ 6.33 and 7.09 (2H, 2s, 2NH), 7.42-8.00 (9H, m, 9CH aromatic), 9.95 (1H, s, OH). ^{13}C NMR (100 MHz, DMSO): δ 84.61 (C), 125.41, 138.46 and 140.72 (6C aromatic), 129.04, 129.90, 133.21 and 134.31 (6C aromatic), 169.35 (C=O), 196.43 (2C=O).

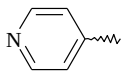
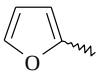
***Isonicotinic acid N'-(2-Hydroxy-1,3-dioxoindan-2-yl)hydrazide* (3c)**
Yellow Powder, Yield: 88%; m.p. 102-104˚C. IR (KBr) (ν_{max}, cm^{-1}): 3332, 3105 (OH, NH), 1719, 1640 (C=O). Calcd. for $C_{15}H_{11}N_3O_4$: C, 60.61; H, 3.73; N, 14.14%. Found: C, 60.77 H, 3.80; N, 14.25 %. MS (m/z, %): 297 (M, 3). ^{1}H NMR (400 MHz, DMSO): δ 6.40 and 7.00 (2H, 2s, 2NH), 7.66 (2H, d, $^3J_{HH}$= 5Hz, 2CH Pyridine), 7.99-8.01 (4H, m, 4CH aromatic), 8.70 (2H, d, $^3J_{HH}$= 5Hz, 2CH Pyridine),10.24 (1H, s, OH).^{13}C NMR (100 MHz, DMSO): δ 84.25 (C), 125.43, 138.49, 140.66 (6C aromatic), 123.00, 141.62, 151.75 (5C Pyridine),167.04 (C=O), 196.85 (2C=O).

***Furan-2-carboxylic acid N'-(2-Hydroxy-1,3-dioxoindan-2-yl)hydrazide* (3d)**
White Powder, Yield: 86%; m.p. 113-116˚C. IR (KBr) (ν_{max}, cm^{-1}): 3370, 3125 (OH, NH), 1716, 1639 (C=O). Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.75; H, 3.52; N, 9.79%. Found: C, 58.70 H, 3.63; N, 9.90 %. MS (m/z, %): 286 (M, 6). ^{1}H NMR (400 MHz, DMSO): δ 6.27 and 7.02 (2H, 2s, 2NH), 7.66 (2H, d, $^3J_{HH}$= 5Hz, 2CH Pyridine), 7.84-7.99 (4H, m, 4CH aromatic), 6.60, 7.15 and 7.84 (3H, 3CH Furan), 9.67 (1H, s, OH).^{13}C NMR (100 MHz, DMSO): δ 84.29 (C), 113.42, 115.88, 147.11 and 147.81 (4C Furan), 125.45, 133.48 and 140.61 (6C aromatic), 159.94 (C=O), 196.90 (2C=O).

RESULTS AND DISCUSSION

Ninhydrin reacts with hydrazides in ILs as solvent to produce N'-(2-Hydroxy-1,3-dioxoindan-2-yl)hydrazide derivatives in nearly quantitative yields (Figure 1).



2,3	Z	%Yield
a	OEt	90
b		91
c		88
d		86

* Isolated yield

Figure 1: Addition reaction between ninhydrin and hydrazides in ILs as solvent.

The structures of compounds **3a–d** were all new and deduced from their elemental analyses and their IR, ^{1}H NMR, ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m/z* values. For example, the ^{1}H NMR spectrum of **3a** exhibited two single signals were observed at 5.81 and 6.77 ppm that disappeared after addition of a few drops of D_2O to the d_6-DMSO solution of compound **3a**. These signals were related to NH protons. The aromatic protons resonated between 7.98 and 8.04 ppm. A broad singlet is observed at δ = 8.33 ppm for OH proton which was disappeared after the addition of D_2O to the d_6-DMSO solution of **3a**. Ethyl protons were observed as a triplet ($^{3}J_{HH}$ = 7 Hz) at 1.11 ppm and a quartet ($^{3}J_{HH}$ = 7 Hz) at 3.92 ppm. The ^{13}C NMR spectrum of **3a** showed 8 distinct resonances in agreement with the proposed structure. The mass spectrum of **3a** displayed the molecular ion peak at *m/z* = 264. The IR spectrum of compound **3a** also supported the suggested structure. Strong absorption bands were observed at 1711 and 1620 cm^{-1} for the carbonyl groups. also showed two absorption bonds at 3320 and 3065 cm^{-1} for NH and OH groups.

Conclusion

In summary, we report herein that Ionic liquids such as 1, 3-dialkylimidazolium bromides and make excellent solvents for addition reaction between ninhydrin and hydrazides. The present method does not involve any hazardous organic solvent. Therefore, this procedure could be classified as green chemistry. Very simple and rapid with excellent yields and easy work.

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