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 allowed 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) (νmax, cm⁻¹): 3320, 3065 (OH, NH), 1711, 1620 (C=O). Calcd. for C₁₉H₁₂N₂O₅: 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). ¹H NMR (400 MHz, DMSO): δ 1.11 (3H), 2.10 (2H, 2s, 2NH). 13C NMR (100 MHz, DMSO): δ 15.35 (CH), 58.41 (C), 60.92 (OCH), 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: 86%; m.p. 113-116°C. IR (KBr) (νmax, cm⁻¹): 3370, 3105 (OH, NH), 1719, 1640 (C=O). Calcd. for C₁₉H₁₁N₂O₅: C, 60.61; H, 3.73; N, 9.95%. Found: C, 60.77 H, 3.80; N, 10.15 %. MS (m/z, %): 296 (M, 10). ¹H 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). ¹³C NMR (100 MHz, DMSO): δ 84.61 (C), 125.41, 126.26, 129.03 (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. 150-153°C. IR (KBr) (νmax, cm⁻¹): 3332, 3105 (OH, NH), 1719, 1640 (C=O). Calcd. for C₁₉H₁₁N₂O₅: C, 60.61; H, 3.73; N, 9.95%. Found: C, 60.77 H, 3.80; N, 10.15 %. MS (m/z, %): 297 (M, 10). ¹H NMR (400 MHz, DMSO): δ 6.40 and 7.00 (2H, 2s, 2NH), 7.66 (2H, d, JHH=5Hz, 2CH Pyridine), 7.99-8.01 (4H, m, 4CH aromatic), 8.70 (2H, d, JHH=5Hz, 2CH Pyridine), 10.24 (1H, s, OH). ¹³C 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) (νmax, cm⁻¹): 3370, 3105 (OH, NH), 1719, 1639 (C=O). Calcd. for C₁₉H₁₆N₂O₅: 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). ¹H NMR (400 MHz, DMSO): δ 6.27 and 7.02 (2H, 2s, 2NH), 7.66 (2H, d, JHH=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). ¹³C 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).

![Figure 1: Addition reaction between ninhydrin and hydrazides in ILs as solvent.](image_url)
Research Article

The structures of compounds 3a-d were all new and deduced from their elemental analyses and their IR, 1H NMR, 13C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate m/z values. For example, the 1H 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 D2O to the d6-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 D2O to the d6-DMSO solution of 3a. Ethyl protons were observed as a triplet (JHH = 7 Hz) at 1.11 ppm and a quartet (JHH = 7 Hz) at 3.92 ppm. The 13C 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 ninyhydrin 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.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support from the Research Council of Islamic Azad University of Zahedan of Iran.

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