



Selective iodination of 2-acetyl-1-naphthol using iodine and iodic acid under solvent-free grinding technique

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ABSTRACT

Selective electrophilic iodination of 2-acetyl-1-naphthol was achieved using iodine and iodic acid in combination with grinding at room temperature under solvent-free conditions to yield 1-(1-hydroxy-4-iodo-naphthalen-2-yl)-ethanone. Grinding mode of reactions has not only of interest from economical point of view, in many cases they also offer considerable advantages in terms of yield, mild reaction conditions, selectivity and simplicity of reaction procedure.

1. Introduction

Aromatic iodo compounds are valuable and versatile synthetic intermediates in organic chemistry [1]. They are useful for the preparation of organometallic reagents, and some are potential intermediates for the synthesis of pharmaceutical and bioactive materials [2,3]. They are also important and the most reactive intermediates for various cross-coupling reactions and especially useful for formation of carbon-carbon and carbon-heteroatom bonds [4]. Recently the reagents reported for iodination of arenes include, iodine-nitrogen dioxide [5], iodine F-TEDA-[1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2,2,2] octane-bis-(tetrafluoroborate)] [6], bis-N-iodosuccinimide [7], trichloroisocyanuric acid-I₂-Wet SiO₂ [8], mercury(II)-oxide-iodine [9], iodine-monochloride [10], bis(pyridine)iodonium(I), tetrafluoroborate CF₃SO₃H [11], NIS-CF₃SO₃H [12], iodine silver sulfate [13], iodine-mercury salts [14] and NaOCl-NaI [15]. However, most of these methods suffer from major drawbacks such as use of harsh conditions, toxic heavy-metal catalysts, non-selectivity and longer reaction times. Use of iodine in combination with iodic acid found to be an efficient iodinating agent for iodination for aromatic compounds. In view of these observations we report here the selective iodination of 2-acetyl-1-naphthol (bicyclic arene) using iodine and iodic acid under solvent-free environment using grinding technique (Scheme 1).

2. Experimental

2.1. Instrumentation

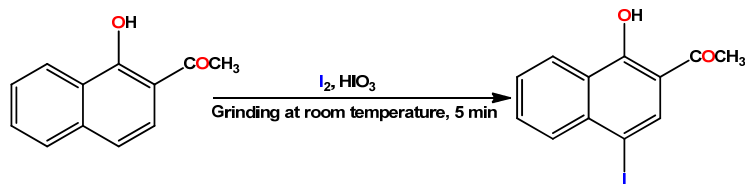
Melting point was determined in an open capillary tube and is uncorrected. IR spectra were recorded in KBr pellets on a Shimadzu FT-IR spectrometer. ¹H and ¹³C NMR spectra were

obtained in DMSO-*d*₆ on Avance 300 MHz spectrometer using TMS as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC-MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 Perkin-Elmer model 240 analyzer.

2.2. Synthesis

Mixture of 2-acetyl-1-naphthol (50 mmol), iodine (20 mmol), taken in open mortar and grind with pestle for 2 min. To this reaction mixture saturated solution of iodic acid (10 mmol) was added and grinding was continued up to disappearance of reactant spot on thin layer chromatography (TLC). After completion of grinding saturated solution of Na₂S₂O₃ (10 mL) was added to remove excess of iodine to obtain solid product. Resultant solid product was filtered through simple büchner funnel, washed with cold water and crystallized from ethanol to yield 1-(1-hydroxy-4-iodo-naphthalen-2-yl)-ethanone (Scheme 1). The purity of compound was checked by TLC, using hexane/ ethyl acetate as the mobile phase.

1-(1-Hydroxy-4-iodo-naphthalen-2-yl)-ethanone: Color: Light greenish. Yield: 94%. M.p.: 156 °C. FT-IR (KBr, ν, cm⁻¹): 3070, 1726, 1622, 1583, 1494, 1442, 1411, 1232, 831, 759. ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 14.0 (s, 1H, OH), 8.2 (s, 1H, Ar-H), 8.4-7.2 (m, 4H, Ar-H), 2.7 (s, 3H, CH₃). ¹³C NMR (75 MHz DMSO-*d*₆, δ, ppm): 196.24 (C of C=O), 156.35 (C of Ar-OH), 137.63 (C of Ar-C), 135.37 (C of Ar-C), 132.73 (C of Ar-C), 131.86 (C of Ar-C), 129.70 (C of Ar-C), 127.48 (C of Ar-C), 124.58 (C of Ar-C), 120.14 (C of Ar-C), 93.89 (C of Ar-I), 24.17 (C of CH₃). MS (EI, *m/z* (%)): 312 (M⁺, 100), 297 (60), 294 (20), 269 (10), 241 (20), 186 (5), 167 (10), 142 (20), 128 (40), 114 (65), 74 (20), 63 (30). Anal. calcd. for C₁₂H₉O₂I: C, 46.15; H, 2.88. Found: C, 45.18; H, 2.86 %.



Scheme 1

3. Result and discussion

In continuation of earlier research work [16-19], we report here in a simple, rapid, efficient and environmentally benign solvent-free iodination of 2-acetyl-1-naphthol using iodine and iodic acid in combination with grinding at room temperature. The iodination occur selectively at electron rich centre i.e. *para*-position to -OH group. The corresponding product 1-(1-hydroxy-4-iodo-naphthalen-2-yl)-ethanone obtained in 94% yield. In grindstone technique, reaction occurs through generation of local heat by grinding of crystals of substrate and reagent. Reactions are initiated by grinding, with the transfer of very small amount of energy through friction. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and may regarded as more economical and ecologically favorable procedure in chemistry [20]. Obtained iodo product established on the basis of spectral characterization, IR, ¹H NMR, ¹³C NMR, MS, and elemental analysis.

4. Conclusion

In summary, we have described selective iodination of 2-acetyl-1-naphthol using iodine and iodic acid under solvent-free grindstone technique.

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