Conversion of indoline-2-thione and oxindole to isatin – some new observations

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Indoline-2-thione (1) and oxindole, when treated separately with ceric ammonium nitrate adsorbed on silica gel (CAN-SiO₂) in acetonitrile, furnished isatin (2) as the sole product, whereas Montmorillonite K10 clay alone converted oxindole to isatin in a dry reaction.

Ceric ammonium nitrate (CAN) is a well documented one-electron oxidant used in organic synthesis. The strong oxidising power of cerium(IV) salts, however, leads to undesired and overoxidised products. The concept of moderating the effect of reagents by using them adsorbed on inorganic solid supports has consequently been developed since long and applied successfully in organic syntheses. It has been earlier demonstrated that CAN adsorbed on silica gel (CAN-SiO₂) is a more selective and efficient oxidant and nitrating agent than CAN alone due to its mildness and ease of work-up. In continuation of our ongoing interest in the study of CAN-mediated reactions of various heterocyclic systems with or without adsorption (of CAN) on solid supports, we report herein the action of CAN-SiO₂ on indoline-2-thione (1) and oxindole in acetonitrile solution. The conversion of oxindole on an acidic clay is also being reported herein.

Results and discussion

Indoline-2-thione (1) was prepared from oxindole by Lawesson's reagent. When a solution of 1 in dry acetonitrile was treated with two equivalents of CAN-SiO₂ at 60° for a few hours, isatin (2) was isolated as the only product, although in low yield (Scheme 1).

Ceric ammonium nitrate - SiO₂ may have initially dethionated 1 to oxindole which subsequently underwent CAN-SiO₂-mediated oxidation to 2. This notion of ours proved to be correct when a somewhat similar treatment of oxindole with CAN-SiO₂ in acetonitrile furnished 2 in 25% yield (Scheme 2).

Since the conversion of oxindole to isatin on the acidic surface of silica gel alone by autoxidation was a distinct possibility, we repeated the above reaction but without using CAN. But there was no change, which demonstrated the inability of silica gel itself to bring about the observed oxidation.

Since the commercially available Montmorillonite K10 clay is reported to have a larger specific area (500–760 m²/g) and higher Bronsted acidity (Hammet acidity function, H₀ = −6 to −8) than those of silica gel, we became curious to know if this acidic clay could induce autoxidation of oxindole to isatin. As planned, oxindole was adsorbed on M.K10 clay and kept at room temperature until it was fully consumed. Leaching of the clay with a suitable solvent furnished a single product which was identified as isatin by usual comparisons (Scheme 3).
Our results demonstrated for the first time the vulnerability of indoline-2-thione and oxindole to CAN-SiO₂ and also of oxindole to Montmorillonite clay. These findings may be of use to the community of chemists.

Experimental

Lawesson's reagent was purchased from Aldrich, U.S.A. The NMR spectra were recorded on a Bruker DRX 500 spectrometer and the low resolution mass spectrum in an AEI MS 30 mass spectrometer. Silica gel G (Merck, India) was used for TLC and silica gel (60–120 mesh, Qualigens, India) for column chromatography was used for the CAN-SiO₂ process (m.m.p. and co-TLC).

Reaction of indoline-2-thione (I): A solution of oxindole (2 mmol, 266 mg) in dry acetonitrile containing Lawesson's reagent (4 mmol, 1.6 g) was stirred at 60° for 5 h. The reaction mixture was then poured into saturated sodium bicarbonate solution and extracted with ethyl acetate (3 x 20 ml). The organic layer was washed with water, dried (anhyd. Na₂SO₄), filtered and the filtrate was distilled. The resulting residue was crystallised from pet. ether-CH₂Cl₂ to furnish indoline-2-thione (I) as pale yellow prisms (60%), m.p. 145°–147° (lit.¹¹ m.p. 148°–150°).

Reaction of oxindole with CAN-SiO₂: A solution of oxindole (2 mmol, 1.1 g) in CH₃CN (4 ml) was added to I (1 mmol, 150 mg) in dry acetonitrile (7 ml). The reaction mixture was stirred at 60° for 5.5 h. On completion of the reaction (TLC), the above mixture was adsorbed on fresh silica gel and the solvent was allowed to evaporate at RT. Leaching with CH₂Cl₂ (3 x 20 ml) and distilling off the solvent gave a residue which was crystallised from pet. ether-CH₂Cl₂ to furnish isatin (2) as orange prisms (15%), m.p. 196°–198° (lit.¹² m.p. 203.5°); its identity was confirmed by direct comparison (m.m.p. and co-TLC).

MS: m/z 147 (M+, 59%), 119 (89), 92 (100); ¹H (500 MHz, d₆-DMSO) δ 10.97 (1H, br s, NHCO), 7.35, (1H, t, J 7.5 Hz, H-6), 7.26 (1H, d, J 7.5 Hz, H-4), 6.85 (1H, t, J 7.5 Hz, H-5), 6.71 (1H, d, J 7.5 Hz, H-7); ¹³C (125 MHz) δ 185.0 (CO), 160.3 (NHCO), 151.3 (C-7a), 139.5 (C-6), 125.7 (C-4), 124.0 (C-5), 118.4 (C-3a), 113.2 (C-7). The ¹³C NMR data agreed well with those reported in literature.¹³

Reaction of oxindole with CAN-SiO₂: The same procedure as applied to I was adopted, except CAN (1 mmol, 18 mg) and oxindole (0.5 mmol, 67 mg) were used. The reaction took 5 h and, after usual work-up, isatin (2) was obtained in 25% overall yield.

Oxidation of oxindole on M.K10 clay surface: Oxindole (1 mmol, 133 mg) was dissolved in CH₂Cl₂ (5 ml) and M.K10 clay (3 g) was added to the solution. The solvent was allowed to evaporate at RT and kept for 24 h. On completion of the reaction (TLC), leaching with CH₂Cl₂ (3 x 20 ml) furnished isatin in 82% overall yield.

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