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A Convenient Synthesis of β-Ketosulfoxides

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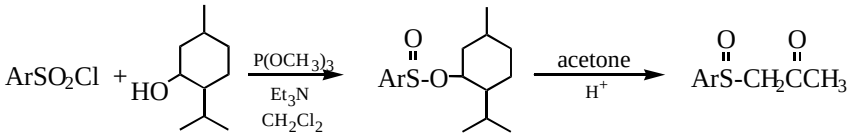
Abstract: β-Ketosulfoxides were synthesized by the reaction of acetone with aryl sulfinate esters in the presence of hydrochloric acid and the structure of title compounds were finally confirmed by IR, ^{1}HNMR and ^{13}CNMR spectra.

Keywords: β-ketosulfoxide, sulfinate ester.

β-Ketosulfoxides have attracted many organic chemists because of their wide use in synthesis of ketones, α-ketols, glyoxals, α-keto acids, glycols, α-hydroxy acids and so on[1]. Generally, β-ketosulfoxides can be prepared by the reaction of ester with sulfoxide[1, 2], acyl chloride with sulfoxide[3] and sulfinyl chloride with acetone[4,5].

In our previous papers, we reported using β-ketosulfoxide for synthesis of α-ketohemithioacetal, followed by reacting with ureas and thioureas to afford 2, 4-imidazolidinediones and 2-thioxo-4-imidazolidinones[6,7], which have a variety of bioactivities[8,9]. Here, we wish to report a new convenient method for synthesis of β-ketosulfoxide *via* reaction of sulfinate esters with acetone in the presence of hydrochloric acid in good yield (**Scheme 1**).

Scheme 1



1a-c **2a-c** **3a-c**

Ar: a, *o*-nitrophenyl; b, *p*-nitrophenyl; c, *p*-tolyl

General Procedure

To a stirred solution containing sulfinate ester[10] **2a-c** (20mmol) and acetone (20mL), concentrated hydrochloric acid (1mL, 12mmol) was added. The mixture was heated to 45°C and kept for 25h. Removal of solvent gave a residue, which was dissolved in

dichloromethane, washed with saturated sodium bicarbonate and brine, dried over anhydrous magnesium sulfate. After removing dichloromethane, white solid **3a-c** was given over night and purified by recrystallization from acetone.

3a: m.p. 122-123°C, yield 55%. IR (KBr): ν 3080, 2980, 1720, 1600, 1530, 1470, 1400 cm^{-1}. ^{1}HNMR ($CDCl_3$/TMS): δ 8.4-7.7 (m, 4H, ArH), 2.9 (s, 2H, CH_2), 2.4 (s, 3H, CH_3) ppm. ^{13}CNMR ($CDCl_3$/TMS): δ 199.0 (C=O), 145.0, 143.0, 136.0, 132.0, 127.0, 125.0 (Ar), 66.0 (CH_2), 31.0 (CH_3) ppm. Ms: 227 (M^+, 26).

3b: m.p. 124-126°C, yield 56%. IR (KBr): ν 3105, 2986, 1720, 1609, 1532, 1450 cm^{-1}. ^{1}HNMR ($CDCl_3$/TMS): δ 8.4 (d, 2H, ArH), 8.1 (d, 2H, ArH), 2.9 (s, 2H, CH_2), 2.2 (s, 3H, CH_3) ppm. ^{13}CNMR ($CDCl_3$/TMS): δ 204.0 (C=O), 152.0, 141.0, 133.0, 124.0 (Ar), 64.0 (CH_2), 33.0 (CH_3) ppm.

3c: m.p. 93-95°C, yield 50%. IR (KBr): ν 3030, 2983, 1713, 1595, 1450 cm^{-1}. ^{1}HNMR ($CDCl_3$/TMS): δ 7.7 (d, 2H, ArH), 7.3 (d, 2H, ArH), 2.9 (s, 2H, CH_2), 2.4 (s, 3H, CH_3), 2.2 (s, 3H, CH_3) ppm. ^{13}CNMR ($CDCl_3$/TMS): δ 204.7 (C=O), 144.9, 131.3, 130.6, 129.5 (Ar), 45.3 (CH_2), 32.1 (CH_3), 21.5 (CH_3) ppm.

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