Supplementary Material (ESI) for Chemical Communications

Supporting Information

New reactions in water: metal-free conversion of alcohols and ketones into α-iodoketones

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Typical procedure for:

Iodination of ketones.

Cycloheptanone (5 mmol, 1 equiv, 0.56 g) was added to a solution of NaI (5.15 mmol, 1.03 equiv, 0.77 g) in water (15 mL). The flask was cooled down in an ice-water-bath and H_2SO_4 (20 mmol, 8 equiv, 1.06 mL) and H_2O_2 33 % solution (30 mmol, 6 equiv, 3 mL) were sequentially added. The resulting mixture was heated in an oil bath (40ºC) over 7 h. The reaction mixture was then allowed to cool, transferred to a separation funnel and extracted with CH_2Cl_2 (3x25 mL). The combined organic layers were washed with H_2O (2x50 mL) and $Na_2S_2O_3$ 5 % solution in water (2x50 mL) and dried over anhydrous sodium sulfate. Concentration of solvents affords crude 2-iodocycloheptanone which was further purified by reduced pressure (64ºC,~10^{-3} mm Hg) distillation (4.6 mmol, 1.1 g, 92 %).

Tandem oxidation-halogenation reaction:

Cyclododecanol (5 mmol, 1 equiv, 0.92 g), NaI (5.25 mmol, 1.05 equiv, 0.78 g) and H_2O (40 mL) were placed in a 100 mL round-bottoned flask which was cooled in an ice-water bath. Amberlyst-15-wet® (2.5 g) and H_2O_2 33 % solution (0.1 mol, 20 equiv, 10 mL) were sequentially added and the resulting mixture was heated in an oil bath (60ºC) over 16 h. The mixture was then allowed to cool and the solid resin was recovered upon filtration and washed with CH_2Cl_2 (2x5 mL). The filtrate was transferred to a separation funnel and the aqueous phase was further extracted with CH_2Cl_2 (4x25 mL). The combined organic layers were sequentially washed with H_2O (2x50 mL), $Na_2S_2O_3$ 5 % solution in water (2x50 mL) and H_2O (2x50 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by column chromatography (hexane/CH_2Cl_2:3/1) gives rise to 2-iodocyclododecanone (4.5 mmol, 1.4 g, 90 %); m.p. = 50-53ºC (from pentane) [(lit. 52-52.5ºC)].[1]

1 G. M. Rubbottom, R. C. Mott, H. D. Juve, Jr., *J. Org. Chem.* **1981**, *46*, 2717.