SUPPORTING INFORMATION

Catalyst-free conjugate addition of thiols to α,β -unsaturated carbonyl compounds in water

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Entry 10, Table 1, ^1H NMR

[illegible]

Entry 12, Table 1, ^1H NMR

Entry 12, Table 1, ^{13}C NMR

Entry 12, Table 1, IR

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*** Mass Spectrum ***

PKNO : 1 Peak # : 35 Ret. Time : 7.000
Scan # : 553
Base Peak : 54 (256838)

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Entry 20, Table 1, IR

Entry 20, Table 1, MS

Experimental

General details

The ^1H and ^{13}C NMR spectra were recorded on 300 MHz spectrometer in CDCl_3 using TMS as internal standard. The IR spectra were recorded as KBr pellets for solid samples and neat for liquid samples. The reactions were monitored by TLC (silica gel-G). MS spectral data were recorded on EI and MALDI-TOF-TOF. Evaporation of solvents was performed at reduced pressure, using a rotary evaporator. Solid products were purified by recrystallization from MeOH and chromatographic purification (EtOAc:Hexane; 3:97) was done in case of liquid products.

Representative procedure for 3-Phenylthiocyclohexan-1-one¹ (entry 1, table 1):

Cyclohexenone (0.24 g, 2.5 mmol) in water (5 mL) was treated with thiophenol (0.303 g, 2.75 mmol, 1.1 equiv) under magnetic stirring at room temperature (30-35°C) till complete consumption of the starting material (5 min: TLC, IR). The reaction mixture was extracted with EtOAc (3 $\times$ 10 mL). The combined EtOAc extracts were dried (Na_2SO_4) and concentrated under reduced pressure to afford an oil which on passing through a column of silica-gel and elution with EtOAc-hexane afforded β -phenylthiocyclohexanone (0.464 g, 90%) as colorless oil, identical (IR, NMR and MS) with an authentic sample. Colorless oil, yield 90%; ^1H NMR (CDCl_3 , 300 MHz) δ : 1.68-1.74 (m, 2H), 2.07-2.14 (m, 2H), 2.26-2.39 (m, 3H), 2.63-2.69 (m, 1H), 3.40-3.45 (m, 1H), 7.23-7.32 (m, 3H), 7.39-7.42 (m, 2H).

The remaining reactions were carried out following this general procedure. The physical data (mp, IR, NMR and MS) of all reported compounds were identical with those of the literature reports.

3-(4-Methylphenylthio)-cyclohexan-1-one² (entry 2, table 1): Colorless oily liquid, yield 90%; ^1H NMR (CDCl_3 , 300 MHz) δ : 1.62-1.75 (m, 2H), 2.06-2.13 (m, 2H), 2.20-2.37 (m, 6H), 2.60-2.67 (m, 1H), 3.30-3.34 (m, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H).

3-(4-Nitro-phenylsulfanyl)-cyclohexanone (entry 3, table 1): Yellow solid, yield 90%; IR (KBr) ν : 2954, 2926, 1706 cm^{-1} ; ^1H NMR (300 MHz; CDCl_3) δ : 1.89-1.91 (m, 2H), 2.16-2.50 (m, 5H), 2.76-2.82 (m, 1H), 3.69-3.76 (m, 1H), 7.41 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz; CDCl_3) δ : 26.5, 33.5, 43.4, 47.0, 49.8, 126.7,

131.7, 147.0, 148.6, 210.1. Calcd for C₁₂H₁₃NO₃S: C, 57.35; H, 5.21; N, 5.57; S, 12.76. Found C, 57.33; H, 5.24; N, 5.56; S, 12.74.

3-Benzylthio-cyclohexan-1-one² (entry 4, table 1): Colorless oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.60-1.74 (m, 2H), 2.06-2.09 (m, 2H), 2.28-2.43 (m, 3H), 2.62-2.68 (m, 1H), 2.92 (br s, 1H), 3.74 (s, 2H), 7.22-7.30 (m, 5H).

3-(2-Furfurylthio)cyclohexan-1-one³ (entry 5, table 1): Colorless oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.65-1.73 (m, 2H), 2.05-2.16 (m, 2H), 2.29-2.41 (m, 3H), 2.65-2.71 (m, 1H), 3.00-3.05 (m, 1H), 3.76 (s, 2H), 6.17 (d, *J* = 3.1 Hz, 1H), 6.29-6.31 (m, 1H), 7.34-7.38 (m, 1H).

3-Ethylthio-cyclohexan-1-one¹ (entry 6, table 1): Colorless oily liquid, yield 95%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.25 (t, *J* = 7.6 Hz, 3H), 1.72-1.78 (m, 2H), 2.13-2.16 (m, 2H), 2.33-2.42 (m, 3H), 2.54-2.61 (m, 2H), 2.67-2.73 (m, 1H), 3.05-3.13 (m, 1H).

Entry 7, Table 1⁴: Oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.70-1.77 (m, 4H), 2.11-2.17 (m, 4H), 2.34-2.42 (m, 4H), 2.68-2.76 (m, 6H), 3.12 (br s, 2H).

Entry 8, Table 1⁴: Colorless oily liquid, yield 80%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.69-1.75 (m, 4H), 1.82-1.87 (m, 2H), 2.12-2.16 (m, 4H), 2.31-2.41 (m, 6H), 2.63-2.73 (m, 6H), 3.06-3.07 (m, 2H).

3-Phenylsulfanyl-cyclopentanone⁵ (entry 9, table 1): Oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.91-1.98 (m, 1H), 2.12-2.30 (m, 3H), 2.36-2.45 (m, 1H), 2.49-2.58 (m, 1H), 3.79-3.87 (m, 1H), 7.19-7.28 (m, 3H), 7.32-7.35 (m, 2H).

3-p-Tolylsulfanyl-cyclopentanone⁶ (entry 10, table 1): Oily liquid; yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.89-1.98 (m, 1H), 2.08-2.23 (m, 2H), 2.27 (s, 1H), 2.29-2.40 (m, 1H), 2.43-2.54 (m, 2H), 3.71-3.79 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H).

3-Benzylsulfanyl-cyclopentanone⁷ (entry 11, table 1): Oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ: 1.87-2.10 (m, 1H), 2.11-2.55 (m, 5H), 3.24-3.29 (m, 1H), 3.76-3.82 (m, 2H), 7.31-7.32 (m, 5H).

3-Ethylsulfanyl-cyclopentanone (entry 12 table 1): Oily liquid, yield 90%; IR (neat) ν: 1745 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ: 1.29 (t, *J* = 7.3 Hz, 3H), 2.16-2.26 (m, 1H), 2.35-2.41 (m, 2H), 2.43-2.51 (m, 2H), 2.56-2.65 (m, 2H), 3.44-3.51 (m, 1H); ¹³C NMR

(CDCl₃, 75 MHz) δ : 14.7, 25.2, 29.8, 37.1, 39.9, 45.7, MS (EI): m/z 144 (M⁺). Anal. Calcd for C₇H₁₂OS: C, 58.29; H, 8.39; S, 22.23, Found: C, 58.31; H, 8.40; S, 22.25.

4-Phenylthio-butan-2-one⁵ (entry 13, table 1): Colorless oil liquid, yield 95%; ¹H NMR (CDCl₃, 300 MHz) δ : 2.10 (s, 3H), 2.72 (t, J = 7.2 Hz, 2H), 3.10 (t, J = 7.1 Hz, 2H), 7.14-7.33 (m, 5H).

4-(4-Methylphenylthio)-butan-2-one⁴ (entry 14, table 1): Colorless oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ : 2.11 (s, 3H), 2.31 (s, 3H), 2.71 (t, J = 7.2 Hz, 2H), 3.07 (t, J = 7.2 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 7.5 Hz, 2H).

4-Benzylthio-butan-2-one⁸ (entry 15, table 1): Colorless oily liquid, yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ : 2.10 (s, 3H), 2.63 (s, 4H), 3.71 (s, 2H), 7.21-7.27 (m, 2H), 7.29 (s, 3H).

4-Ethylthio-butan-2-one³ (entry 16, table 1): Colorless oily liquid, Yield 90%; ¹H NMR (CDCl₃, 300 MHz) δ : 1.25 (t, J = 7.2 Hz, 3H), 2.17 (s, 3H), 2.54 (q, J_{AB} = 14.7 Hz, 2H), 2.74 (s, 4H).

Methyl-3-phenylsulfanylpropanoic acid⁴ (entry 17, table 1): Colorless oil, yield 95%; ¹H NMR (CDCl₃, 300 MHz) δ : 2.62 (t, J = 7.4 Hz, 2H), 3.16 (t, J = 7.3 Hz, 2H), 3.67 (s, 3H), 7.17-7.23 (m, 1H), 7.25-7.31 (m, 2H), 7.34-7.38 (m, 2H).

3-(4-Methylphenylsulfanyl)propionic acid methyl ester (entry 18, table 1): Colorless liquid, yield 95%; IR (neat) ν : 2951, 2923, 1738 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz) δ : 2.31 (s, 3H), 2.58 (t, J = 7.41 Hz, 2H), 3.10 (t, J = 7.41 Hz, 2H), 3.66 (s, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ : 20.9, 29.7, 34.2, 51.7, 129.7, 130.9, 131.2, 136.8, 172.1. MS (EI): m/z = 210 (M⁺). Calcd for C₁₁H₁₄O₂S: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.81; H, 6.70; S, 15.23.

Methyl-3-benzylsulfanylpropanoic acid (entry 19, table 1): Colorless oily liquid, yield 90%; IR (Neat) ν : 1738 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ : 2.50-2.57 (m, 2H), 2.64-2.69 (m, 2H), 3.65 (s, 3H), 3.70 (s, 2H), 7.19-7.27 (m, 1H), 7.29-7.30 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) δ : 26.1, 34.2, 36.1, 51.6, 126.9, 128.4, 128.7, 137.9, 172.1; MS (EI) m/z 210 (M)⁺. Calcd for C₁₁H₁₄O₂S: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.82; H, 6.73; S, 15.24.

3-Ethylsulfanypropionic acid methyl ester (entry 20, table 1): Colorless liquid, yield 80%; IR (neat) ν : 2952, 2928, 1737 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ : 1.26 (t, $J = 7.30$ Hz, 3H), 2.52-2.64 (m, 4H), 2.79 (t, $J = 7.30$ Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 14.5, 25.8, 26.4, 34.5, 51.6, 172.3. MS (EI): $m/z = 148$ (M^+). Calcd for $\text{C}_6\text{H}_{12}\text{O}_2\text{S}$: C, 48.62; H, 8.16; S, 21.63. Found: C, 48.60; H, 8.18; S, 21.64.

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