A Direct Preparation of 6-Methylene-2-cyclohexenones

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Abstract: The reaction of enol silyl ethers with Eschenmoser’s salt, followed by methylation and elimination, provides ready access to 6-methylene-2-cyclohexenones.

Key words: Eschenmoser’s salt, 6-methylene-2-cyclohexenones, enol silyl ethers

In the course of studying tandem reactions on dienones, we needed substituted 6-methylene cyclohexenones 1a–c.1 There are few literature reports of compounds of this class. Wiberg and coworkers prepared 1c by the reaction of ketene with 1,4-bicyclo[2.2.0]hexene.2 Reddy reported the preparation of 1b as a by-product in a transition metal mediated rearrangement.3

Initially, we tried both the Gras methylenation reaction4 and the McMurry methylation reaction5 with cyclohexenone. Although we had employed the latter reaction successfully with substituted cyclohexanones, neither reaction provided 1a. We eventually discovered that the reaction of enol silyl ethers of cyclohexenone with Eschenmoser’s salt6 followed by methylation and elimination afforded good overall yields of the desired products. The overall yields from 3a, 3b,7 and 3c were 65%, 54% and 49%, respectively (Scheme 1).

Dienones 1a–c can be prepared in a one-pot reaction from the corresponding enol silyl ethers.8 The ready availability of these novel cross-conjugated dienones will make possible new pathways to complex bridged- and spiro systems.

General Experimental Procedure

To a cooled solution (0 °C) of Eschenmoser’s salt (1.3 mmol) in CH₂Cl₂ (0.4 M solution) was added the silyl enol ether (1 mmol). After stirring for 24 h at r.t., the reaction mixture was diluted with CH₂Cl₂ (5 mL) and 1 N HCl (6 mL). After 10 min at r.t., a 2 N solution of NaOH was slowly added to the aqueous phase (until pH 14). The aqueous phase was extracted with CH₂Cl₂ (4 × 10 mL) and the combined organic layers were dried (MgSO₄) and concentrated in vacuo to give amine 2, which was dissolved in anhyd MeOH (1 M solution). Mel (1.75 mmol) was added slowly with stirring at 0 °C. The resulting solution was warmed to r.t. and stirred for 1 h to give the ammonium salt as a white precipitate. After removing the solvent and the excess Mel, the crude salt was dissolved in H₂O (10 mL) and Et₂O (10 mL). To the solution of salt was added NaHCO₃ (4.5 mmol) and the reaction was stirred vigorously for 2 h at r.t. The aqueous layer was extracted with Et₂O (3 × 20 mL) and the combined organic layers were dried (MgSO₄) and concentrated in vacuo. Further purification by short path column chromatography on silica gel (hexane–Et₂O = 10:1–5:1) gave compound 1 as a colorless volatile oil.

6-Methylene Cyclohexenone (1a)

Rᵣ = 0.35 (hexane–Et₂O, 2:1).

1H NMR (400 MHz, CDCl₃): δ = 7.06 (dt, J = 10, 4 Hz, 1 H), 6.15 (d, J = 10 Hz, 1 H), 5.96 (d, J = 1.2 Hz, 1 H), 5.29 (d, J = 1.2 Hz, 1 H), 2.75 (t, J = 6.4 Hz, 2 H), 2.46 (m, 2 H).

13C NMR (100 MHz, CDCl₃): δ = 188.7, 150.7, 142.9, 130.5, 120.1, 31.0, 26.4.


2-Methyl-6-methylene Cyclohexenone (1b)

Rᵣ = 0.62 (hexane–Et₂O, 2:1).

1H NMR (400 MHz, CDCl₃): δ = 6.81 (br s, 1 H), 5.95 (s, 1 H), 5.25 (d, J = 1.6 Hz, 1 H), 2.71 (t, J = 6.4 Hz, 2 H), 2.40 (dd, J = 4.4, 2 Hz, 2 H), 1.85 (d, J = 0.8 Hz, 3 H).

13C NMR (100 MHz, CDCl₃): δ = 189.5, 150.7, 143.5, 136.9, 119.7, 31.7, 26.3, 16.4.

HRMS (EI): m/z [M]+ calcd for C₈H₁₀O: 122.0732; found: 122.0773.

Scheme 1
3-Methyl-6-methylene Cyclohexenone (1c)

R_f = 0.31 (hexane–Et_2O, 2:1).

^1H NMR (400 MHz, CDCl_3): δ = 6.01 (br s, 1 H), 5.96 (d, J = 1.6 Hz, 1 H), 5.27 (d, J = 1.2 Hz, 1 H), 2.73 (tt, J = 6.4, 1.6 Hz, 2 H), 2.38 (t, J = 6 Hz, 2 H), 2.00 (d, J = 0.4 Hz, 3 H).

^13C NMR (100 MHz, CDCl_3): δ = 188.8, 163.0, 142.3, 127.5, 119.1, 31.6, 31.0, 24.8.

HRMS (EI): m/z calcd [M]⁺ for C₈H₁₀O: 122.0732; found: 122.0773.

References