

Synthesis and Photoreactivity of a 2-Pivaloylcyclohex-2-enone†

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2-Pivaloylcyclohex-2-enone **4**, obtained from 2,2-dimethylcyclohexanone in three steps in 70% yield, is converted into tetrahydrobenzo[*c*]furan-4-one **6** on irradiation (254 nm) in propan-2-ol.

2-Acylcyclohex-2-enones should represent valuable synthons, *e.g.* as Michael acceptors.^{1,2} Unfortunately the few known compounds, all *acetyl*cyclohexenones, are unstable as they readily isomerize to dienolic tautomers in the presence of acid or base.^{2–5} Here we report on the synthesis of a non-enolizing 2-pivaloylcyclohexenone and on its photochemical conversion to a (novel) tetrahydrobenzo[*c*]furan-3-one.

Treatment of 2,2-dimethylcyclohexanone (**1**)⁶ with lithium diethylamide (LDA) and pivaloyl cyanide⁷ gives a 1,3-diketone **2**, which on reaction with Br₂ in boiling CCl₄ affords the bromodiketone **3**. Dehydrobromination of **3** to **4** is achieved with Li₂CO₃ in DMF at 130 °C. The overall yield of 6,6-dimethyl-2-(2,2-dimethylpropanoyl)cyclohex-2-enone (**4**) from **1** is 60%. The fact that the olefinic hydrogen of **4** resonates at almost identical chemical shift as that of 2,6,6-trimethylcyclohex-2-enone (6.68 *vs.* 6.62 ppm in CDCl₃) indicates that the (exocyclic) pivaloyl group in **4** is not coplanar with the enone double bonds, the range of chemical shifts for corresponding hydrogens in fully delocalized systems, *e.g.* 2-alkylidenecyclohexane-1,3-diones,⁸ 2-acetylcyclohex-2-enone³ or 2-cyano-6,6-dimethylcyclohex-2-enone,⁹ being 7.7–7.6 ppm. Furthermore, while this latter compound in the presence of base readily yields a dimer resulting from Michael-addition⁹ and reacts with (neutral) H₂O₂ in Me₃CN¹⁰ to give an oxabicycloheptanone, **4** is stable towards base and affords 1-pivaloyl-7-oxabicycloheptanone **5** only on classical treatment¹¹ with H₂O₂–NaOH in MeOH. Finally, while the above mentioned cyanocyclohexenone affords cycloadducts on irradiation (350 nm) in the presence of alkenes,^{12,13} no such reaction is observed for **4** in the presence of excess 2,3-dimethylbut-2-ene or isobutene, neither on *n*–*π** (300–350 nm) nor on *π*–*π** (254 nm) excitation. Nevertheless on irradiation with light of 254 nm in propan-2-ol, **4** is converted in > 90% yield into the

1,6,7,7a-tetrahydrobenzo[*c*]furan-4(5*H*)-one **6**. The formation of this novel heterocyclic system most probably involves (a) reductive addition of a solvent molecule to C_β of the enone, *i.e.*, H-abstraction from propan-2-ol by one of the carbonyl oxygen atoms of excited **4** and coupling of the 2-hydroxypropyl radical to the unsubstituted allylic C-atom in the radical pair,¹⁴ followed by (b) cyclization to a 2-hydroxytetrahydrofuran and elimination of water.

Experimental

NMR spectra (Bruker DRX500 spectrometer: ¹H, 500 MHz; ¹³C, 125.77 MHz) were recorded in CDCl₃ as solvent. High-resolution mass spectra were recorded at 70 eV on a 311A (Varian MAT) spectrometer. Photolyses were run in a Rayonet RPR-100 photoreactor equipped with 254 nm lamps.

6,6-Dimethyl-2-(2,2-dimethylpropanoyl)cyclohexanone (2).—A solution of **1** (2.0 g, 15.8 mmol), pivaloyl cyanide (1.93 g, 17.4 mmol) and LDA (1.8 g, 17.4 mmol) in THF (20 ml) was stirred at 0 °C for 90 min. After conventional work-up (hydrolysis, extraction with diethyl ether), subsequent chromatography (SiO₂, pentane–diethyl ether 2:1) afforded 2.8 g (87%) of **2**, mp 70 °C; δ_H 4.19 (dd, *J* 5.6, 12.8 Hz), 2.07 (m, 1H), 1.87 (m, 3H), 1.80 (m, 3H), 1.65 (ddd, *J* 3.5, 13, 13.5 Hz), 1.26 (s, 3H), 1.11 (s, 9H); 1.05 (s, 3H); δ_C 213 (CO), 212 (CO), 53 (CH), 46 (> C <), 45 (> C <), 41 (CH₂), 31 (CH₂), 26, 25 and 25 (CH₃), 21 (CH₂) (Found: M⁺, 210.1621. C₁₃H₂₂O₂ requires M_r, 210.1620).

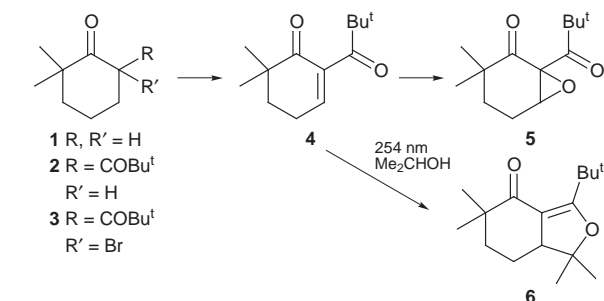
6,6-Dimethyl-2-(2,2-dimethylpropanoyl)cyclohex-2-enone (4).—A solution of **2** (1.0 g, 4.76 mmol) and bromine (0.761 g, 4.76 mmol) in CCl₄ (20 ml) was stirred at 90 °C for 60 min. The solvent was evaporated, and the crude bromoketone **3** and Li₂CO₃ (0.387 g, 5.2 mmol) were stirred in DMF (10 ml) at 120 °C for 5 h. After addition of water, extraction with pentane and evaporation of the solvent, chromatography (SiO₂, pentane–diethyl ether 4:1) afforded 0.702 g (71%) **4**, mp 29–30 °C; δ_H 6.68 (t, *J* 4.1 Hz), 2.44 (dt, *J* 4.1, 6.1 Hz, 2H), 1.87 (t, *J* 6.1 Hz, 2H), 1.16 (s, 6H), 1.15 (s, 9H); δ_C 212 (CO), 202 (CO), 144 (CH), 141 (C-2), 44 (> C <), 42 (> C <), 36 (CH₂), 27 and 24 (CH₃), 23 (CH₂) (Found: M⁺, 208.1464. C₁₃H₂₀O₂ requires M_r, 208.1463).

3,3-Dimethyl-1-(2,2-dimethylpropanoyl)-7-oxabicyclo[4.1.0]heptan-2-one (5).—Treatment of **4** with H₂O₂–NaOH in MeOH according to ref. 11 followed by chromatography (SiO₂, pentane–diethyl ether 4:1) afforded **5** in 33% yield as colourless liquid; δ_H 3.48 (dd, *J* 1, 2 Hz), 2.20 (m, 1H), 2.10 (m, 1H), 1.81 (ddd, *J* 5, 13, 13.5 Hz), 1.40 (ddd, *J* 2, 5, 13 Hz), 1.20 (s, 9H), 1.13 (s, 3H), 1.12 (s, 3H); δ_C 210 (CO), 207 (CO), 63 (C-1), 59 (CH), 45 and 42 (> C <), 29 (CH₂), 26, 25 and 24 (CH₃), 20 (CH₂) (Found: M⁺, 224.1413. C₁₃H₂₀O₃ requires M_r, 224.1412).

3-(1,1-Dimethylethyl)-1,1,5,5-tetramethyl-1,6,7,7a-tetrahydrobenzo[*c*]furan-4(5*H*)-one (6).—An argon-degassed solution of **4** (0.208 g, 1 mmol) in propan-2-ol (10 ml) was irradiated for 45 h. After evaporation of the solvent, chromatography (SiO₂, pentane–diethyl ether 4:1) afforded 0.101 g (40%) of **6** as a colourless oil; δ_H 2.98 (dd, *J* 5, 12 Hz), 1.71–1.61 (m, 4H), 1.44 (s, 3H), 1.21 (s, 9H), 1.16 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H); δ_C 202 (CO), 175 (C-3), 107 (C-3a), 88 (C-1), 54 (CH), 39 (CH₂), 28, 27.5, 27, 26 and 22 (CH₃), 21 (CH₂) (Found: M⁺, 250.1933. C₁₆H₂₆O₂ requires M_r, 250.1933).

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