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Sequence of bromination of (*E*)-4,4-dimethyl-6-isobutylidenecyclohex-2-en-1-one

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Experimental

Materials and methods

All preparations were carried out in the reagent grade solvents. The progress of all reactions was monitored on Silufol UV-254 plates using ethyl acetate/*n*-hexane as the solvent system. Melting points (mp) were taken in open capillaries on a Stuart melting point apparatus SMP11 and are uncorrected. Elemental analyses were performed on a Vario MICRO cube CHNS/O Elementar. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and Agilent 400-MR spectrometers (at 400 MHz for ^{1}H or 100 MHz for ^{13}C) at 23 C using $CDCl_3$ as a solvent. Chemical shift (δ) values are given in ppm with the TMS (for ^{1}H) or solvent resonance as internal standard; coupling constants (*J*) are given in Hz. IR spectra were recorded on a UR-20 spectrometer, UV spectra – on Specord M-40 spectrometer in EtOH ($1.2 \cdot 10^{-3}$ M).

(*E*)-6-Isobutylidene-4,4-dimethylcyclohex-2-en-1-one (**1**) was synthesized according to the reported procedurte.[1] Colourless oil. R_f 0.64 (benzene/ether 4:1). IR (film), ν, cm^{-1}: 1638, 1685, 1740. NMR ^{1}H, δ, ppm: 1.04 d (6H, $CH\underline{Me}_2$, ^3J 6.7 Hz), 1.14 s (6H, 4-Me), 2.53 dd (2H, CH_2, ^4J 1.7, 0.9 Hz), 2.63 d sept (H, $C\underline{H}Me_2$, ^3J 9.9, 6.7 Hz), 5.96 d (H, H^2, ^3J 10.0 Hz), 6.53 dt (H, H^7, ^3J 9.9, ^4J 1.7 Hz) , 6.71 dt (H, H^3, ^3J 10.0, ^4J 0.9 Hz). NMR ^{13}C-{^{1}H}, δ_C, ppm: 22.08 ($CH\underline{Me}_2$), 26.72 ($\underline{C}HMe_2$), 28.19 (4-Me), 34.26 (C^4), 39.68 (CH_2), 127.73 (C^2), 130.67 (C^6), 145.35 (C^7), 158.90 (C^3), 188.76 (C=O). UV, λ_{max}: 240 nm (lgε 4.01), 267 nm (lgε 3.87).

Compound **1** was first characterized in detail by NMR data.[1] Based on indirect data, the authors thought dienone **1** to be an *E*-isomer. We confirmed this by NMR NOESY1D (see Supplementary information, Figure S1). Irradiation of the methyl group doublets of the isopropyl substituent gives rise to NOEs for the HC^7, C*H*Me$_2$ and HC^5 (the numbering is in accordance with that for Schemes 1 and 2). These data are consistent with the results of our quantum-chemical calculations of the molecule **1** by DFT (B3LYP/6-31G (d, p)), according to which the *E*-isomer is up to 2.5 kJ/mol more stable than the *Z*-isomer. Note that the C^3 and C^7 signal assignments are actually the opposite of those made previously.[1] Our results were verified with a two-dimensional correlation HSQC experiment.

2-Bromo-6-isobutylidene-4,4-dimethylcyclohex-2-en-1-one (**3**). Mp 44.5 °C (pentane), transparent needles. R_f 0.26 (benzene/Et_2O 5:1). IR (Nujol), ν, cm^{-1}: 1605, 1635, 1685. NMR ^1H, δ, ppm: 1.04 d (6H, $CH\underline{Me}_2$, ^3J 6.7 Hz), 1.18 s (6H, 4-Me), 2.56 dd (2H, CH_2, ^4J 1.6, 0.6 Hz), 2.61 d sept. (H, $C\underline{H}Me_2$, ^3J 10.0, 6.7 Hz), 6.63 dt (H, H^7, ^3J 10.0, ^4J 1.6 Hz) , 7.17 t (H, H^3, ^4J 0.6 Hz). NMR ^{13}C-{^1H}, δ_C, ppm 22.06 ($CH\underline{Me}_2$), 27.29 ($\underline{C}HMe_2$), 28.02 (4-Me), 37.19 (C^4), 39.60 (CH_2), 123.56 (C^2), 129.50 (C^6), 147.90 (C^7), 158.84 (C^3), 181.77 (C=O). UV, λ_{max}: 263 nm (lgε 4.05), 284 nm (lgε 3.97). Found, %: C 56.30; H 6.77. $C_{12}H_{17}BrO$. Calculated, %: C 56.03; H 6.61.

2,6-Dibromo-6-(1-bromo-2-methylpropyl)-4,4-dimethylcyclohex-2-en-1-one (**5**). Mp 106 °C (hexane). R_f 0.86 (benzene/Et_2O 5:1). IR (Nujol), ν, cm^{-1}: 268. NMR ^1H, δ, ppm: 1.10 d and 1.12 d (3H, $CH\underline{Me}_2$, ^3J 6.6 Hz), 1.23 s and 1.51 s (3H, 4-Me), 2.44 dd (H, H^5, ^2J 15.9, ^4J 1.7 Hz), 2.64 d sept. (H, $C\underline{H}Me_2$, ^3J 6.6, 1.5 Hz), 3.02 d (H, H^5, ^2J 15.9 Hz), 4.93 d (H, H^7, ^3J 1.5 Hz) , 7.14 d (H, H^3, ^4J 1.7 Hz). NMR ^{13}C-{^1H}, δ_C, ppm: 20.34, 24.02, 26.91, 32.34 ($CH\underline{Me}_2$, 4-Me), 29.47 ($\underline{C}HMe_2$), 35.67 (C^4), 43.59 (CH_2), 64.87 (C^6), 66.22 (C^7), 119.07 (C^2), 158.68 (C^3), 182.61 (C=O). UV, λ_{max}: 268 nm (lgε 3.57). Found, %: C 34.87; H 4.33. $C_{12}H_{17}Br_3O$. Calculated, %: C 34.53; H 4.07.

2-Bromo-6-(1-bromo-2-methylpropyl)-4,4-dimethylcyclohexa-2,5-dien-1-one (**6**). Colourless oil. R_f 0.76 (benzene). IR (film), ν, cm^{-1}: 1610, 1670. NMR ^1H, δ, ppm: 0.98 d and 0.99 d (3H, $CH\underline{Me}_2$, ^3J 6.5 Hz), 1.33 s and 1.34 s (3H, 4-Me), 2.10 octet (H, $C\underline{H}Me_2$, ^3J 6.5 Hz), 5.05 dd (H, H^7, ^3J 6.3, ^4J 0.8 Hz) , 7.07 dd (H, H^5, ^4J 2.8, 0.8 Hz), 7.29 d (H, H^3, ^4J 2.8 Hz). NMR ^{13}C-{^1H}, δ_C, ppm: 19.24, 20.99 ($CH\underline{Me}_2$), 26.34, 33.70 (4-Me), 26.59 ($\underline{C}HMe_2$), 41.11 (C^4), 57.02 (C^7), 122.98 (C^2), 135.92 (C^6), 155.47, 156.12 ($C^{3,5}$), 176.63 (C=O). UV, λ_{max}: 200 nm (lgε 4.01), 254 nm (lgε 4.03). Found, %: C 42.61; H 4.70. $C_{12}H_{16}Br_2O$. Calculated, %: C 42.85; H 4.76.

References

1 H.O. Krabbenhoft, *J. Org. Chem.*, 1979, **44**, 4050.