Organic Chemistry

Alkylation of $\beta$-dicarbonyl compounds with 1,2-dibromocyclohexane

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Alkylation of acetylacetone, ethyl acetoacetate, and diethyl malonate with 1,2-dibromocyclohexane in the presence of $K_2CO_3$ in DMSO occurs only as C-alkylation accompanied by dehydrobromination, whereas a similar reaction of dimedone follows both C- and O-alkylation pathways.

Key words: $\beta$-dicarbonyl compounds, alkylation with 1,2-dibromocyclohexane.

Alkylation of $\beta$-dicarbonyl compounds with $\alpha,\omega$-dibromoalkanes in the $K_2CO_3$--DMSO system has been studied fairly comprehensively. However, no systematic data on the alkylation of $\beta$-dicarbonyl compounds with cyclic dibromides have been reported. This work is devoted to the study of alkylation of some $\beta$-dicarbonyl compounds with 1,2-dibromocyclohexane in the $K_2CO_3$--DMSO system.

Previously, it has been noted that the direction of alkylation of $\beta$-dicarbonyl compounds with $\alpha,\omega$-dibromoalkanes depends both on the structure of the initial $\beta$-dicarbonyl compound and on the number of C atoms in the dibromide. By analogy with published data, it might be expected that alkylation of $\beta$-dicarbonyl compounds with 1,2-dibromocyclohexane in the $K_2CO_3$--DMSO system would give C-mono-, C,C-di-, C,C-cyclo-, O-, and C,O-alkylation products. We found that the alkylation of acyclic $\beta$-dicarbonyl compounds, *viz.*, acetylacetone, ethyl acetoacetate, and diethyl malonate, occurs mainly as C-monoalkylation and gives compounds 1, 3, 5 as the major products and compounds 2, 4, 6 as minor C,C-dialkylation products (Scheme 1).

Scheme 1

The structures of products 1—6 were confirmed by synthesizing them by an alternative route, *i.e.*, by alkylation...
tion of the above-mentioned β-dicarbonyl compounds with 3-bromocyclohexene in the K₂CO₃—DMSO system (Scheme 2).

![Scheme 2]

To elucidate the order in which alkylation and dehydrobromination occur during the reaction of β-dicarbonyl compounds with 1,2-dibromocyclohexane, we studied the behavior of the latter compound under the alkylation conditions (80 °C, 10 h) and found that it remains unchanged. Hence, it can be assumed that the carbocation generated from a dicarbonyl compound under the action of the catalytic system attacks the 1,2-dibromocyclohexene molecule to give the intermediate 2-bromocyclohexyl derivative, which is then debrominated.

Unlike the alkylation of acetylacetone, ethyl acetoacetate, and ethyl malonate, the alkylation of dimedone with 1,2-dibromocyclohexane carried out under the same conditions follows both O- and C-alkylation pathways and affords compounds 7 and 8 in nearly equal yields (Scheme 3).

![Scheme 3]

Thus, the direction of alkylation of β-dicarbonyl compounds with 1,2-dibromocyclohexane in the K₂CO₃—DMSO system depends on the structure of the substrate.

### Experimental

NMR spectra were recorded on an FT-80A spectrometer (80 and 20 MHz for ¹H and ¹³C nuclei, respectively) in CDCl₃ using tetramethylsilane as the internal standard.

The starting 1,2-dibromocyclohexene and 3-bromocyclohexene were obtained by known procedures.³,⁴

General procedure of alkylation. 1,2-Dibromocyclohexene (24.2 g, 0.1 mol) was added to an intensely stirred mixture of a β-dicarbonyl compound (0.1 mol) and calcined potassium carbonate (34.3 g, 0.25 mol) in 30 mL of DMSO. The reaction with 3-bromocyclohexene (16.1 g, 0.1 mol) was carried out in the presence of 21 g (0.15 mol) of K₂CO₃. The reaction mixture was stirred for 10 h at 80 °C, cooled, diluted with water until K₂CO₃ dissolved, and extracted with benzene. The benzene extracts were washed with water and dried with anhydrous CaCl₂. After evaporation of the benzene, the residue was distilled in vacuo.

The reaction of acetylacetone (10 g) and 1,2-dibromocyclohexene gave compounds 1 and 2.

3-(Cyclohex-2-enyl)pentane-2,4-dione (1), yield 13.8 g (76.3%), b.p. 77–79 °C (2 Torr), ν₉07 1.6972, d₁₀0 1.0501.

Found (%): C, 73.09; H, 8.91. C₁₂H₂₀O₂. Calculated (%): C, 73.33; H, 8.89. ¹H NMR, 8: 1.27–1.65 (m, 4 H, 2 CH₂); 1.97 (m, 2 H, CH₂); 2.18 (s, 6 H, 2 CH₃); 3.00 (m, 1 H, CH=); 3.61 (d, 1 H, CH=); 5.18 (d, 1 H, CH=); 5.75 (m, 1 H, CH=).

¹³C NMR, 8: 20.25, 24.49, 26.18, 29.68 (C(sp³) of the cyclohexene ring); 35.18 and 35.24 (2 CH₃); 74.14 (CH=); 126.80 (CH=); 129.42 (CH=); 149.71 (C=O); 149.38 (C=O).

3,3-Di(cyclohex-2-enyl)pentane-2,4-dione (2), yield 2.2 g (8.6%), b.p. 102–103 °C (1 Torr), ν₉07 1.4897, d₁₀0 1.0974.

Found (%): C, 87.42; H, 9.22. C₁₃H₂₄O₂. Calculated (%): C, 87.46; H, 9.23. ¹H NMR, 8: 1.12–1.69 (m, 8 H, 4 CH₂); 1.99 (m, 4 H, CH₂); 2.20 (s, 6 H, 2 CH₃); 3.08 (m, 2 H, 2 CH₂); 5.20 (d, 2 H, 2 CH=); 5.71 (m, 2 H, 2 CH=).

The reaction of acetylacetone (10 g) with 3-bromocyclohexene gave compounds 1 (yield 14.6 g, 81.1%) and 2 (yield 3.1 g, 11.9%), whose characteristics coincided with those given above.

The reaction of ethyl acetoacetate (13 g) and 1,2-dibromocyclohexene gave compounds 3 and 4.

Ethyl 2-(cyclohex-2-enyl)pentane-2,4-dione (3), yield 15.24 g (72.6%), b.p. 97–99 °C (2 Torr), ν₉07 1.4722, d₁₀0 1.0553.

Found (%): C, 68.48; H, 8.33. C₁₂H₂₀O₂. Calculated (%): C, 68.57; H, 8.57. ¹H NMR, 8: 1.25 (t, 3 H, CH₃); 1.27–1.75 (m, 4 H, CH₂); 1.99 (m, 2 H, CH₂); 2.21 (s, 3 H, CH₃); 2.95 (m, 1 H, CH); 3.40 (d, 1 H, CH); 4.21 (q, 2 H, CH₂O); 5.42 (t, 1 H, CH); 5.70 (d, 1 H, CH=); 13C NMR, 8: 13.56 (CH₂); 20.36, 24.48, 26.18, 29.09 (C(sp³) of the cyclohexene ring); 34.44 (CH₃); 34.52 (CH₃); 60.63 (CH₂); 64.61 (CH₂); 126.95 (CH=); 129.01 (CH=); 168.11 (C=O); 168.14 (C=O).

Ethyl 2,2-di(cyclohex-2-enyl)acetoacetate (4), yield 4.5 g (15.5%), b.p. 132–134 °C (2 Torr), ν₉07 1.4850, d₁₀0 1.0303.

Found (%): C, 74.49; H, 8.97. C₁₈H₂₆O₄. Calculated (%): C, 74.49; H, 8.97. ¹H NMR, 8: 1.42 (t, 3 H, CH₃); 1.25–1.79 (m, 8 H, 4 CH₂); 2.00 (m, 4 H, 2 CH₂); 2.30 (s, 3 H, CH₃); 2.99 (m, 2 H, 2 CH₂); 4.25 (q, 2 H, CH₂O); 5.40 (m, 2 H, 2 CH=); 5.70 (d, 2 H, 2 CH=).

The reaction of ethyl acetoacetate and 3-bromocyclohexene gave compounds 3 (yield 16.2 g, 77.1%) and 4 (yield 3.9 g, 13.4%), whose characteristics coincided with those given above.

The reaction of diethyl malonate (16 g) and 1,2-dibromocyclohexene gave compounds 5 and 6.

Diethyl cyclohex-2-enylmalonate (5), yield 17.8 g (74.2%), b.p. 109–111 °C (2 Torr), ν₉07 1.4610, d₁₀0 1.0542.

Found (%): C, 64.03; H, 8.37. C₁₈H₂₆O₄. Calculated (%): C, 64.03; H, 8.33. ¹H NMR, 8: 1.15 and 1.17 (t, 6 H, 2 CH₃); 1.19–1.27 (m, 4 H, 2 CH₂); 2.30 (m, 1 H, CH); 3.22 (d, 1 H, CH=); 4.20 and 4.22 (q, 4 H, 2 CH₂O); 5.57 (d, 1 H, CH=); 5.79 (d, 1 H, CH=). ¹³C NMR, 8: 13.58 and 13.68 (2 CH₂); 20.38, 24.54, 26.22, 34.85 (C(sp³) of the cyclohexene ring); 56.67