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The Deacylation of β-Diketones in the Presence of Copper(II)-β-Diketonates in Methanol[1]

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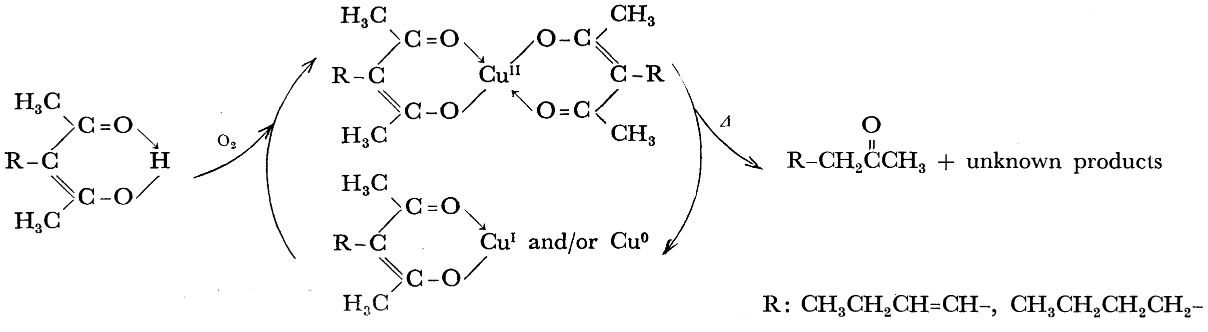
In a previous paper[2] we reported that the copper(II) chelate of 3-α-butenylacetylacetone shows a high activity as an initiator of the radical polymerization of styrene and methyl methacrylate, that the polymerization proceeds *via* the reduction of Cu(II), and that the ligand is bound to the polymer chain. Furthermore, it has been found that the copper(II) chelate of 3-*n*-butylacetylacetone shows a moderate activity, while the chelate of acetylacetone, $Cu(acac)_2$, is an inefficient initiator.[2] We now wish to report a novel reaction of these β-diketones catalyzed by their copper(II) chelates.

When 3-α-butenylacetylacetone was heated with its copper(II) chelate in methanol under atmospheric air at 70°C, 4-hepten-2-one was obtained. In the course of the reaction, some metallic copper was precipitated. In the reaction carried out under pure oxygen, however, 4-hepten-2-one was formed without the precipitation of metallic copper. It was found that the copper(II) chelate decomposed in methanol to give 4-hepten-2-one, that metallic copper and/or cuprous oxide was precipitated when the solution was heated, and that the precipitation was delayed by the addition of a free ligand. It has also been reported that when the ligand is added to the metallic copper or cuprous oxide in hot methanol under atmospheric air, the copper(II) chelate is reformed.[3]

The deacylation of 3-α-butenylacetylacetone was very slow in tetrahydrofuran or benzene, and did not occur in the absence of the copper(II) chelate.

When 3-*n*-butylacetylacetone was heated with its copper(II) chelate in methanol, 2-heptanone was obtained. The reaction was slower than that of 3-α-butenylacetylacetone. When acetylacetone was heated with $Cu(acac)_2$ in methanol, however, no reaction occurred.

The experimental results in the present study suggest that the deacylation of β-diketones catalyzed by their copper(II) chelates proceeds *via* the reduction of Cu(II); the following cycle may be considered, although the reaction mechanism is yet unclear. The present reaction seems to be interesting as a new route of forming β,γ-unsaturated ketones.



Experimental

Materials. The 3-α-butenylacetylacetone, the 3-*n*-butylacetylacetone, and their copper(II) chelates were prepared in the way described in a previous paper.[2] The acetylacetone and $Cu(acac)_2$ were G.R.-grade reagents. The solvents were purified by the ordinary method and were distilled before use.

Deacylation of 3-α-butenylacetylacetone. A solution of 3-α-butenylacetylacetone (37 g, 0.24 mol) and its copper(II) chelate (3.6 g, 0.01 mol) in methanol (200 m*l*) was heated under reflux at 70°C for 24 hr, during which period metallic copper was gradually precipitated. The reaction mixture was then subjected to distillation. From the volatile fraction, methanol was recovered. From the second fraction (bp 52—55°C/18 mmHg, n_D^{25} 1.4297, d_4^{25} 0.8423), 4-hepten-2-one (**1**) was obtained in a yield of 31% (8.4 g).

Semicarbazone of **1**, mp 105.5°C; Found: C, 57.32; H, 9.09; N, 24.74%, Calcd for $C_8H_{15}ON_3$: C, 56.78; H, 8.93; N, 24.89%. 2,4-Dinitrophenylhydrazone of **1**, mp 121°C; Found: C, 52.77; H, 5.21; N, 19.45%, Calcd for $C_{13}H_{16}O_4N_4$: C, 53.42; H, 5.52; N, 19.18%. The IR spectrum of **1** showed sharp absorption peaks at 1714 cm^{-1} and 970 cm^{-1}. The former was attributed to the C=O group, and the latter, to the *trans* C=C group. The UV spectrum of **1** showed an absorption at 277 mμ (methanol). The NMR spectrum of **1** showed signals at 9.00 (3H, t, $CH_2C\underline{H}_3$), 7.95 (3H, s, $COC\underline{H}_3$), 7.90 (2H, m, $CH_3C\underline{H}_2CH=$), 6.98 (2H, d, $-C\underline{H}_2-CO-$), and 4.50 (2H, q, CH=CH). The mass spectrum of **1** showed the parent peak at *m/e* 112 and fragment peaks at *m/e* 97 $(CH_2CH=CHCH_2COCH_3)^+$, *m/e* 83 $(CH=CHCH_2COCH_3)^+$, *m/e* 69 $(CH_3CH_2CH=CHCH_2)^+$, *m/e* 55 (CH_3CH_2-

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[1] Paper XVI in a series of "Catalytic Behavior of Metal Chelate Compounds."

[2] K. Uehara, T. Matsumura, T. Nishi, F. Tamura, and N. Murata, *Kogyo Kagaku Zasshi*, **69**, 2027 (1966); K. Uehara, T. Matsumura, Y. Murata, M. Tanaka, and N. Murata, *ibid.*, **72**, 1825 (1969).

[3] K. Uehara, M. Tanaka, and N. Murata, *ibid.*, **70**, 1564 (1967).

CH=CH)$^+$, and m/e 43 $(CH_3CO)^+$.

Deacylation of Copper(II) Chelate of 3-α-Butenylacetylacetone. A 0.1-g portion of the copper(II) chelate of 3-α-butenylacetylacetone was dissolved in 5 m*l* of methanol, and then the mixture was heated under reflux at 70°C for 24 hr, during which period a mixture of metallic copper and cuprous oxide precipitated and the green color of the solution disappeared. After the precipitate had then been filtered off, the methanol was evapolated from the filtrate. The residue was analyzed by gas chromatography. 4-Hepten-2-one was identified by a comparison of its retention time with that of an authentic sample prepared above by means of a Shimadzu GC 4APT gas chromatograph using a silicon gum SE 52 column.

*Deacylation of 3-*n*-Butylacetylacetone.* A solution of 3-*n*-butylacetylacetone (15 g, 0.095 mol) and its copper(II) chelate (1.5 g, 0.006 mol) in methanol (500 m*l*) was heated under reflux at 70°C for 48 hr. The reaction mixture was then subjected to distillation. From the volatile fraction, methanol was recovered. From the second fraction (bp 47—50°C/18 mmHg, n_D^{25} 1.4189, d_4^{25} 0.8394), 2-heptanone (**2**) was obtained in a yield of 4.5% (1.0 g). Semicarbazone of **2**, mp 105.5°C; Found: C, 55.94; H, 9.54; N, 24.17%. Calcd for $C_8H_{17}ON_3$: C, 56.11; H, 10.00; N, 24.55%. The IR, UV, NMR, and mass spectra of **2** were closely analogous to those of an authentic sample of 2-heptanone (G.R.-grade reagent).

Spectral Measurements. The IR spectra were measured as a liquid film by means of a Hitachi Model EPI-S2 infrared spectrometer. The UV spectra were measured using a Hitachi recording spectrophotometer, Model EPS-3T. The NMR spectra were determined by means of a Hitachi Model R-20 spectrometer. Tetramethylsilane was used as the internal standard, and CCl_4 was used as the solvent. The mass spectra were recorded on a Hitachi Model RMU-6E mass spectrometer under the following conditions: chamber voltage 80 V, total emission current 80 μA, vacuum 2×10^{-6} mmHg, sample temp. 160°C.