Introduction of oxygen-functions into the $\alpha$ position of $\beta$-diketones, 8:\footnote{1}

Acyloxylation of copper(II) acetylacetonate with diacyl peroxides.

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Replacement of only one hydrogen of the methylene group of 2,4-pentanedione (1) (acetylacetone) can be obtained by conversion of copper(II) acetylacetonate (2) with peroxycarboxylic acids \footnote{6} whereas dibenzoylperoxide (3) (DBPO) leads to geminal disubstitution.

Opposite to selective introductions of halogen substituents into organic molecules the corresponding introduction of oxygen substituents instead of hydrogen appears sometimes difficult. Though alkali salts of 1,3-dicarbonyl compounds are easily acyloxylated by means of diacyl peroxides \footnote{2,3}, usually the reaction cannot be stopped at the stage of monoacyloxylation if a second attack is principally possible. On the other hand separation of mixtures of mono- and bisacyloxylation products and their rearrangement products is sometimes difficult. Conversion of 2 with DBPO leads to the same result\footnote{4,5,6}. However, application of peroxycarboxylic acids \footnote{6} instead of DBPO leads to selective monoacyloxylation of 2 yielding the corresponding copper(II) chelates 7:

\[
\begin{align*}
&\text{CH}_3\text{C}==\text{O} \quad \text{C}==\text{O} \quad \text{CH}_3 \\
&\text{H} - \text{C} - \text{o} \quad \text{Cu} - \text{C} - \text{H} \\
&\text{H}_2\text{C} - \text{C} - \text{O} \quad \text{O} == \text{C} - \text{H} \\
\end{align*}
\]

This selective monoacyloxylation appears rather surprising as even enaminones from 1,3-diketones and primary amines\footnote{7} or secondary amines\footnote{8} suffer simultaneous mono- and bisacyloxylation. Unfortunately, hydrogenolysis of benzylester 7b to yield copper(II) chelate 8 does not occur as in the enaminone conversions\footnote{7,8}. Thus, an in situ generation of a reductone: copper 2:1-complex instead of the usual 1:1-complexes fails by this way.

Melting points are determined by means of a Fus-O-mat (Heraeus), IR spectra are recorded on a Beckman IR-33. Elemental analyses are obtained by the method of Walisch\footnote{10},

\[
\begin{align*}
&\text{Cu} - \text{OCOC}_6\text{H}_5 \quad (44\%) \\
&\text{CH}_3\text{COCH}_2\text{COCH}_3 \quad (44\%) \\
&\text{H}_2\text{Pd-C} (10\%) \\
&\text{CH}_3\text{OH, r.t.} \\
&\text{OH-C}==\text{O} \quad \text{O} == \text{C} - \text{H} \\
&\text{H}_2\text{C} - \text{C} - \text{O} \quad \text{O} == \text{C} - \text{H} \\
\end{align*}
\]
peroxydicarbonates 6 are prepared according to ref.11). DC controls of the reaction mixtures are carried out using DC foils Alugram Sil G/UV254 from Macherey and Nagel.

3.3-Bis(benzoyloxy)pentane-2,4-dione (5): A solution of DBPO (3) (4.8 g, 20 mmol) in absol. chloroform (50 ml) was added slowly under dry nitrogen to a boiling solution of copper(II) acetylacetonate (2) (2.6 g, 10 mmol) in absol. chloroform (20 ml). No peroxide was detectable after refluxing the mixture for 20 h. The solvent was removed i. vac. and the residue was treated with ethyl acetate leaving copper(II) benzoate (4) undissolved. After filtration the ethyl acetate extract was evaporated i. vac. until crystallization occurred. Crystallization was completed overnight at -18°C, yield 1.5 g (44%) 5, colorless crystals, m.p. 141-142°C (ref.6) 142-143°C.

Copper(II) 3-(methoxycarbonyloxy) pentane-2,4-dionate (7a): A solution of dimethyl peroxydicarbonate (6a) (20 mmol, iodometric determination) in dichloromethane - prepared according to ref.11) - was added dropwise to a boiling solution of copper(II) acetylacetonate (2) (2.6 g, 10 mmol) in dichloromethane (50 ml) and boiling was continued until a peroxide test proved to be negative (15-20 h). The solvent was evaporated after cooling and the resulting crystals of 7a were recrystallized from ethyl acetate and dried in a desiccator over potassium hydroxide; yield 2.1 g (52%) 7a, blue-grey crystals, m.p. 195°C.

C_{14}H_{18}O_{10}Cu (409.8) Calc. 41.03 H 4.43 Found 41.10 H 4.35; IR (KBr): ν = 1750 (C=O); 1595, 1485 (O=C-C=C); 1160 (C-O-C) cm^{-1}.

Copper(II) 3-(benzyloxycarbonyloxy) pentane-2,4-dionate (7b): According to the preceding prescription copper(II) acetylacetonate (2) (2.6 g, 10 mmol) in dichloromethane (50 ml) and a solution of dibenzyl peroxydicarbonate 6b (20 mmol) in dichloromethane afford 2.7 g (48%) blue-grey crystals of 7b, m.p. 205°C. This substance was identical with a species which had been obtained earlier by conversion of the monobenzyloxycarbonyloxylation product of 1 (independently formed together with the corresponding bisacyloxylation product from the sodium salt of 1) with copper(II) acetate, m.p. 206°C after recrystallization from ethanol. C_{26}H_{26}O_{10}Cu (562.0) Calc. C 55.56 H 4.66 Found C 55.60 H 4.61; IR (KBr): ν = 1745 (C=O); 1590, 1485 (O=C-C=C) cm^{-1}.

We are indebted to Thomas Heisel for graphical processing.

(5) Beck, H., Diplomarbeit, Universität Saarbrücken, 1983: 44% yield, m.p. 141- 142°C; ref. 6; m.p. 142-143 °C).