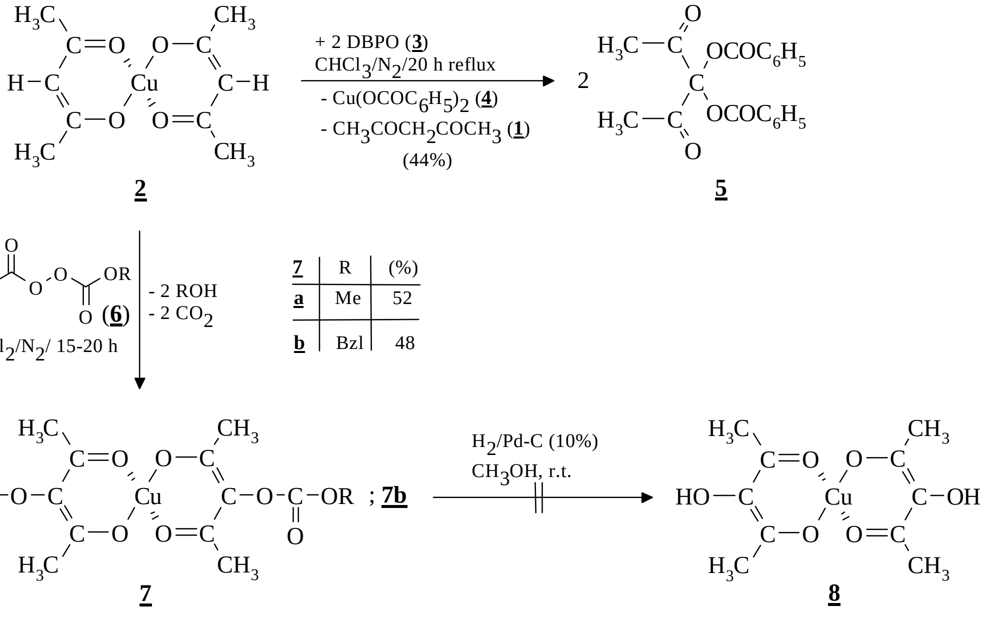
Introduction of oxygen-functions into the α position of ß-diketones, 8[1)]: Acyloxylation of copper(II) acetylacetonate with diacyl peroxides.

Kurt Schank*, Horst Beck
Fachrichtung 11.2 Organische Chemie der Universität des Saarlandes, D-66041 Saarbrücken

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 peroxydicarbonates **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[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[4)5)6)]. However, application of peroxydicarbonates **6** instead of DBPO leads to selective monoacyloxylation of **2** yielding the corresponding copper(II) chelates 7:



7	R	(%)
a	Me	52
b	Bzl	48

This selective monoacyloxylation appears rather surprising as even enaminones from 1.3-diketones and primary amines[7)] or secondary amines[8)] suffer simultaneous mono- and bisacyloxylations. Unfortunately, hydrogenolysis of benzylester **7b** to yield copper(II) chelate **8** does not occur as in the enaminone conversions[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 spetra are recorded on a Beckman IR-33. Elemental analyses are obtained by the method of Walisch[10)], peroxydicarbonates **6** are prepared according to ref.[11]. DC controls of the reaction mixtures are carried out using DC foils Alugram Sil G/UV$_{254}$ 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**) (2.6g, 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): $\nu = 1750$ (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[11] afforded 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[12].

$C_{26}H_{26}O_{10}Cu$ (562.0) Calc. C 55.56 H 4.66 Found C 55.60 H 4.61; IR (KBr): $\nu = 1745$ (C=O); 1590, 1485 (O=C-C=C) cm^{-1}.

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