138. *The Preparation of Some β-Diketones from Copper Complexes and Nitrobenzoyl Chlorides.*

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The copper complexes of pentane-2,4-dione and 1-phenyl- and 1-*p*-methoxyphenyl-butane-1,3-dione with nitrobenzoyl chlorides in chloroform give triketones which can be de-acetylated to β-diketones; the ethyl acetoacetate copper complex yields β-diketo-esters. For some of these compounds this is the most convenient method of preparation.

For substitution at the methylene group of β-diketones the sodio-derivatives are generally used, the copper complexes having received little attention although reported yields have been good.[1] Only Michael and Carson [2] have studied the reaction of acid chlorides and the copper complexes. It is now clear that the method is simple and gives good yields of pure products.

The pentane-2,4-dione copper complex (I; $R^1 = R^2 = Me$) (0·5 mol.) when shaken with *m*- or *p*-nitrobenzoyl chloride (1 mol.) in chloroform for 12—24 hr. gives the triketone (II; $R^1 = R^2 = Me$) which on treatment with aqueous ammonia [3] and then acidification gives the β-diketone (III; $R^1 = Me$) in good overall yield, though they are difficult to obtain pure by the usual methods [4] whilst boron trifluoride is needed as catalyst to acylate the nitroacetophenones.[5] 1-*o*-Nitrophenylbutane-1,3-dione could not be prepared in this way; the unstable triketone gave only tars on hydrolysis.

$$\begin{array}{lcl} [R^1\cdot CO\cdot CH\cdot CO\cdot R^2]Cu_{0\cdot5} + Ar\cdot COCl & \longrightarrow & R^1\cdot CO\cdot CH(COAr)\cdot COR^2 \ (II) \\ (I) & \longrightarrow & R^1\cdot CO\cdot CH_2\cdot COAr \ (III) \end{array}$$

The 1-phenylbutane-1,3-dione copper complex similarly gave the triketones (II; $R^1 = Ph$, $R^2 = Me$, Ar = 1-*m*- or 1-*p*-$NO_2\cdot C_6H_4$), but only the *p*-compound was purifiable. The grouping $CH(CO)_3$ caused strong infrared absorption between 1639 and 1530 cm.$^{-1}$, in

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[1] Vaillant, *Compt. rend.*, 1894, **119**, 647; Barry, Finar, and Simmonds, *J.*, 1956, 4974; Morgan, Drew, and Barker, *J.*, 1922, **121**, 2456.

[2] Michael and Carson, *J. Amer. Chem. Soc.*, 1936, **58**, 353.

[3] Cf. Claisen, *Annalen*, 1893, **277**, 203.

[4] Simmonds, Thesis, London, 1957.

[5] Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 2742.

keeping with the suggestion by Birch *et al.*[6] that this may be characteristic of such compounds. There was also considerable hydroxyl absorption from 3650 to 3330 cm.$^{-1}$, and a carbonyl peak at 1653 cm.$^{-1}$. The crude triketones, however, were de-acetylated nearly quantitatively by 30% ethanolic sulphuric acid [7] to the diones (III) which were characterized by conversion into 5-*m*-nitrophenyl-1,3-diphenylpyrazole [8] and *p*-nitrodiphenylisoxazole [9] respectively. Again no satisfactory product was obtained with *o*-nitrobenzoyl chloride.

1-*p*-Nitrophenylbutane-1,3-dione copper complex did not condense with *p*-nitrobenzoyl chloride even in boiling nitrobenzene, but 1-*p*-methoxyphenylbutane-1,3-dione copper complex gave the triketone (III; $R^1 = p\text{-MeO}\cdot C_6H_4$, $Ar = p\text{-NO}_2\cdot C_6H_4$). The ethyl acetoacetate copper complex gave excellent yields of acyl derivatives with *o*-, *m*-, and *p*-nitrobenzoyl chloride; here 1 mol. of each reactant was used, the greater acidity of the diketo-nitro-ester leading to the copper complex of the ethyl nitrobenzoylacetoacetate.

EXPERIMENTAL

*Preparations from Pentane-*2,4-*dione Copper Complex.*—The complex (1 mol.) in dry chloroform (10% solution) was shaken with the appropriate nitrobenzoyl chloride in chloroform (10% solution) at room temperature for 12—24 hr. The precipitated cupric chloride was shaken with 3N-sulphuric acid until the extract was colourless. The chloroform layer was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was heated for 10—15 min. with 3N-ammonia, then acidification with 3N-hydrochloric acid gave 1-*m*- (92%), m. p. 115—116° (from methanol), and 1-*p*-nitrophenylbutane-1,3-dione (82%), m. p. 112—114° (from methanol), the identities being confirmed by mixed m. p.s.

Preparations from 1-*Phenylbutane*-1,3-*dione Copper Complex.*—A similar procedure afforded a greenish solution containing precipitated cupric chloride and a little triketone copper complex, not in solution. Treatment with 5N-hydrochloric acid and evaporation of the chloroform layer gave 2-acetyl-1-*m*-nitrophenyl-3-phenylpropane-1,3-dione, spontaneously deacetylated in air and therefore not purifiable, and 2-*acetyl*-1-p-*nitrophenyl*-3-*phenylpropane*-1,3-*dione* (52%), m. p. 121—122° (from ethanol) (Found: C, 65·8; H, 4·1; N, 4·4. $C_{17}H_{13}O_5N$ requires C, 65·6; H, 4·2; N, 4·5%). 2-Acetyl-1-*p*-methoxyphenyl-3-*p*-nitrophenylpropane-1,3-dione (55%), obtained similarly, also underwent spontaneous decomposition.

Hydrolysis of the Triketones.—The triketones were heated with excess of 30% ethanolic sulphuric acid for 10—15 min. at 100°, reaction being complete when the odour of ethyl acetate had disappeared. Cooling gave 1-*m*-nitrophenyl-3-phenylpropane-1,3-dione, m. p. 135—136° (identified by conversion with phenylhydrazine in acetic acid into 5-*m*-nitrophenyl-1,3-diphenylpyrazole, m. p. 131—132°), 1-*p*-nitrophenyl-3-phenylpropane-1,3-dione, m. p. 159—160° (identified by conversion with hydroxylamine into the *p*-nitrodiphenylisoxazole, m. p. 220—221°), and 1-p-*methoxyphenyl*-3-p-*nitrophenylpropane*-1,3-*dione*, m. p. 180° (from benzene) (Found: C, 64·5; H, 4·1; N, 4·5. $C_{16}H_{13}O_5N$ requires C, 64·2; H, 4·3; N, 4·7%), which was strongly fluorescent. The yields from these hydrolyses were nearly quantitative.

Preparations from Ethyl Acetoacetate Copper Complex.—Ethyl acetoacetate copper complex (1 mol.) and the nitrobenzoyl chloride (1 mol.) gave the diketo-ester as the copper complex. Ethyl 2-*p*-nitrobenzoylacetoacetate copper complex was insoluble in the chloroform and was filtered off, washed with water to remove cupric chloride, and then with ethanol and ether. Shaking the solid with ether and 3N-sulphuric acid, and evaporating the dried ether layer, gave ethyl *p*-nitrobenzoylacetoacetate (72%), m. p. 49—50° (from methanol) (identified by mixed m. p. and comparison of its infrared spectrum with that of an authentic specimen). The *o*- and the *m*-complex, being soluble in the chloroform, were decomposed by shaking the reaction mixture with 3N-sulphuric acid until the aqueous layers were colourless. The chloroform layer, containing a mixture of ethyl nitrobenzoylacetoacetate and ethyl acetoacetate, was shaken with cupric acetate solution (pH 2), and the copper complex of the nitro-ester was filtered off, washed free from ethyl acetoacetate with ethanol and ether, and decomposed in the usual way.

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[6] Birch, *J.*, 1951, 3026; Birch and Elliott, *Austral. J. Chem.*, 1956, **9**, 95; Birch and English, *J.*, 1957, 3805.

[7] Cf. Hassall, *J.*, 1948, 51.

[8] Bodforss, *Ber.*, 1916, **49**, 2804.

[9] Wieland, *Ber.*, 1904, **37**, 1151.

Evaporation of the ether layer gave ethyl *m*-nitrobenzoylacetoacetate (72%), m. p. 73—75° (from methanol) (converted by boiling 5% phosphoric acid in 6 hr. into 1-*m*-nitrophenylbutane-1,3-dione (infrared spectrum identical with that of an authentic specimen), and ethyl *o*-nitrobenzoylacetoacetate (72%), an oil, converted by phenylhydrazine in acetic acid into ethyl 3-methyl-1,5-diphenylpyrazole-4-carboxylate, m. p. and mixed m. p. 146°.

The author thanks Mr. Pyszora of the National College of Rubber Technology for the spectroscopic data.

THE NORTHERN POLYTECHNIC, HOLLOWAY, LONDON, N.7.

[*Received, July* 14*th*, 1959.]