# 891. *Acylation of Metal Chelates. Part II.*[1] *The Anomalous Behaviour of Copper*(II) *Chelates.*

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Copper(II) chelates of β-diketones have been shown to react with acyl chlorides to give initially the chlorocopper(II) chelate of the diketone. This then reacts with a further molecule of acyl chloride to give either the chlorocopper(II) chelate of the *C*-acylated diketone or copper(II) chloride together with the *C*-acylated diketone and/or the enol ester of the diketone.

METAL chelates of β-diketones react with acyl chlorides to give the metal chloride together with triacylmethane and/or the enol ester of the diketone.[1, 2] Copper(II) chelates, however, exhibit two anomalies: first, the frequent formation of cuprous chloride [2, 3] and, secondly, the occasional isolation of a complex which contains copper, chlorine, and an organic residue.[3] The present work involves a closer examination of these reactions.

Copper(II) chelates of a variety of β-diketones react with acyl chlorides in refluxing toluene or cyclohexane to give, in every instance, hydrogen chloride and copper(II) chloride, independently of the ratio of triacylmethane to enol ester formed as the organic product.[2] In these reactions copper(II) chloride is formed initially and this then reacts with substances from which hydrogen atoms can be readily abstracted, *e.g.*, toluene, cyclohexane, and 9,10-dihydroanthracene, giving copper(I) chloride and hydrogen chloride. Evidence for this is that reactions of copper(II) di-isobutyrylmethane and copper(II) dipivaloylmethane with *p*-nitrobenzoyl chloride in toluene or cyclohexane at room temperature led to copper(II) chloride. This was also obtained by stopping the reaction of copper(II) di-isobutyrylmethane with *p*-nitrobenzoyl chloride in refluxing cyclohexane after five minutes and by performing the reaction in refluxing carbon tetrachloride. The reaction in refluxing carbon tetrachloride in the presence of 9,10-dihydroanthracene gave copper(I) chloride and anthracene. Copper(II) chloride reacts with anthracene, to give 9-chloroanthracene [4] and this was obtained from the reaction of copper(II) dipivaloylmethane and benzoyl chloride in the presence of anthracene.

This represents an over-simplified picture since copper(II) acetylacetone reacted with *p*-nitrobenzoyl chloride in refluxing toluene to give copper(I) chloride and diacetyl-*p*-nitrobenzoylmethane, whilst in toluene at room temperature and in refluxing carbon tetrachloride a copper-containing complex [which is formulated as chlorocopper(II) diacetyl-*p*-nitrobenzoylmethane] and diacetyl-*p*-nitrobenzoylmethane were obtained. This complex

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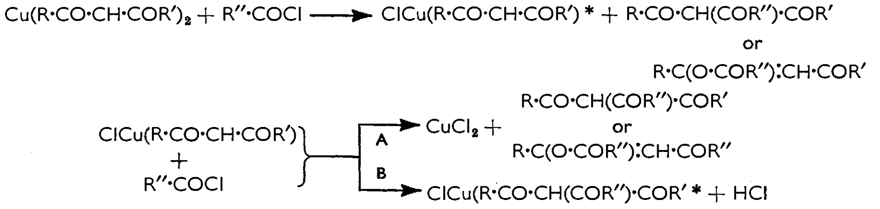
[1] Part I, Murdoch and Nonhebel, *J.*, 1962, 2153.
[2] Hammond and Nonhebel, unpublished work.
[3] Michael and Carlson, *J. Amer. Chem. Soc.*, 1936, **58**, 353.
[4] Nonhebel, *Proc. Chem. Soc.*, 1961, 307.

was also obtained when the reaction in refluxing toluene was stopped after five minutes, indicating a common reaction path. Acid hydrolysis of the complex gave *p*-nitrobenzoylacetone, indicative of the diacetyl-*p*-nitrobenzoylmethyl group. Under similar conditions diacetyl-*p*-nitrobenzoylmethane gave *p*-nitrobenzoylacetone. The infrared spectrum in the 4000—700 cm.$^{-1}$ region was identical with that of the copper chelate of diacetyl-*p*-nitrobenzoylmethane, from which it was differentiated by melting point and solubility. Although it was not possible to obtain a satisfactory analysis because of the difficulty of purifying the complex analysis did support the formulation of the complex as chlorocopper(II) diacetyl-*p*-nitrobenzoylmethane. The infrared spectrum in the 700—200 cm.$^{-1}$ region showed absorption bands characteristic of both copper(II) diacetyl-*p*-nitrobenzoylmethane and copper(II) chloride though the frequencies of the absorptions were somewhat displaced. This indicates that the compound is a true complex and not merely a mixture of copper(II) diacetyl-*p*-nitrobenzoylmethane and copper(II) chloride. It was converted into copper(I) chloride and diacetyl-*p*-nitrobenzoylmethane when heated in toluene, which supports the fact that it is an intermediate in the reaction in toluene leading to copper(I) chloride.

In chloroform at room temperature, copper(II) acetylacetone and *p*-nitrobenzoyl chloride gave a second complex, which is formulated as chlorocopper(II) acetylacetone because its infrared spectrum in the 4000—700 cm.$^{-1}$ region is similar to that of copper acetylacetone and because in the 700—200 cm.$^{-1}$ region there are absorption bands characteristic, though somewhat displaced, of both copper(II) acetylacetone and copper(II) chloride. Chlorocopper(II) acetylacetone, a green material insoluble in chloroform, disproportionated in presence of water to give copper(II) acetylacetone (a blue chloroform-soluble substance) and copper(II) chloride. Heating the chlorocopper complex in acetylacetone gave copper(II) acetylacetone and hydrogen chloride. Michael and Carlson,[3] and Wislicenus,[5] have suggested similar types of complexes.

On the basis of these results the following reaction scheme is suggested:



$$\mathrm{Cu(R{\cdot}CO{\cdot}CH{\cdot}COR')_2 + R''{\cdot}COCl \longrightarrow ClCu(R{\cdot}CO{\cdot}CH{\cdot}COR')^{*} + R{\cdot}CO{\cdot}CH(COR''){\cdot}COR'\ \text{or}\ R{\cdot}C(O{\cdot}COR''){:}CH{\cdot}COR'}$$

$$\left.\begin{array}{c}\mathrm{ClCu(R{\cdot}CO{\cdot}CH{\cdot}COR')}\\ +\\ \mathrm{R''{\cdot}COCl}\end{array}\right\}\begin{array}{l}\xrightarrow{\mathrm{A}}\mathrm{CuCl_2 + R{\cdot}CO{\cdot}CH(COR''){\cdot}COR'\ \text{or}\ R{\cdot}C(O{\cdot}COR''){:}CH{\cdot}COR''}\\ \xrightarrow{\mathrm{B}}\mathrm{ClCu(R{\cdot}CO{\cdot}CH(COR''){\cdot}COR'^{*} + HCl}\end{array}$$

* The chlorocopper(II) chelates probably have a dimeric or polymeric structure, as 3-co-ordinate copper is unlikely.

Metal chelates react by co-ordination of the acyl halide to the central metal atom.[1,2] In the case of copper(II) chelates it appears that only one molecule of acyl halide co-ordinates to the copper. Copper chelates form monosolvates with pyridine and quinoline in which the co-ordination number of copper is five.[6,7] Chelates of other bivalent metals in which the co-ordination number of the metal is four or six show no evidence for this type of complex formation. The chlorocopper(II) chelate of the diketone reacts by path B to give the chlorocopper(II) chelate of the triacylmethane if the latter is insoluble; otherwise reaction proceeds by path A, giving copper(II) chloride. That the solubility of the chlorocopper(II) triacylmethane is important in determining the reaction path is borne out by the results shown in the Table. Copper chelates with branched alkyl groups

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[5] Wislicenus, *Ber.*, 1898, **31**, 3151.
[6] Bradley and Robinson, *J.*, 1926, 2356.
[7] Morgan and Moss, *J.*, 1914, 189.

Reactions of copper chelates of β-diketones with *p*-nitrobenzoyl chloride at room temperature.

| Metal chelate | Solvent | Product |
|---|---|---|
| $Cu(AA)_2$ * | Toluene | Chlorocopper(II) diacetyl-*p*-nitrobenzoylmethane |
| $Cu(DIBM)_2$ * | Cyclohexane | Copper(II) chloride |
|  | Toluene | Copper(II) chloride |
|  | $CCl_4$ | Copper(II) chloride |
| $Cu(DNBM)_2$ * | Cyclohexane | Chlorocopper(II) di-n-butyryl-*p*-nitrobenzoylmethane |
|  | Toluene | Copper(II) chloride |
|  | $CCl_4$ | Copper(II) chloride |
| $Cu(BIBM)_2$ * | Cyclohexane | Chlorocopper(II) benzoylisobutyryl-*p*-nitrobenzoylmethane |
|  | Toluene | Copper(II) chloride |
| $Cu(BNBM)_2$ * | Cyclohexane | Chlorocopper(II) benzoyl-n-butyryl-*p*-nitrobenzoylmethane |
|  | Toluene | Chlorocopper(II) benzoyl-n-butyryl-*p*-nitrobenzoylmethane |
| $Cu(BA)_2$ * | Cyclohexane † | Chlorocopper(II) acetyl-*p*-nitrodibenzoylmethane |

* AA = Acetylacetone; DIBM = di-isobutyrylmethane; DNBM = di-n-butyrylmethane; BIBM = benzoylisobutyrylmethane; BNBM = benzoyl-n-butyrylmethane; BA = benzoylacetone.

† Reaction in refluxing cyclohexane.

are more soluble than those with linear alkyl groups, and these are more soluble than those with phenyl groups. This is also true of the chelates of the *C*-*p*-nitrobenzoylated diketones. The identity of the chlorocopper(II) triacylmethanes was demonstrated in the same way as for chlorocopper(II) diacetyl-*p*-nitrobenzoylmethane.

*p*-Nitrobenzoyl chloride was chosen for acylations because it reacted at room temperature.

## EXPERIMENTAL

Infrared spectra were determined for Nujol mulls and ultraviolet spectra for ethanol solutions, unless otherwise stated.

*Preparation of Copper Chelates.*—These were prepared by shaking an ethanol solution of the diketone with an aqueous solution of copper acetate (cf. ref. 1).

*Reaction of Copper Dipivaloylmethane and* p-*Nitrobenzoyl Chloride in Toluene at Room Temperature.*—A mixture of copper dipivaloylmethane (0·43 g., 0·001 mole) and *p*-nitrobenzoyl chloride (0·37 g., 0·002 mole) in toluene (100 ml.) was left at room temperature for two weeks. The precipitate was filtered off and washed with hot toluene to dissolve any organic product. A brown residue (0·13 g.) of copper(II) chloride remained. The combined filtrate and washings were evaporated; the residue crystallised from methanol as white flat needles (0·60 g.) of *p*-nitrobenzoyldipivaloylmethane, m. p. and mixed m. p. 192°.

*Reaction of Copper Dipivaloylmethane and Benzoyl Chloride in Benzene in Presence of Anthracene.*—Copper dipivaloylmethane (0·6 g.), benzoyl chloride (5 ml.), and anthracene (5 g.) in benzene (100 ml.) were refluxed for 24 hr. Copper(I) chloride was filtered off from the hot mixture and the filtrate was evaporated. The residue was extracted with hot light petroleum (b. p. 40—60°). Anthracene crystallised from these extracts and the filtrate was then chromatographed on alumina. Elution with light petroleum (b. p. 40—60°) gave 9-chloroanthracene (0·9 g.), m. p. and mixed m. p. 107°. The insoluble portion of the residue crystallised from methanol in needles of benzoyldipivaloylmethane, m. p. and mixed m. p. 177°.

*Reaction of Copper Di-isobutyrylmethane and* p-*Nitrobenzoyl Chloride.*—(*a*) *In cyclohexane at room temperature.* Copper di-isobutyrylmethane (1·36 g.) and *p*-nitrobenzoyl chloride (1·36 g.) in cyclohexane (70 ml.) were left at room temperature for 48 hr. The brown precipitate of copper(II) chloride (0·45 g.) was filtered off and the filtrate evaporated to dryness. The residue gave fine white needles [from light petroleum (b. p. 60—80°)] of *di-isobutyryl*-p-*nitrobenzoylmethane* (1·90 g.), m. p. 109—110° (Found: C, 62·5; H, 6·4; N, 4·6. $C_{16}H_{19}NO_5$ requires C, 62·9; H, 6·3; N, 4·6%), $\nu_{max.}$ 1660 cm.$^{-1}$ (C=O). This, with aqueous alcoholic copper acetate, gave *copper di-isobutyryl*-p-*nitrobenzoylmethane*, m. p. 215—217°, crystallising from methanol as green prisms (Found: C, 56·85; H, 5·8; Cu, 9·4; N, 3·8. $C_{32}H_{38}CuN_2O_{10}$ requires C, 57·2; H, 5·4; Cu, 9·5; N, 4·2%), $\nu_{max.}$ 1655 (C=O) and 1565 cm.$^{-1}$ (chelate C=O).

(*b*) *In refluxing cyclohexane.* Copper di-isobutyrylmethane (1.36 g.) and *p*-nitrobenzoyl chloride (1·36 g.) in cyclohexane (100 ml.) were refluxed for 30 min. Copper(I) chloride was filtered off from the hot solution and the filtrate gave di-isobutyryl-*p*-nitrobenzoylmethane.

The reaction was repeated with a reaction time of 5 min. The brownish solution was cooled, giving copper(II) chloride (0·4 g.) and di-isobutyryl-*p*-nitrobenzoylmethane.

(*c*) *In toluene.* Copper di-isobutyrylmethane (0·74 g.) and *p*-nitrobenzoyl chloride (0·74 g.) in toluene (50 ml.) were left at room temperature for 48 hr. before removal of copper(II) chloride (0·22 g.). The filtrate gave di-isobutyryl-*p*-nitrobenzoylmethane (0·57 g.).

(*d*) *In carbon tetrachloride.* Copper di-isobutyrylmethane (0·74 g.) and *p*-nitrobenzoyl chloride (0·74 g.) in carbon tetrachloride (50 ml.) were refluxed for 2½ hr. Copper(II) chloride (0·22 g.) and di-isobutyryl-*p*-nitrobenzoylmethane (0·87 g.) were isolated.

The reaction was repeated in the presence of 9,10-dihydroanthracene (1·8 g.); copper(I) chloride (0·18 g.) was obtained. Anthracene was detected in the recovered 9,10-dihydroanthracene from its ultraviolet spectrum ($\lambda_{max.}$ 250 mμ).

*Reaction of Copper Acetylacetone and* p-*Nitrobenzoyl Chloride.*—(*a*) *In refluxing toluene.* Copper acetylacetone (1·31 g.) and *p*-nitrobenzoyl chloride (1·85 g.) in toluene (100 ml.) were refluxed for 6 hr. Copper(I) chloride (0·50 g.) was filtered off and the filtrate evaporated to dryness. Crystallisation of the residue from light petroleum (b. p. 40—60°) gave yellow prisms of *diacetyl*-p-*nitrobenzoylmethane* (1·10 g.), m. p. 104° (Found: C, 57·8; H, 4·45; N, 5·6. $C_{12}H_{11}NO_5$ requires C, 58·0; H, 4·5; N, 5·4%), $\nu_{max.}$ 1665 (C=O). Treatment with copper acetate gave *copper diacetyl*-p-*nitrobenzoylmethane* as green needles (from chloroform) (Found: Cu, 11·7; N, 5·1. $C_{24}H_{20}CuN_2O_{10}$ requires Cu, 11·4; N, 5·0%), $\nu_{max.}$ 1660 (C=O), 1590 (chelate C=O), 658, 614, 568, 556, 518, 485, 451, 431, 417, 408, 397, and 298 cm.$^{-1}$. Recrystallisation of the triketone from methanol gave white needles of *p*-nitrobenzoylacetone, m. p. and mixed m. p. 115°.

The reaction was repeated with a reaction time of 10 min. A green precipitate of chlorocopper(II) diacetyl-*p*-nitrobenzoylmethane, insoluble in chloroform, was obtained, having $\nu_{max.}$ 1660 (C=O), 1590 (chelate C=O), 641, 602, 568, 550, 510, 485, 451, 431, 415, 397, and 294 (v. broad) cm.$^{-1}$ [copper(II) chloride has a very broad band in the 345—250 cm.$^{-1}$ region]. The filtrate gave diacetyl-*p*-nitrobenzoylacetone. Hydrolysis of the chloro-chelate with dilute aqueous methanolic sulphuric acid gave *p*-nitrobenzoylacetone, m. p. and mixed m. p. 115°. Hydrolysis with nitric acid followed by addition of silver nitrate gave a precipitate of silver chloride. A suspension of the chloro-chelate in toluene was refluxed for 8 hr., after which a white precipitate of copper(I) chloride was filtered off. The filtrate gave diacetyl-*p*-nitrobenzoylmethane.

(*b*) *In toluene at room temperature.* The above reaction was repeated at room temperature by shaking the mixture periodically during 7 days. Chlorocopper diacetyl-*p*-nitrobenzoyl methane was filtered off and washed with chloroform to remove any unchanged copper acetylacetone. The filtrate gave diacetyl-*p*-nitrobenzoylmethane.

(*c*) *In carbon tetrachloride.* The reaction was repeated in carbon tetrachloride by refluxing the mixture for 4 hr. Diacetyl-*p*-nitrobenzoylmethane (0·9 g.) and chlorocopper diacetyl-*p*-nitrobenzoylmethane were isolated.

(*d*) *In chloroform.* Copper acetylacetone (2·62 g.) and *p*-nitrobenzoyl chloride (3·71 g.) in chloroform (60 ml.) were left for 18 hr. at room temperature. The green precipitate consisting chiefly of chlorocopper(II) acetylacetone was filtered off; it had $\nu_{max.}$ 1590, 1520, 1022, 938, 782, 641, 599, 417, 415, and 287 (v. broad) cm.$^{-1}$. When this was washed with water, part of it dissolved, to give a blue solution of copper(II) chloride and a residue of (mainly) copper acetylacetone, $\nu_{max.}$ 1582, 1553, 1527, 1021, 940, 782, 649, 610, 455, 431, and 287 cm.$^{-1}$; the latter was soluble in chloroform, leaving a trace of chlorocopper diacetyl-*p*-nitrobenzoylmethane. The filtrate gave diacetyl-*p*-nitrobenzoylmethane. Chlorocopper acetylacetone, when heated in acetylacetone, gave copper acetylacetone and hydrogen chloride.

*Reaction of Copper Di-n-butyrylmethane and* p-*Nitrobenzoyl Chloride.*—(*a*) *In cyclohexane.* Copper di-n-butyrylmethane (0·37 g.) and *p*-nitrobenzoyl chloride (0·37 g.) in cyclohexane (50 ml.) were left at room temperature for 24 hr. The green precipitate of chlorocopper di-n-butyryl-*p*-nitrobenzoylmethane was filtered off; it had $\nu_{max.}$ 1656 (C=O) and 1580 cm.$^{-1}$ (chelate C=O). The filtrate was evaporated to dryness; the residue crystallised from light petroleum (b. p. 40—60°) as yellow tablets of *di-n-butyryl*-p-*nitrobenzoylmethane* (0·27 g.), m. p. 76° (Found: C, 62·8; H, 6·1; N, 4·6. $C_{16}H_{19}NO_5$ requires C, 62·9; H, 6·3; N, 4·6%),

$\nu_{max.}$ 1660 cm.$^{-1}$ (C=O). With copper acetate, this gave blue-green needles (from benzene) of *copper di-n-butyryl-p-nitrobenzoylmethane*, m. p. 236° (Found: Cu, 9·9; N, 3·9. $C_{32}H_{36}CuN_2O_{10}$ requires Cu, 9·5; N, 4·2%), $\nu_{max.}$ 1656 (C=O) and 1580 cm.$^{-1}$ (chelate C=O). Acid hydrolysis of the chloro-chelate gave di-n-butyryl-*p*-nitrobenzoylmethane.

(*b*) *In toluene or carbon tetrachloride.* Copper di-n-butyrylmethane (0·37 g.) and *p*-nitrobenzoyl chloride (0·37 g.) in one of these solvents (50 ml.) was left at room temperature for 48 hr. before removal of copper(II) chloride. The filtrate gave di-n-butyroyl-*p*-nitrobenzoylmethane.

*Reaction of Copper Benzoyl-n-butyrylmethane and* p-*Nitrobenzoyl Chloride in Toluene and in Cyclohexane.*—Copper benzoyl-n-butyrylmethane (0·42 g.) and *p*-nitrobenzoyl chloride (0·37 g.) in one of the solvents (50 ml.) were left at room temperature for 48 hr. A green precipitate of chlorocopper benzoyl-n-butyryl-*p*-nitrobenzoylmethane was filtered off; it had $\nu_{max.}$ 1656 (C=O) and 1567 cm.$^{-1}$ (chelate C=O), and on acid hydrolysis gave *benzoyl-n-butyryl-*p*-nitrobenzoylmethane*, m. p. 90—91°, yellow needles [from light petroleum (b. p. 60—80°)] (Found: C, 67·3; H, 5·0; N, 4·35. $C_{19}H_{17}NO_5$ requires C, 67·3; H, 5·0; N, 4·1%), $\nu_{max.}$ 1660 cm.$^{-1}$ (C=O). Treatment of this with copper acetate gave *copper benzoyl-n-butyryl-*p*-nitrobenzoylmethane*, m. p. 257° (decomp.), as blue-green needles (from benzene) (Found: C, 62·1; H, 4·8; N, 3·9. $C_{38}H_{32}CuN_2O_{10}$ requires C, 61·6; H, 4·4; N, 3·8%), $\nu_{max.}$ 1656 (C=O) and 1572 cm.$^{-1}$ (chelate C=O). The filtrate from the last reaction gave benzoyl-n-butyryl-*p*-nitrobenzoylmethane.

*Reaction of Copper Benzoylisobutyrylmethane and* p-*Nitrobenzoyl Chloride.*—(*a*) *In cyclohexane.* Copper benzoylisobutyrylmethane (0·42 g.) and *p*-nitrobenzoyl chloride (0·37 g.) in cyclohexane (50 ml.), when kept at room temperature for 48 hr., yielded a green precipitate of chlorocopper benzoylisobutyryl-*p*-nitrobenzoylmethane, $\nu_{max.}$ 1656 (C=O) and 1570 cm.$^{-1}$ (chelate C=O). The filtrate gave yellow needles [from light petroleum (b. p. 40—60°)] of *benzoylisobutyryl-*p*-nitrobenzoylmethane*, m. p. 99—100° (Found: C, 67·6; H, 5·35; N, 4·4. $C_{19}H_{17}NO_5$ requires C, 67·25; H, 5·05; N, 4·2%), $\nu_{max.}$ 1661 cm.$^{-1}$ (C=O). This gave, with copper acetate, blue-green needles (from benzene) of *copper benzoylisobutyryl-*p*-nitrobenzoylmethane*, m. p. 226° (Found: C, 61·6; H, 4·6; N, 3·9. $C_{38}H_{32}CuN_2O_{10}$ requires C, 61·6; H, 4·4; N, 3·8), $\nu_{max.}$ 1656 (C=O) and 1575 cm.$^{-1}$ (chelate C=O). Acid hydrolysis of the chloro-chelate gave benzoylisobutyryl-*p*-nitrobenzoylmethane.

(*b*) *In toluene.* The reaction in toluene at room temperature gave copper(II) chloride and benzoylisobutyryl-*p*-nitrobenzoylmethane.

*Reaction of Copper Benzoylacetone and* p-*Nitrobenzoyl Chloride in Cyclohexane.*—Copper benzoylacetone (3·85 g.) and *p*-nitrobenzoyl chloride (3·71 g.) in cyclohexane (200 ml.) were refluxed for 1 hr. A green precipitate of chlorocopper acetylbenzoyl-*p*-nitrobenzoylmethane (3·7 g.), $\nu_{max.}$ 1645 (C=O) and 1572 cm.$^{-1}$ (chelate C=O), was filtered off. The filtrate gave acetylbenzoyl-*p*-nitrobenzoylmethane, m. p. 124° (lit.,[5] 121—122°), yellow needles (from benzene), which with copper acetate gave *copper acetylbenzoyl-*p*-nitrobenzoylmethane*, m. p. 292° (Found: Cu, 8·8; N, 3·9. $C_{34}H_{24}CuN_2O_{10}$ requires Cu, 9·3; N, 4·1%), $\nu_{max.}$ 1645 (C=O) and 1572 cm.$^{-1}$ (chelate C=O). Crystallisation from ethanol gave *p*-nitrodibenzoylmethane, m. p. and mixed m. p. 164° (Barry[8] reported that acetylbenzoyl-*p*-nitrobenzoylmethane crystallised from ethanol). Acid hydrolysis of the chloro-chelate gave acetylbenzoyl-*p*-nitrobenzoylmethane.

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[8] Barry, *J.*, 1961, 670.