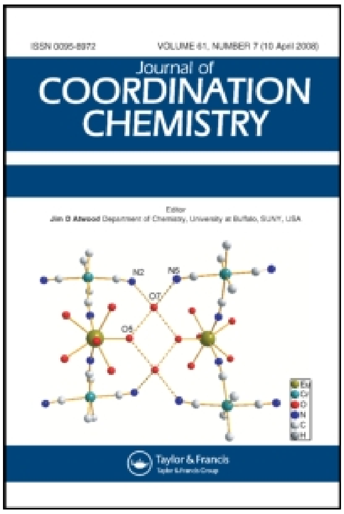

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PHOTOLYSIS OF COPPER(II) CHELATES OF β-DIKETONES IN THE PRESENCE OF OXYGEN†

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The photolysis of solutions of bis(acetylacetonato)copper(II) (**I**), bis(benzoylacetonato)copper(II) (**II**), bis(dipivaloylmethanato)copper(II) (**III**), and bis(dibenzoylmethanato)copper (II) (**IV**) in the presence of oxygen has been studied. The destructive photooxidation of these chelates gives copper(II) complexes of unidentified structure and a variety of organic products. The reaction course seems similar to that described for the destructive photooxidation of iron(III) chelates with β-diketones and the autooxidation of metal chelates of β-diketones at 100° in diphenyl ether.

INTRODUCTION

Metal chelates of β-diketones are useful as flotation agents in metallurgy[1] and in the analysis of metals by precipitation, colorimetry, or photometry.[2–4] Examples of the various applications of copper(II) chelates include their use as antiinflammatory agents,[5] as antifungal agents in cotton and linen supports for paintings,[6] and as catalysts in the polymerization of styrene,[7] for deacylation of β-diketones,[8] for decomposition of diazo compounds,[9] and for acceleration of polyurethane formation from diisocyanates.[10] Metal chelates containing ligands derived from β-diketones show variable reactivity as quenchers in the photoreduction of benzophenone by benzhydrol.[11,12] Because of the practical and theoretical importance of metal chelates of β-diketones, it seemed of interest to study their photochemical behavior and their stability upon exposure to light in the presence and in the absence of oxygen.

Only a few experimental studies related to our work have been published in the literature. Several papers were devoted to the oxidation of various metal chelates derived from β-diketones.[13–19] Also the photolysis of some iron(III) chelates in the absence of oxygen was studied but no defined products were isolated.[20] The results of a recent photochemical study of chromium(III) β-diketonate complexes have been reported.[21]

The photosensitivity of copper(II) chelates with β-diketones was investigated in ethanol and *tert*-butyl alcohol. Whereas no reaction was observed on irradiation with visible light, their irradiation in the LMCT band (~240 nm) led to the photoreduction of the chelates to metallic copper.[22] A more detailed study of this reaction showed that the primary photochemical process is the reduction of Cu(II) to Cu(I) followed by thermal reduction of Cu(I) to the copper metal.[23] The course of the reaction depended on the presence or absence of oxygen and, in addition to metallic copper, the respective β-diketones were isolated as reaction products.[23]

In one of our previous papers[24] we have shown that photolysis of the benzene solution of tris(dibenzoylmethanato)iron(III) in the presence of oxygen gives basic ferric salt of diphenyltartaric acid, benzoic acid, and phenyl benzoate as the main reaction products, with phenylglyoxylic acid as the intermediate. Similarly, the destructive photooxidation of tris(dipivaloylmethanato)iron(III) carried out under analogous conditions yielded pivalic acid and the corresponding ferric salt in the form of a brownish-yellow precipitate, along with other reaction products.[25]

The present work represents a continuation of our previous photochemical studies of metal chelates.[24,25] The following copper(II) chelates have been synthesized and their photolysis in the presence of oxygen has been studied: bis(acetylacetonato)copper(II) [$Cu(acac)_2$, **I**], bis(benzoylacetonato)copper(II) [$Cu(bzac)_2$, **II**], bis(dipivaloylmethanato)copper(II) [$Cu(dpm)_2$, **III**], and bis(dibenzoylmethanato)copper(II) [$Cu(dbm)_2$, **IV**].

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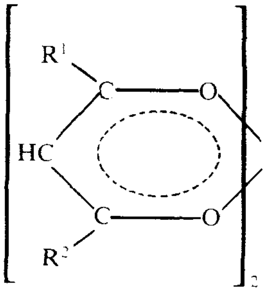


Copper β-diketonates

I. $R^1 = R^2 = CH_3$ **III.** $R^1 = R^2 = (CH_3)_3C$

II. $R^1 = C_6H_5$; $R^2 = CH_3$ **IV.** $R^1 = R^2 = C_6H_5$

EXPERIMENTAL

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were carried out by the Heterocyclic Chemical Corporation, Harrisonville, Missouri, and the microanalytical laboratory of the Institut de Pétroléochimie et de Synthèse Organique Industrielle, Faculté des Sciences et Techniques de Saint-Jérôme, Université d'Aix-Marseille III, Marseille, France. Ultraviolet and visible spectra were recorded on a Cary 118 spectrophotometer. Infrared spectra were measured on Perkin-Elmer model 710A and model 221 spectrometers. NMR spectra were obtained with a Perkin-Elmer R12 spectrometer and mass spectra were recorded on a DuPont 21-491 double-focussing instrument. A Chemtrix 40 pH-meter was used to measure pH during the synthesis of copper chelates.

Irradiations

All irradiations were carried out in a Rayonet model RPR-208 preparative photochemical reactor using the merry-go-round unit and quartz vessels. Three sets of interchangeable lamps were available, with the maximum radiation intensitities at 254, 300, and 350 nm, respectively. In all irradiation experiments, the course of the photooxiation of copper(II) chelates was followed spectrophotometrically (uv).

Bis(acetylacetonato)copper(II) (I)

$Cu(acac)_2$ (**I**) was obtained from acetylacetone and cupric chloride in water, with ammonia added to the reaction mixture (77% yield).[26,27] The product was recrystallized twice from chloroform. Blue crystals, m.p. >250° (dec.); uv, visible, and ir spectra in agreement with the literature.

Bis(benzoylacetonato)copper(II) (II)

$Cu(bzac)_2$ (**II**) was prepared from benzoylacetone and cupric chloride in 50% aqueous ethanol, with ammonia added to the reaction mixture (83% yield).[28-30] The product was recrystallized twice from a benzene-ligroin mixture. Green crystals, m.p. 192°; uv, visible, and ir spectra in agreement with the literature.

Bis(dipivaloylmethanato)copper(II) (III)

$Cu(dpm)_2$ (**III**) was synthesized from dipivaloylmethane and cupric chloride in 50% aqueous ethanol, with ammonia added to the reaction mixture (30% yield).[28,31] The product was recrystallized twice from a benzene-ligroin mixture. Dark blue crystals, m.p. 196°; uv, visible, and ir spectra in agreement with the literature.

Bis(dibenzoylmethanato)copper(II) (IV)

$Cu(dbm)_2$ (**IV**) was obtained from dibenzoylmethane and cupric sulfate in 50% aqueous ethanol, in the presence of ammonia (87% yield).[12,27,28] It was recrystallized twice from a methylene chloride-ligroin mixture. Yellow-green crystals, m.p. 319°; uv, visible, and ir spectra in agreement with the literature.

Photooxidation of $Cu(acac)_2$ (I)

A 5×10^{-3} M solution of **I** (0.196 g) in methanol (150 ml) was irradiated in a quartz vessel with 300 nm wavelength for 86 h. A stream of oxygen was bubbled through the reaction mixture and the course of the reaction was followed spectrophotometrically.

The blue precipitate formed during the irradiation was filtered off (0.060 g) and a green solution was obtained.[32] The methanolic solution after the removal of the precipitate was evaporated to dryness and treated with 4 ml of ether. The undissolved green substance was filtered off.[32]

Acetic acid was identified as one of the reaction products in the following manner. After evaporation of methanol, the residue was dissolved in carbon disulfide and analyzed by gas chromatography on a DEGS column (3 m) at 150°. The presence of acetic acid was determined by comparison with an authentic sample and by adding this sample to the solution.

Biacetyl was identified in the reaction mixture in the form of its yellow 2,4-dinitrophenylhydrazone, m.p. 316° (in agreement with lit.[33]) and as the brown-yellow *p*-nitrophenylhydrazone, m.p. 233° (in agreement with lit.[33]). Uv spectrum of biacetyl: λ_{max}, nm 288, 326 sh (lit.[34] gives λ_{max} at 290 nm).

Photooxidation of Cu(bzac)$_2$ (**II**) *in Methanol*

A 5×10^{-3}M solution of **II** (0.300 g) in methanol (150 ml) was irradiated for 110 h similarly as in the previous experiment. No precipitate was formed. The reaction mixture was evaporated to dryness, the residue (0.221 g) was dissolved in a small amount of benzene, and the undissolved green substance (0.057 g) was filtered off.[32]

The benzene solution was then chromatographed on alumina using cyclohexane, benzene, ether, and methanol as the eluents. In addition to trace amounts of three organic substances which were not identified, benzoic acid was eluted as the last compound (with ether-methanol). White needles (0.017 g), m.p. 120° (sublimed at 95°); uv, ir, and mass spectra in agreement with the literature.

Photooxidation of Cu(bzac)$_2$ (**II**) *in Benzene*

Photooxidation of **II** carried out under analogous conditions as above but in benzene (108 h) produced a brown precipitate (0.055 g) and a green substance (0.024 g) after the evaporation of benzene.[32]

Column chromatography of the residue carried out in the same way as before gave the following identified fractions, in addition to small amounts of other unidentified compounds.

trans-Stilbene (0.021 g), white crystals, m.p. 124–126°; uv, ir, and mass spectra identical with those reported in the literature and with the spectra of an authentic sample of *trans*-stilbene.

Benzophenone (0.032 g), white crystals, m.p. 46°; uv, ir, NMR, and mass spectra in agreement with the literature and with the spectra of an authentic sample of benzophenone.

Benzaldehyde (0.071 g), oily liquid; uv, ir, and NMR spectra identical with those of an authentic sample of benzaldehyde.

Benzoic acid (0.024 g) was identified in the same manner as before.

Photooxidation of Cu(dpm)$_2$ (**III**)

A 5×10^{-3}M solution of **III** (0.323 g) in methanol (150 ml) was irradiated at 300 nm for 86 h. A green precipitate (0.033 g) was formed.[32] It was filtered off and the filtrate was evaporated to dryness. The oil residue (0.216 g) was dissolved in 4 ml of cyclohexane and chromatographed on alumina. The following fractions were identified.

Dipivaloyl (0.073 g), yellowish oil, was identified by direct comparison of its uv, ir, NMR, and mass spectra with those of an authentic sample of dipivaloyl synthesized independently.

Pivalic acid (0.011 g), m.p. 35°, was identified by comparison of its uv and ir spectra with those reported in the literature.

Photooxidation of Cu(dbm)$_2$ (**IV**)

A 1.8×10^{-3}M solution of **IV** (0.280 g) in methylene chloride (300 ml) was irradiated at 350 nm for 100 h. No precipitate was formed. The yellow-green solution was evaporated to dryness, the residue was treated with benzene, and the undissolved green substance (0.44 g) was filtered off.[32] Chromatography of the benzene solution of alumina after the removal of the green compound gave the following products.

Benzil (0.083 g), yellow prisms, m.p. 94–95° (sublimed at 75°), identified by comparison of its uv, ir, and mass spectra with those reported in the literature for this compound.

Benzoic acid (0.020 g) was identified as before.

Irradiation of Copper(II) Chelates **I–IV** *in the Absence of Oxygen*

A 10^{-2}M solution of Cu(acac)$_2$ (**I**) was placed in a quartz vessel and degassed by several repeated freeze-pump-thaw cycles. Then it was irradiated at 300 nm. A stream of purified, oxygen-free nitrogen was bubbled through the solution during irradiation. Practically no change of the uv spectrum was observed after 100 h. After 420 h, only a 25% drop of absorption at 294 nm was observed.

The other chelates, **II–IV**, have been found equally stable under analogous conditions.

Dark Oxidation Experiments

A stream of oxygen was bubbled through solutions of the chelates **I–IV** under the same conditions as those used in the irradiation experiments but in the dark. The volume of the solutions was kept constant by adding the corresponding solvent whenever necessary. No changes were observed after 10 days.

RESULTS AND DISCUSSION

A number of studies have been concerned with the electronic absorption spectra of metal β-diketonates.[28,35–47] The electronic absorption spectra of the four copper chelates, **I–IV**, studied in the present work have been measured in the uv and visible region and the absorption maxima and their respective intensities are summarized in Table I. Also, the experimental

TABLE I
Ultraviolet and visible absorption spectra of copper(II) β-diketonates

No.	Compound	Solvent	λ_{max}, nm (log ε)
I	$Cu(acac)_2$	Methanol	201 sh (3.64),[a] 240 (4.09), 294 (4.39), 635 (1.69)
II	$Cu(bzac)_2$	Methanol	230 sh (4.12),[a] 251 (4.36), 322 (4.50), 640 (1.63)
III	$Cu(dpm)_2$	Cyclohexane	201 sh (4.11), 249 (4.26), 297 (4.30), 306 sh (4.26), 640(1.69)
IV	$Cu(dbm)_2$	Methylene chloride	263 (4.50), 279 sh (4.45), 348 (4.62), 611 (2.01)[b]

[a] In cyclohexane. [b] In dioxane, see ref. 45.

absorption curves of $Cu(acac)_2$ (**I**) and $Cu(bzac)_2$ (**II**) are presented in Figure 1 as examples.

In general, these complexes possess two major bands at 240–265 and 290–350 nm, respectively, in the uv region and a shoulder at about 201 nm. There is some lack of agreement concerning the assignment of the absorption at 201 nm which was proposed to be a $\pi_L \rightarrow \pi_L^*$ transition or a $d_{yz} \rightarrow \pi_L^*$ metal-to-ligand transition.[37,38,42] There has been at least some controversy concerning the band at 240–265 nm which originally was interpreted as a $\pi_L \rightarrow \pi_L^*$ band but which has now been reassigned to the charge transfer $\pi_L \rightarrow 3d_{xy}^*$ transition.[46] On the other hand, there is a general agreement that the band at 290–350 nm originates from the lowest $\pi_L \rightarrow \pi_L^*$ transition.[46]

The blue or green color of these chelates is due to the absorption in the visible region in the 600–800 nm range. This absorption in the visible region consists of at least three or four bands of comparable intensity belonging to $d \rightarrow d^*$ transitions, and possibly a stronger intensity fifth band corresponding to a ligand transition.[35,39,42]

The assignments of the individual bands are supported by the results of MO calculations.[37,38,41,42,48–50]

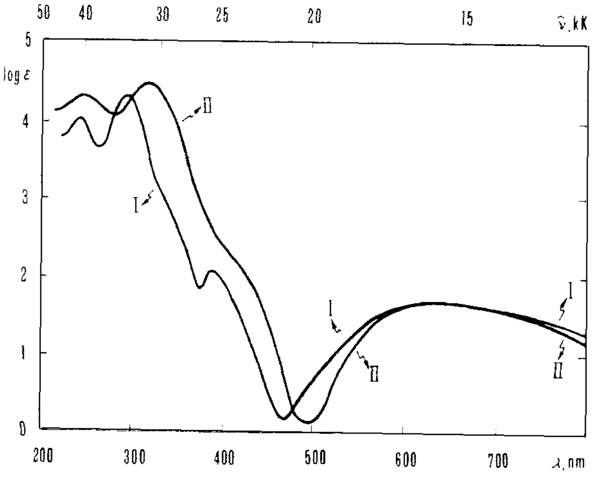


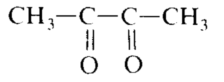
FIGURE 1 Ultraviolet and visible absorption spectra of $Cu(acac)_2$ (**I**) and $Cu(bzac)_2$ (**II**) in methanol.

The results of our experiments indicate that the copper(II) chelates **I–IV** are remarkably stable towards oxidation in the dark at room temperature as well as towards photolysis in the absence of oxygen. However, they all undergo destructive photooxidation when irradiated in the presence of oxygen with uv light of the wavelength corresponding to their most intense absorption band in the uv region (290–350 nm), i.e. a band corresponding to a $\pi_L \rightarrow \pi_L^*$ transition.

The copper-containing products isolated in the photooxidation of chelates **I–IV** are amorphous copper(II) salts of varying composition which do not give satisfactory analytical data and are difficult to characterize. They have not been identified. Also, no attempt has been made to identify the gaseous products formed in the photooxidations.

In addition to the copper(II) salts, complex mixtures of organic oxidation products have been obtained.

Photooxidation of $Cu(acac)_2$ (**I**) gives biacetyl (**V**)

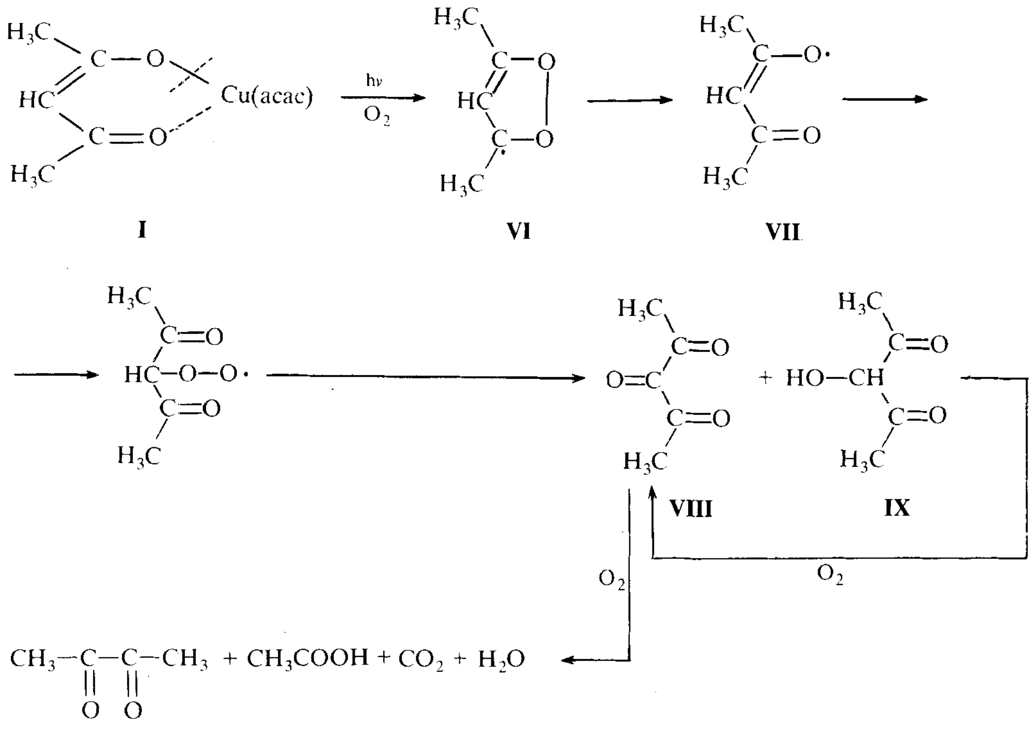


$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

V

and acetic acid as the major organic products. This result is quite analogous to the results of studies of metal β-diketonates of several metals which undergo autooxidation at 100° in diphenyl ether.[15–18] In the case of tris(acetylacetonato)iron(III), the chelate studied most extensively, biacetyl, acetic acid, water, and carbon dioxide were found among the oxidation products.[18]

By analogy with the mechanism of autooxidation reactions,[18] it is possible to assume that photochemical cleavage of the chelate **I** generates free radical **VI** which isomerizes into **VII**. Radical **VII** is subsequently oxidized to the corresponding trione — 2,3,4-pentanetrione (**VIII**). The trione **VIII** is a powerful reducing agent and reacts with oxygen to give the above-



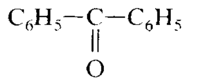
I **VI** **VII** **VIII** **IX** **V**

mentioned final oxidation products. The hydroxydione **IX** can undergo further oxidation to **VIII**.

Photooxidation of $Cu(bzac)_2$ (**II**) gives *trans*-stilbene (**X**), benzophenone (**XI**), benzaldehyde (**XII**), and benzoic acid (**XIII**).

$C_6H_5-CH=CH-C_6H_5$ (*trans*)

X



$C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5$

XI

$C_6H_5-CH=O$

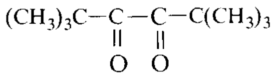
XII

C_6H_5-COOH

XIII

The formation of benzaldehyde and benzoic acid is not difficult to explain on the basis of the above mechanism. *trans*-Stilbene and benzophenone are obtained by recombination of the various free radicals generated during the photolysis. *cis*-Stilbene, although not isolated from the reaction mixture, is clearly one of the reaction products as well and *cis-trans*-photoisomerization of the two isomers is undoubtedly involved in the entire processs.[51–53]

The photoxidation of $Cu(dpm)_2$ (**III**) yields, in complete analogy with the photooxidation of **I**, dipivaloyl (**XIV**) and pivalic acid (**XV**). In the destructive photooxidation of tris(dipivaloylmethanato)iron(III), pivalic acid was obtained as one of the products.[25]

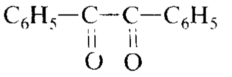


$(CH_3)_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C(CH_3)_3$

XIV

$(CH_3)_3C-COOH$

XV



$C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-C_6H_5$

XVI

Finally, the photooxidation of $Cu(dbm)_2$ (**IV**) gives benzil (**XVI**) and benzoic acid (**XIII**), again in agreement with expectations based on the above mechanism. Benzoic acid was obtained as one of the products in the photooxidation of tris(dibenzoylmethanato)iron(III) as well.[24]

In conclusion, it should be pointed out that the systems studied in the present work are somewhat less complicated than metal-diketonate photochemistry in general.

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