

Metal-catalysed Organic Photoreactions. Photo-oxidations of $\alpha\beta$ -Unsaturated Ketones and *o*-Methylacetophenone in the Presence of Copper(II) Salts¹

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Dyprone (β -methylchalcone), *para*-substituted dyprones, and mesityl oxide (4-methylpent-3-en-2-one) underwent photo-oxidation in methanol only with catalytic assistance by metal salts. The reaction is compared with the photo-oxidation of *o*-methylacetophenone, and the role of the metal compounds is discussed.

THERE has been considerable recent interest in photo-reactions catalysed by metal compounds.² Dimerization,³ isomerization,⁴ and reduction⁵ of olefins by irradiation in the presence of copper(I) or d^6 -metal carbonyls are typical examples. In most such systems, an interaction between metal and substrate in the ground state is believed to exist even in cases where the corresponding co-ordination compound cannot be isolated. We consider that even when this interaction is not evident, the metal can influence the reaction pattern and induce the formation of products different from those obtained in its absence, if *any* kind of interaction exists at *any* stage during the reaction. Such an effect has been found in the photo-oxidation of $\alpha\beta$ -unsaturated ketones and *o*-methylacetophenone, described in the present paper.

RESULTS AND DISCUSSION

When a methanolic solution of dyprone (1a) containing copper(II) sulphate was irradiated with Pyrex-filtered light for 6 h while air was bubbled through, the methanol-insoluble bifurandione (2a) crystallized out. In a similar way compounds (2b and c) were obtained from (1b and c), respectively. The structures of the products (2a—c) were determined from elemental analyses and spectroscopic data (Table and Experimental section). Structure (2a) was further established by comparison (mixed m.p. and i.r. spectrum) with an authentic sample.⁶ The stereochemistry at positions 2 and 2' however, remains undetermined.

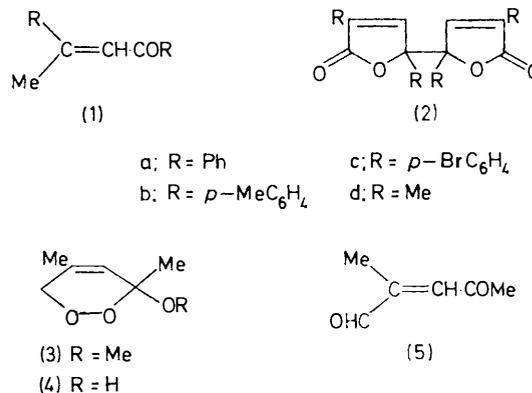
¹ Preliminary report, T. Sato, K. Tamura, K. Maruyama, and O. Ogawa, *Tetrahedron Letters*, 1973, 4221.

² Review: T. Sato, *J. Synthetic Org. Chem., Japan*, 1974, **32**, 989.

³ R. G. Salomon, K. Folting, W. E. Streib, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 1145.

⁴ M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organometallic Chem.*, 1974, **70**, 283.

This photo-oxidation proceeds only under the influence of irradiation, copper(II) sulphate, and oxygen; when



copper(II) sulphate and/or air were lacking, *cis-trans*-isomerization of dyprone was the sole reaction. The

Yields and properties of the bifurandiones (2a—c)

Product	Yield (%)	Cryst. solvent	M.p. (°C) †	ν_{max} (KBr)/cm ⁻¹
(2a)	42	Me ₂ N·CHO	288—289 ‡	1 764, 1 500, 1 453, 1 150, 1 100, 965
(2b)	34	CHCl ₃	240—241	1 760, 1 513, 1 149, 1 084, 818
(2c)	49	Me ₂ N·CHO	242—243	1 762, 1 490, 1 398, 1 148, 1 069, 820

† Decomp. ‡ Lit.,⁶ 288—289°.

maximum yield of the bifurandione (2a) was obtained when 0.1 mol. equiv. of copper(II) sulphate was used.

⁵ G. Platbrood and L. Wilputte-Steinert, *J. Organometallic Chem.*, 1974, **70**, 407.

⁶ M. Tanaka, T. Nagai, and N. Tokura, *J. Org. Chem.*, 1972, **37**, 4106.

Inhibition of absorption of light by the dyppnone through a filter effect of the copper(II) sulphate might be responsible for the retardation of the reaction at higher catalyst concentration. The reaction was clean and no appreciable amounts of products (<5%) other than *cis*- and *trans*-isomers of the starting dyppnone were detected by n.m.r. and t.l.c. analysis after the crystals of (2a) had been filtered off.

The same type of oxidation also occurred in toluene in the presence of bis(acetylacetonato)copper(II). But in the absence of the copper(II) catalyst, in benzene, *cis*-*trans*-isomerization was again the sole reaction. Copper(I) iodide-triethyl phosphite, copper(II) chloride, and iron(III) chloride were also effective catalysts for the photo-oxidation of dyppnone (1a) in methanol, affording the bifurandione (2a) in 30, 40, and 17% yield, respectively. However, nickel(II) sulphate, mercury(II) chloride, and cadmium(II) chloride had little effect: very low yields of (2a) were obtained during the same reaction period.

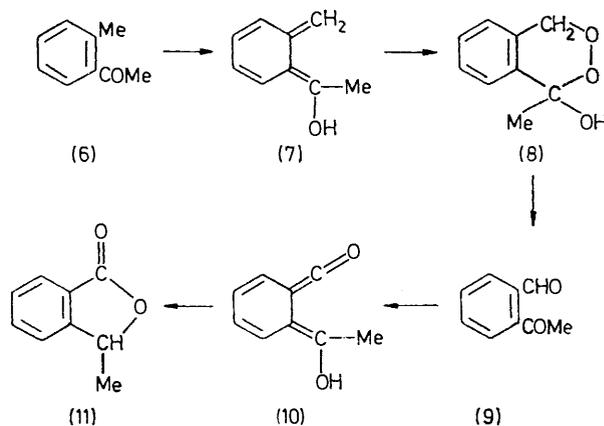
Mesityl oxide (1d), treated under the same conditions, reacted more than 100 times slower than the dyppnones. Two products (3) and (4) were isolated, although the latter (4) seems to be a secondary product formed during work-up, since the n.m.r. spectrum of the crude reaction mixture prior to the distillation indicated the presence of only (3) and starting material. The cyclic peroxides (3) and (4) could be distilled under reduced pressure, but at higher temperature in g.l.c., they decomposed to give an aldehyde [probably (5) from its n.m.r. spectrum], which, on isolation, decomposed gradually (in 10 h) to unidentifiable polymeric products at room temperature. As in the case of dyppnones, the photo-oxidation did not proceed when copper(II) sulphate was lacking.

Neither singlet-oxygen oxidation (Rose Bengal or Methylene Blue with tungsten lamp, or sodium hypochlorite-hydrogen peroxide) nor radical-initiated oxidation (benzoyl peroxide at 100 °C) of the dyppnone (1a) and mesityl oxide (1d) effected the present oxidation. It has been reported that dyppnone (1a) gives benzoic acid on auto-oxidation in the presence of t-butoxide ion,⁷ and that (1d) gives an epoxide and a five-membered cyclic peroxide by oxidation with alkaline hydrogen peroxide oxidation.⁸ However, these products were not detected in the present reactions.

Yates *et al.*⁹ reported the photo-oxidation of methyl-anthraquinone to a lactone dimer. In a similar reaction with *o*-methylacetophenone (6), they isolated a cyclic peroxide (8) which was further photoconverted into a lactone (11); the proposed reaction paths are shown in Scheme 1. The mechanism seems reasonable since photo-enolisation of *ortho*-methyl aromatic ketones has been demonstrated by trapping the dienol as a Diels-Alder adduct with maleic anhydride.¹⁰ Photo-enolis-

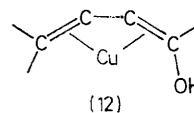
ation of an *ortho*-oxo-aromatic aldehyde [(9) → (10)] has also been reported.¹¹

The photo-oxidations of dyppnones and mesityl oxide are similar to these reactions and can be assumed to proceed in a similar fashion. Presumably cyclic peroxide (3) formed from mesityl oxide was isolable because of its transparency to the light employed, whereas those



formed from dyppnones further absorbed u.v. light to afford bifurandiones.

In open-chain systems the photo-oxidation proceeds only in the presence of metal catalyst, whereas in aromatic systems the same type of reaction proceeds without catalytic assistance. We consider that the most likely role of copper in the open-chain system might be to stabilise the substrate as the *s-cis*-dienol form (12). In aromatic systems, the *s-cis*-dienol form would be attained more easily through electronic and steric assistance by the ring structure.



The absence of interaction between copper(II) sulphate and ground-state $\alpha\beta$ -unsaturated ketones was evident from the u.v. spectrum of the mixture of dyppnone (1a) and copper(II) sulphate, which coincided exactly with the 'sum' of the spectra of the two compounds.

The postulate that co-ordination plays an important role in the present reaction was substantiated by the observation that the oxidation was inhibited by substances having high co-ordinating power such as triphenylphosphine or acetonitrile (as solvent). When the reaction of dyppnone was carried out in the presence of triphenylphosphine, an induction period was observed before the oxidation product began to crystallize out, and *cis*-*trans*-isomerization could be observed in the

⁷ W. von Doering and R. M. Haines, *J. Amer. Chem. Soc.*, 1954, **76**, 482.

⁸ G. B. Payne, *J. Org. Chem.*, 1958, **23**, 310.

⁹ P. Yates, A. C. Mackay, and F. X. Garneau, *Tetrahedron Letters*, 1968, 5389; cf. M. Pfau, E. W. Sarver, and N. D. Heindel, *Compt. rend.*, 1969, **268**, 1167.

¹⁰ (a) B. J. Arnold, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 415; (b) E. Block and R. Stevenson, *Chem. Comm.*, 1971, 711.

¹¹ M. F. Tchir, *J.C.S. Chem. Comm.*, 1974, 514.

earlier stages. These facts indicate that although light absorption by dypnone occurred effectively even in the presence of triphenylphosphine, dypnone underwent only *cis-trans*-isomerization because the photo-oxidation was blocked by the presence of the phosphine. After oxidation of triphenylphosphine to triphenylphosphine oxide, of lower co-ordinating ability,[†] was complete, the oxidation proceeded smoothly. The oxide could be isolated from the reaction mixture at the end of the photo-oxidation.

In view of the postulated role of copper, we were interested to discover whether copper exhibited a catalytic function in the photo-oxidation of the aromatic ketone (6). When this photo-oxidation was performed in methanol with no additive, the reaction proceeded almost in the same manner as in benzene, to give the cyclic peroxide (8) and the lactone (11), in accord with the result reported.⁹ However, when the reaction was carried out in the presence of a catalytic amount of

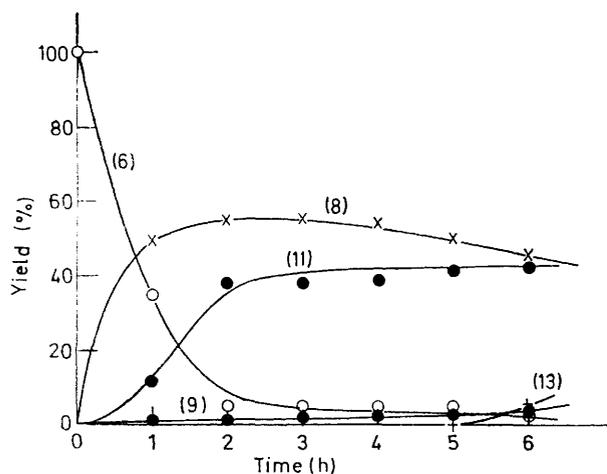


FIGURE 1 Photolysis of the ketone (6) with no additive

copper(II) sulphate, a mixture of *cis*- and *trans*-cyclic acetals (13) became the main product, accompanied by small amounts of compounds (8) and (9); no lactone (11) was detected. The ratio of the two stereoisomers was 45 : 55 (n.m.r. analysis) but the stereochemistry was not established. The structure of the acetals was established by elemental analysis, and n.m.r. spectrum, and by hydrolysis to the aldehyde (9).

The photo-oxidation of the ketone (6) in methanol was performed under three sets of conditions: (a) with no additive, (b) in the presence of copper(II) sulphate, and (c) in the presence of hydrochloric acid; the yields of products, as obtained from n.m.r. analyses, are plotted as a function of time in Figures 1–3. Reaction paths as shown in Scheme 2 can be deduced from these results.

[†] Although triphenylphosphine was recovered intact after bubbling air through the methanolic solution in the dark, it was readily oxidized in the dark to the oxide when copper(II) sulphate was present. The oxidation occurred more rapidly when air was bubbled through an irradiated methanolic solution containing copper(II) sulphate.

Figure 1 shows that the initially formed cyclic peroxide (8) undergoes photolysis to afford the lactone (11). That the reaction of the peroxide (8) is photochemical was

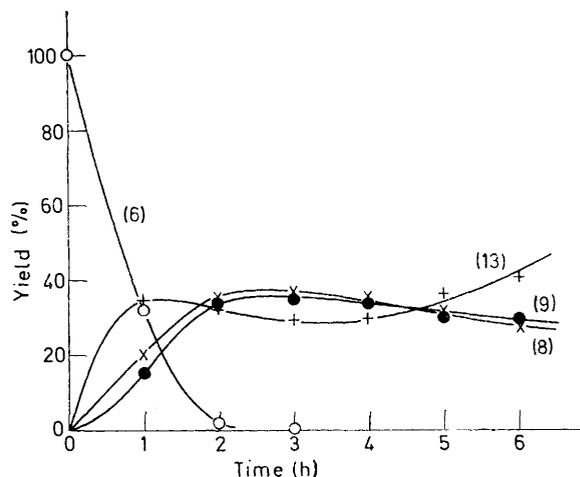


FIGURE 2 Photolysis of the ketone (6) in the presence of copper(II) sulphate

evident because (8) was thermally stable under the reaction conditions. Presumably the reaction path [(9) → (11)] is faster than the process [(6) → (8) → (9)], since no appreciable concentration of the aldehyde (9) was attained. In the presence of copper catalyst (Figure 2), the peroxide (8) and aldehyde (9) accumulated to substantial concentrations, but no trace of the lactone (11) was detected. These facts indicate that, although copper(II) sulphate scarcely affected the photoreaction [(8) → (9)], it inhibited the photo-reaction [(9) → (11)] completely, and led to the

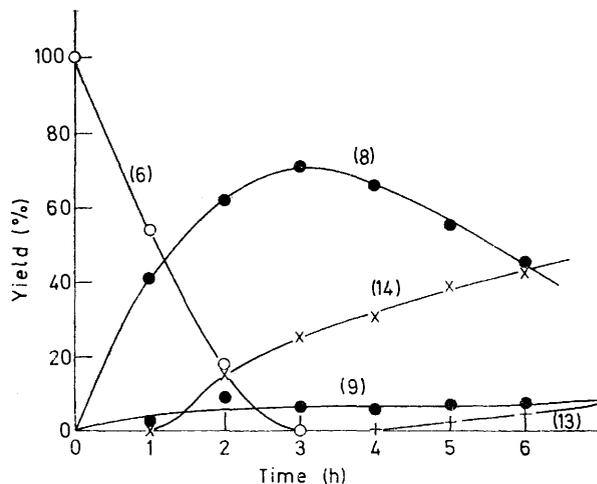
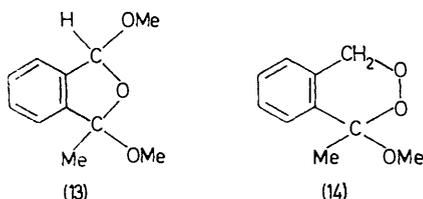


FIGURE 3 Photolysis of the ketone (6) in the presence of hydrochloric acid

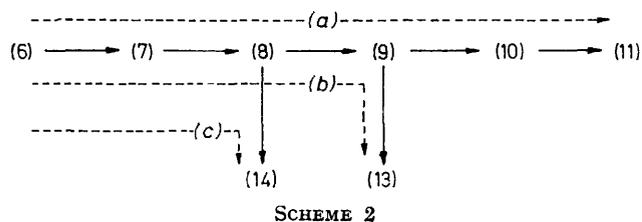
formation of the acetals (13). The process [(9) → (13)] is considered to be thermal because n.m.r. analysis revealed that when the irradiated solution was kept in

the dark, the amount of (13) increased, while that of (9) decreased. The quenching of excited species or a filter effect by the copper(II) sulphate might be responsible for the inhibition, but we have not pursued these points



further. Hydrochloric acid catalysed the reaction from (8), and the peroxide (14) was obtained as the main product (Figure 3).

These observations indicate that, in the aromatic system, copper(II) sulphate does not exert any effect on



SCHEME 2

the oxidation step, and the apparent difference in reaction pattern is a consequence of the different function of copper(II) sulphate from that in the open-chain system.

EXPERIMENTAL

Mass spectra were obtained with a Hitachi RMS-4 spectrometer, i.r. spectra with a JASCO IRS or a Hitachi EPI-G₃ spectrometer, and n.m.r. spectra with a JEOL MH-60 (60 MHz) or a PS-100 (100 MHz) spectrometer (Me₄Si as internal standard). G.l.c. analyses were carried out with a Shimadzu GC-2C or GC-4A gas chromatograph fitted with a 2.5 m × 6 mm stainless column packed with Silicone SE 30 or Carbowax 20M on silanised Chromosorb W. Peak areas were employed for quantitative analyses.

All irradiations were conducted in a Pyrex vessel with a high-pressure mercury vapour lamp {Riko UVL-100HA (100 W) or Ushio UM-452 (450 W)} at running-water temperature.

Photo-oxidations of the Dypnones (1a—c).—A solution of the dypnone (1.1 g) and copper(II) sulphate pentahydrate (0.05—0.5 g) in methanol (150 ml) was irradiated for 6 h while air was bubbled through. In every case a white solid (2) crystallized out in 10—20 min. The mother liquor (filtrate A) was shaken with chloroform, and the solvent evaporated off *in vacuo*. The residue consisted of *cis*- and *trans*-isomers of (1a) contaminated with a small amount of unknown substance (<5%) as revealed by n.m.r. and t.l.c. Another crop of (2) was obtained from filtrate A on further irradiation, but the second crop was usually blue in colour, particularly when the larger amount of catalyst was used. The details are summarized in the Table. The bifurandione (2a) was identical with an authen-

tic sample⁶ (m.p., mixed m.p., and i.r. spectrum). Although the products (2a—c) were poorly soluble in most ordinary organic solvents, a manageable concentration for determinations of spectra and molecular weight could be attained with 2,2',4,4'-tetra-*p*-tolyl-2,2'-bifuran-5,5'-(2H,2'H)-dione (2b); λ_{max} (MeOH) 285 nm (ϵ 24 000), δ (CDCl₃) 2.25 (6 H, s), 2.35 (6 H, s), and 7.1—8.0 (18 H, m), *M* (vapour pressure osmometry) 490 (Found: C, 81.8; H, 5.9. C₃₆H₃₀O₄ requires C, 82.1; H, 5.7%). The *p*-bromophenyl analogue (2c) was only analysed (Found: C, 48.8; H, 2.1. C₃₂H₁₈Br₄O₄ requires C, 48.9; H, 2.3%).

Photo-oxidation of Mesityl Oxide (1d)—A solution of mesityl oxide (1d) (42 ml) and copper(II) sulphate pentahydrate (0.14 g) in methanol (400 ml) was irradiated for 37 h while air was bubbled through. Saturated aqueous sodium chloride was added and the mixture was extracted with ether. The extract was evaporated *in vacuo* and the residue was distilled under reduced pressure. After the main fraction (starting material) two fractions were obtained: (i), b.p. 32—33° at 2 mmHg (1.2 g), almost pure methoxyperoxide (3); and (ii), b.p. 43° at 2 mmHg (1.5 g), a mixture of (3) and the hydroxy-peroxide (4) (1:2 from n.m.r. analyses). Further fractionation afforded pure samples of 3,6-dihydro-3-methoxy-3,5-dimethyl-1,2-dioxin (3), ν_{max} (CCl₄) 1 440, 1 364, 1 122, and 1 045 cm⁻¹, δ (CCl₄) 1.28 (3 H, s), 1.80br (3 H, s), 3.32 (3 H, s), 4.10 and 4.55 (2 H, ABq, *J* 15 Hz), and 5.60 (1 H, m); and the 3-hydroxy-analogue (4), ν_{max} (CCl₄) 3 400, 1 440, 1 344, 1 128, and 900 cm⁻¹, δ (CCl₄) 1.30 (3 H, s), 1.80br (3 H, s), 4.20br (1 H, s), 4.10 and 4.55 (2 H, ABq, *J* 15 Hz), and 5.68 (1 H, m).

Photo-oxidation of Dypnone (1a) in the Presence of Copper(II) Sulphate and Triphenylphosphine.—A solution of dypnone (1a) (0.1 ml), copper(II) sulphate pentahydrate (5 mg), and triphenylphosphine (30 mg) in methanol (7 ml) (solution A) and a similar solution but without the phosphine (solution B) were irradiated under the same conditions while air was bubbled through. Crystals of (2a) began to separate in 15—20 min from solution B, and in 1.5 h from solution A. Almost equal amounts of (2a) were obtained from both solutions after prolonged irradiation. From the mother liquor of solution A, triphenylphosphine oxide was detected by t.l.c. analysis, as well as the *cis*- and *trans*-isomers of (1a).

Photo-oxidation of *o*-Methylacetophenone (6).—(a) *With no additive.* A solution of the ketone (6) (0.6 ml) in methanol (60 ml) was irradiated while air was bubbled through. Samples (8 ml) were periodically taken out, diluted with water, and extracted with methylene chloride. The extracts were evaporated and the yields of each product were obtained from the weight and n.m.r. spectrum of the crude residue. The peroxide (8) decomposed on g.l.c. and afforded *o*-acetylbenzaldehyde (9), ν_{max} (CCl₄) 1 685, 1 360, and 1 250 cm⁻¹, δ (CCl₄) 2.53 (3 H, s), 7.4—7.8 (4 H, m), and 10.08 (1 H, s). N.m.r. data (solvent CCl₄) of compounds (8) and (11), as obtained from the spectrum of the reaction mixture, were as follows: (8) δ 1.53 (3 H, s), 4.0br (1 H), 4.73 and 5.23 (2 H, ABq, *J* 15 Hz), and 7.4—7.8 (4 H, m); (11) δ 1.58 (3 H, d, *J* 8 Hz), 5.50 (1 H, q, *J* 8 Hz), and 7.0—7.9 (4 H, m).

(b) *In the presence of copper(II) sulphate.* A solution of the ketone (6) (0.6 ml) and copper(II) sulphate pentahydrate (10.4 mg) in methanol (60 ml) was irradiated and analysed as above. Vacuum distillation afforded a sample which was shown to be a mixture of *cis*- and *trans*-acetals (13) from its n.m.r. spectrum: δ (CCl₄) 1.60 (3 H, s), 2.87 (3 H, s), 3.50 (3 H, s), 5.75 (1 H, s), and 7.21br (4 H, s) for the major

component (55%), and δ (CCl_4) 1.67 (3 H, s), 2.82 (3 H, s), 3.35 (3 H, s), 6.05 (1 H, s), and 7.21br (4 H, s) for the minor component (45%) (Found: C, 68.2; H, 7.0. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 68.0; H, 7.3%). When 0.1N-hydrochloric acid (5 μl) was added to the solution of (13) in carbon tetrachloride in the n.m.r. tube and the mixture was shaken for 1.5 h at 45 °C, signals assignable to the aldehyde (9) appeared.

(c) *In the presence of hydrochloric acid.* A methanolic solution (60 ml) containing the ketone (6) (0.6 ml) and 0.6N-hydrochloric acid (3.8 ml) was irradiated and analysed as in (a). N.m.r. data for the peroxide (14), as obtained from the spectrum of the mixture were as follows: δ (CCl_4) 1.48 (3 H, s), 3.21 (3 H, s), 4.80 and 5.19 (2 H, ABq, J 15 Hz), and 7.4—7.8 (4 H, m).

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