

THE PHOTOOXIDATION OF DYPNONE AND p-SUBSTITUTED DYPNONES IN
THE PRESENCE OF METALLIC COMPOUNDS

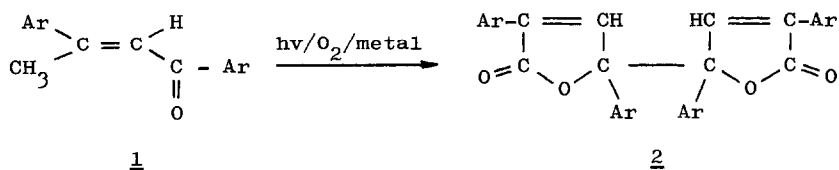
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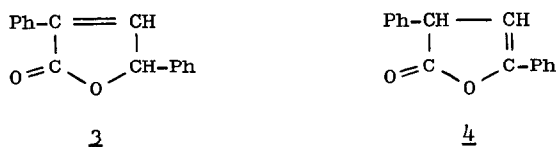
There has been considerable interest in the metallic compound-catalyzed photochemical reactions.¹ In most of these systems, an apparent interaction between metal and organic molecule in the ground state is believed to exist even in cases where no such an interaction can be verified definitely by isolating a coordination compound as a stable and isolable species. We consider that even when metal does not make an evident interaction with organic molecule in the ground state, if the metal makes any kind of interaction with organic molecule in the excited state, it would make an influence on the reaction pattern of the organic molecule and induce to form products different from what can be obtained in the absence of the metal. Such a system was found in the photooxidation of dypnone and p-substituted dypnones, and the results will be reported in this communication.

When a methanol solution (150 ml) of dypnone (1a, 1.1 g) containing 0.5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was irradiated with pyrex-filtered light for 6 hr while bubbling with air, methanol-insoluble material of 2a crystallized out. In a similar way 2b and 2c were obtained from 1b and 1c, respectively. The structures of 2a-2c were determined from elemental analyses and data shown in Table 1. Structure 2a was further established by the undepressed mixture melting point and the identity of its IR spectrum with that of a sample obtained by the thermolytic dimerization of diazoacetophenone.² The stereochemistry of 5,5'-positions, however, remains undetermined.

It should be noted that the present reaction proceeded only under the cooperation of the three elements---irradiation, metallic compound and oxygen; when metallic compound and/or air were lacking in the photoreaction of 1a, cis-trans isomerization was the sole reaction pattern. Furthermore, neither singlet-oxygen oxidation (rose bengal-tungsten lamp or hydrogen peroxide-sodium



a: Ar = phenyl b: Ar = p-tolyl c: Ar = p-bromophenyl



hypochlorite) nor radical-initiated oxidation (benzoyl peroxide at 100°C) of 1a afforded 2a. 1a has been known to afford benzoic acid on autooxidation in the presence of t-butoxide ion,³ but no benzoic acid was identified in the present reaction.

Table 1

product	yield (%)	mp (°C)	IR (cm ⁻¹)	UV	NMR (CDCl ₃ , δ)	MW (vpo)
<u>2a</u>	42	288-289	1760	_a)	_a)	_a)
<u>2b</u>	34	240-241	1760	{ 285 nm ε, 24000	{ 2.3 (12H, s) 7.1-8.0 (18H, m)	490
<u>2c</u>	49	242-243	1760	_a)	_a)	_a)

a) Not determined because of poor solubility in most of organic solvents at room temperature

The absence of monomeric lactones 3 and/or 4, which are known to be precursors for the formation of 2a from diazoacetophenone,² indicates that these lactones are not involved in the present reaction. This fact leads us to assume that the 5,5'-bond in 2a-2c has been formed in the earlier stages of the reaction.

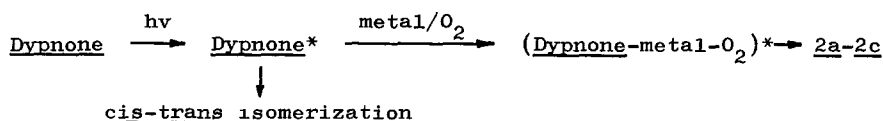
The UV spectrum of the dyprnone-CuSO₄ mixture coincided exactly to the summation of each spectrum, thus indicating that no interaction between these two compounds is involved in the ground states.

It was found that CuI·P(OC₂H₅)₃, CuCl₂ and FeCl₃ were also effective for the photooxidation of 1a, affording 2a in 30%, 40% and 17% yields, respectively. However, NiSO₄, HgCl₂ and CdCl₂ were found to be scarcely effective and less than few percent yields of 2a were obtained during the same reaction time.

Only catalytic amount of CuSO₄ was found sufficient to induce the present reaction. When the photooxidation was carried out with CuSO₄/dyprnone ratio of 0.01, the yield of 2a in a limited reaction time was 2.5 times as large as that obtained when the reaction was carried out with its ratio of 0.1. Evidently, larger amount of CuSO₄ prevented the effective absorption of light by dyprnone, thus affording a lower yield.

p-Bromo compound 1c did not afford 2c in carbon disulfide in the absence of metallic compound, which would eliminate the possibility that the rôle of metallic compound might be to induce a heavy atom effect.

In view of the fact that the effect of metallic compound was not observed in the absence of oxygen, we picturize the transition state as the one including excited dyprnone, metal and oxygen, and would like to propose the reaction scheme as follows.



Dyprnone: 1a-1c

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References

1. As one of the most recent reports: R. G. Salomon and J. K. Kochi, Tetrahedron Letters, 1973, 2529.
2. P. Yates and T. J. Clark, Tetrahedron Letters, 1961, 435.
3. W. von E. Doering and R. M. Haines, J. Amer. Chem. Soc., 76, 482 (1954).