tion of benzaldehyde (Figure 2), and supported a carbonyl radical **4**. Cocivera and Trozzolo have recently suggested the intermediacy of a radical pair ($C_6H_5\dot{C}{=}O + C_6H_5\dot{C}HOH$) in the room-temperature photolysis of benzaldehyde.[10] Our results, however, show that the hydroxybenzyl radical is absent in the low-temperature photochemistry, which must simply involve the formation of a benzoyl radical. Furthermore, hydrogen transfer in **1** taking place intramolecularly (yielding **2** or its diradical equivalent) or intermolecularly (yielding a mixture of **4** and **7**) is not compatible with our results, which are best explained by a radical chain mechanism.[11] For the sake of simplicity we assumed that both **3** and **6** were derived from **5**, but **6** could also have been formed by reaction of **4** with **1**.

Additional evidence for a second radical, such as **5**, in the thermal conversion of **4** to products was obtained by esr during warm-up of the photolyzed sample, whereby the formation of a radical showing hyperfine structure became visible (Figure 3).[12] Our mechanism predicts that a solvent which is a poorer hydrogen donor than **1** should not participate chemically in the conversion of **1** to **3**. Indeed, irradiation of **1** at 77°K in benzene containing CD_3OD and warm-up yielded **3** which was free from deuterium (mass spectrum),[13] in contrast with the results of Pappas and Blackwell,[2] who obtained mostly **3**-d_1 by photolyzing **1** at room temperature in solvents containing CH_3OD[14] or D_2O. The mechanism of the photochemical conversion of **1** to a phthalide-like product (**3** and/or **6**) at 77°K will remain unclear at least until a direct product analysis can be performed at that temperature. We note, however, that since the radical **4** is stable at 77°K, neither it nor **5** can be an intermediate leading to products at that temperature. It is reasonable, therefore, to postulate that the observed photochemistry at 77°K proceeds from the short-lived singlet excited state of **1** and yields **3** and/or **6**.

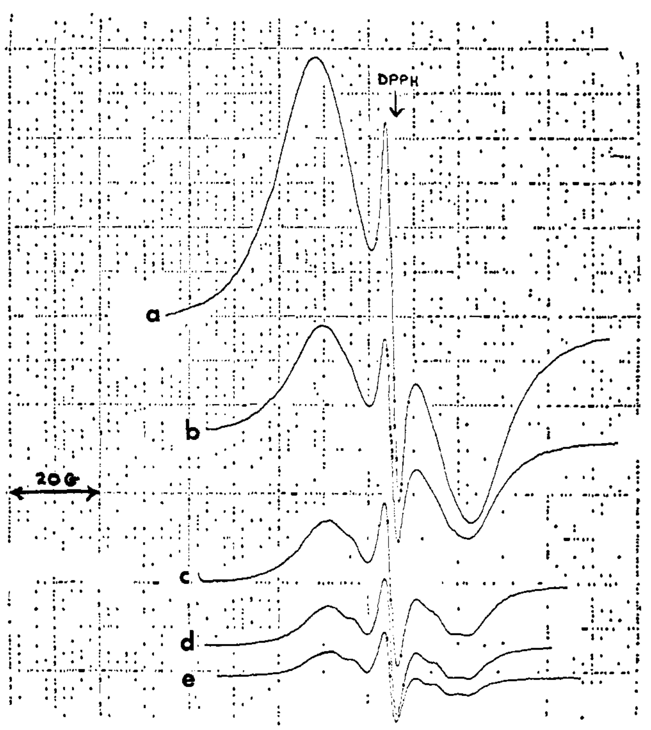

Figure 3. Warm-up of the *o*-phthalaldehyde radical (spectra a–e were recorded as the temperature increased).

The formation of **4** and the subsequent dark reactions would result from intersystem crossing of the initially formed singlet excited species followed by α cleavage of the C–H bond from the triplet.

Acknowledgment. We thank the National Science Foundation (GP 12379), the National Institutes of Health (GM 16759), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to M. Miskevitch for some technical assistance, and to Dr. M. G. Ettlinger for comments.

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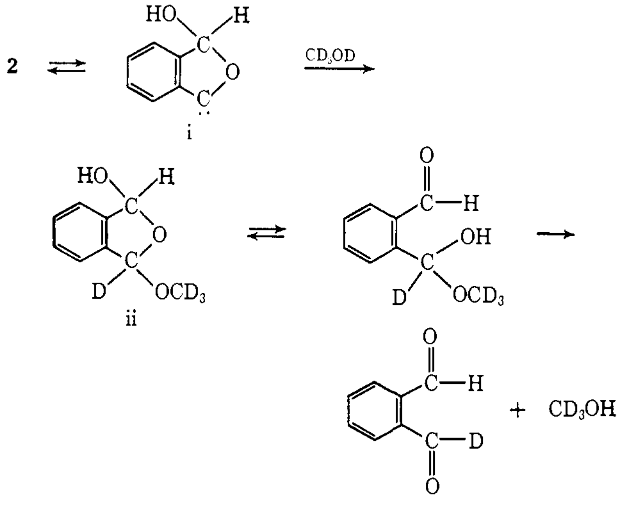
[10] M. Cocivera and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 1772 (1970).

[11] One referee objected to our postulating a free-radical *chain* mechanism. However, the H· formed upon irradiation of **1** was not detected and it is likely that much of it diffused rapidly and was deactivated, *e.g.*, by forming H_2. To the extent that H· is lost, the formation of the observed products derived from **5** requires another hydrogen radical source, and **1** is a reasonable candidate. However, because of the difficulty of getting absolute measurements on the number of free radicals, the average chain length is unknown. The similarity among the fingerprint regions in the spectra of **1**, **3**, and **6** precluded a direct product analysis by ir, and the ratio of **3** to **6** formed in the warm-up could not be compared to that formed at 77°K.

[12] The mass spectra of **1** and **3** are practically indistinguishable, suggesting that a rearrangement similar to that experienced by **1** in the photochemical–thermal process may also occur upon electron impact.

[13] Deuterium was also absent in **1** which was recovered in the experiment, ruling out the participation of the singlet carbene i (obtained by cyclization of **2**[3]) which would have been expected to react with solvent to yield ii, from which **3**-*d* would be generated *via* the hemiacetal.



[14] Irradiation of **1** in pure CH_3OH, contrary to most solvents, yields a dark mixture which contains several products in addition to **3** and dimers.

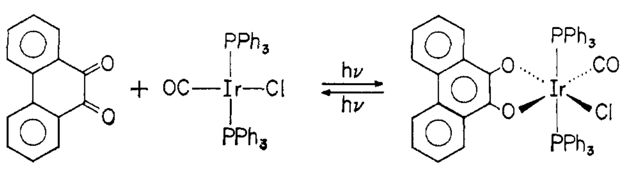
Photoinduced Oxidative Addition of 9,10-Phenanthrenequinone to $Ir(PPh_3)_2(CO)(Cl)$

Sir:

We report in this paper a study of the photoinduced oxidative addition of 9,10-phenanthrenequinone to $Ir(PPh_3)_2(CO)(Cl)$. This and similar reactions we have observed afford convenient syntheses of *o*-quinone complexes and provide examples of a new use of photochemical activation in transition-metal complex synthesis which promises to be of considerable utility.

Photochemical activation has found wide employment in synthesis of transition-metal complexes.[1] The most common use of photochemistry in synthesis has been to promote formation of coordinatively unsaturated intermediates by expulsion of some ligand—usually CO.[2] Thus expulsion of CO is the photochemical primary process in photoinduced substitution of PPh_3 for CO in $Cr(CO)_6$[3] and in photoinduced addition of H_2 to $Ru(PPh_3)_2(CO)_3$ to give $Ru(PPh_3)_2(CO)_2(H)_2$.[4] Less commonly observed processes include linkage isomerization,[5] geometrical isomerization,[6] and photoresolution[7] of complexes and chemical transformations of ligands.[8] We describe here a process in which the metal complex $Ir(PPh_3)_2(CO)(Cl)$ apparently serves to trap electronically excited states of *o*-quinones.

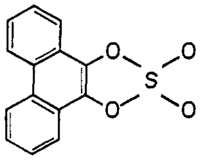
Solutions of 9,10-phenanthrenequinone and $Ir(PPh_3)_2(CO)(Cl)$ (**1**) in 2:1 molar ratio and total concentration of 6×10^{-3} *M* were irradiated under argon for 4–6 hr with a Hanovia medium-pressure mercury arc whose output was filtered through a cylindrical uranium glass sleeve filter to exclude light of wavelengths shorter than 345 nm. The deep red-brown solutions were evaporated under vacuum and the crude residue, which consisted of a mixture of **2** and unreacted starting materials, was crystallized from chloroform–ethanol and then from benzene–hexane to give pure **2** as deep red-brown, air-stable crystals, soluble in benzene and chloroform, insoluble in ethanol and hexane. Little or no reaction occurred between **1** and phenanthrenequinone in benzene at 25° in the dark; some formation of **2** was observed upon reflux of the same solution. Complex **2** gave elemental analyses consistent with the proposed structure (*Anal.*[9] Calcd for $C_{51}H_{38}P_2O_3ClIr$: C, 61.9; H, 3.85; Cl, 3.59; mol wt, 988. Found: C, 61.0; H, 3.97; Cl, 3.65; mol wt, 907), and in KBr discs gave ν_{CO} 2024 (vs) cm^{-1}, consistent with an oxidized Ir center. Two sharp bands at 1616 (m) and 1596 (m) cm^{-1} were attributed to the coordinated phenanthrenediol unit; the characteristic bands of the quinone were not observed. The visible–ultraviolet absorption spectrum of **2** was characterized by a strong new band in the visible (λ_{max} 522 nm, ϵ 1.16×10^3). The chemical transformation which occurs upon near-ultraviolet irradiation of solutions of **1** and phenanthrenequinone in benzene is thus evidently



1 **2** (1)

A procedure similar to reaction 1 gave $Ir(PPh_3)_2(CO)(Cl)(1,2\text{-naphthoquinone})$, analogous to **2**. No photochemical reaction was observed between **1** and 1,2-cyclohexanedione or acenaphthenequinone or upon irradiation of **1** for reasonable periods in the absence of other reagents. Chloranil reacted fairly readily with **1** under irradiation to give a mixture of products, none of them analogous to **2**.

That **2** might be prepared photochemically was suggested by the known photochemical reaction of 9,10-phenanthrenequinone and other *o*-quinones with the Lewis base sulfur dioxide in benzene to give cyclosulfates such as **3**. Observation of reaction 1 in turn suggested that the d^{10} complex $Pt(PPh_3)_3$, a more potent Lewis base than **1**, might react spontaneously with *o*-quinones. In fact, brownish-red crystals of $Pt(PPh_3)_2(9,10\text{-phenanthrenequinone})$, **4**, precipitate slowly from solutions of $Pt(PPh)_4$ and the quinone in benzene stored in the dark at 25°. Complex **4** had characteristic infrared absorptions at 1610 (m) and 1588 (m) cm^{-1}. *Anal.* Calcd for $C_{50}H_{38}P_2O_2Pt$: C, 64.7; H, 4.09; mol wt, 927. Found: C, 65.9; H, 4.62; mol wt, 858.



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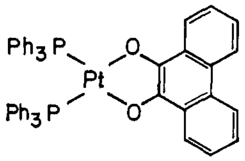

4

Complex **2** is photosensitive under conditions of its formation. Irradiations of solutions of **2** in benzene with the light source used to drive reaction 1 led to production of stoichiometric amounts of **1** but somewhat less than an equivalent of phenanthrenequinone together with a second organic product, as yet unidentified, which absorbs less strongly than the quinone in the near-ultraviolet. When solutions of **1** and quinone in molar ratios 1:2, 1:1, and 2:1 were irradiated, the ratio of **2** to **1** present in the solution eventually became essentially constant. The **2**:**1** ratio in such mixtures and the initial rate of formation of **2** were increased by increasing the quinone concentration. These observations are consistent with, but do not serve to distinguish between, kinetically equivalent mechanisms in which either (or both) **1** or the quinone is photochemically excited and attacks the other partner in the reaction. We incline to the view that photoexcited phenanthrenequinone is trapped by **1** to yield **2**. This would be analogous to trapping of photoexcited quinone by SO_2 in the aforementioned photochemical synthesis of **3** and, when probable lifetimes of photoexcited **1** and quinone triplets are considered, seems more plausible than the alternative in which photoexcited **1** is the active partner. The quantum yield for reaction 1 in the forward direction is about 0.5 ×

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(1) Recent reviews include (a) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968); (b) D. Valentine, *Annu. Rev. Photochem.*, *1967*, **1**, 454 (1969); *1968*, **2**, 341 (1970); see also ref 2.

(2) E. A. Koerner von Gustorf and F. Grevels (*Fortsch. Chem. Forsch.*, **13**, 367 (1969)) present an excellent review of metal carbonyl photochemistry.

(3) See ref 1b and 2 for original papers.

(4) D. Valentine, B. Sarver, and J. P. Collman, manuscript in preparation.

(5) *E.g.*, V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

(6) P. R. Brookes and B. L. Shaw, *Chem. Commun.*, 919 (1968).

(7) K. L. Stevenson and J. F. Verdieck, *Mol. Photochem.*, **1**, 271 (1969); *J. Amer. Chem. Soc.*, **90**, 2974 (1968).

(8) *E.g.*, D. G. Whitten, P. D. Wildes, and I. G. Lopp, *ibid.*, **91**, 3393 (1969).

(9) Elemental analyses were performed by Amherst Microanalytical laboratory, Amherst, Mass.

10^{-2}.[10] Such a relatively efficient reaction, especially at the concentrations used,[11] requires a moderately long-lived excited-state species.[12] The only long-lived complex excited state would presumably have to be the triplet state. Triplet states of square-planar d^8 complexes are almost certainly tetrahedral and can be expected to cross over rapidly into the ground state.[13] It would thus seem that photoexcited quinone is the logical candidate for the active partner in the reaction. This would explain our observation that the reactivity or unreactivity of particular quinones is the same in reaction 1 and in the cyclosulfate synthesis.

Studies of the chemistry of 2 and 4 under various conditions and attempts to expand this synthesis to thiolenes and to other metal complexes will be reported soon.[14]

[10] Estimated at 365 nm relative to the quantum yield for photochemical decomposition of $[(NH_3)_4Co(NH_2,O_2)Co(NH_3)_4]^{4+}$ in 0.1 *M* $HClO_4$ solutions. *Cf.* J. Valentine and D. Valentine, *J. Amer. Chem. Soc.*, in press.

[11] These concentrations produced optimum yields; at higher concentrations separation problems were encountered.

[12] We assume explicitly that neither geometrical isomerization of 1 nor expulsion of a ligand would lead to the observed products.

[13] See ref 1b for further exposition of this point.

[14] We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

[15] National Science Foundation Summer Fellow, 1969.

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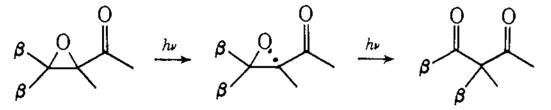
Photoisomerization of Phenalen-1-one Oxide. A New Course of Light-Induced α,β-Epoxy Ketone Rearrangement[1]

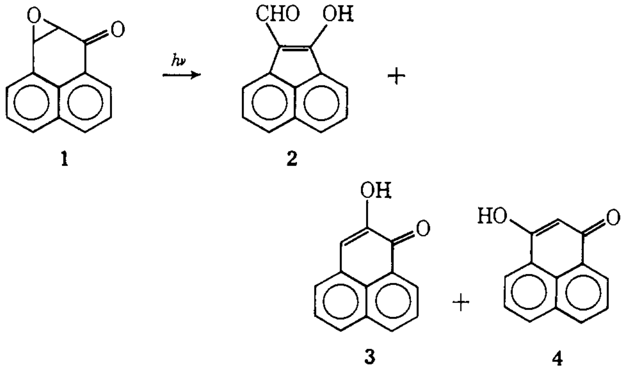
Sir:

The photoisomerization of α,β-epoxy ketones to β-diketones is a subject of considerable interest.[2] A characteristic feature of this reaction is the lack of phenyl migration, which has been interpreted in terms of the mechanism in eq 1, whereby there is complete or pronounced bond breaking at the β carbon prior to rebonding of the migrating group at the α position.[2a,c] On investigating the generality of this feature, we have discovered a new course of photorearrangement of an α,β-epoxy ketone system, which is described herein.



(1)

Irradiation[3] of a 0.5% solution of phenalenone oxide 1[4] in acetonitrile followed by silica gel chromatography provided three products identified as acenaphthen-1-one-2-carboxaldehyde (2),[5] 2-hydroxyphenalen-1-one (3),[4] and 3-hydroxyphenalen-1-one (4)[6] by direct comparison with the known compounds. The products 2, 3, and 4 were obtained in 16, 30, and 5% yields, respectively.

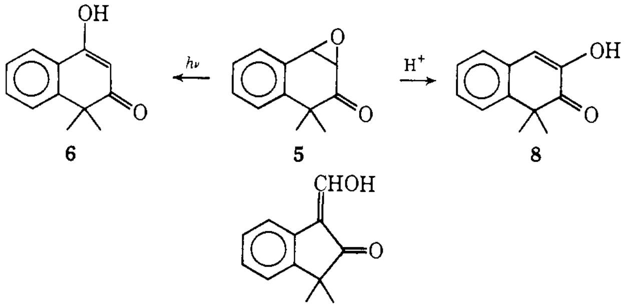


1 2 3 4

The results provide a distinct point of departure from previous findings. Based on the mechanism of eq 1, formation of product 2 requires an aryl migration, which has not been observed previously. The β-diketone 4, predicted to be the major product, was actually produced in minor amount. Furthermore the formation of 3 apparently represents the first example of an α,β-epoxy ketone photorearrangement to an α-diketone, a process which is not readily explicable in terms of eq 1.

These findings suggested that epoxy ketone 1 follows an alternative course of photorearrangement, which was considered either (a) to be unique for this naphthyl carbonyl system, or (b) to reflect a general feature of the system, such as incorporation of the β-aromatic substituent into the cyclic epoxy ketone framework which might reasonably facilitate aryl migration. Thus, it was of interest to investigate 1,1-dimethyl-2-(1H)-naphthalenone oxide (5),[7] which retains the latter feature.

Irradiation[3] of 5[8] in acetonitrile yielded a single crystalline product, mp 199–200°, in 21% yield. Although isomeric with 5, the photoproduct was not identical with either the acid-catalyzed rearrangement product of 5, mp 101–102°, formulated as the β-diketone 6,[7] or the previously unreported formyl ketone 7,



6 5 8

7

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[1] Taken in part from the Ph.D. Thesis of R. M. G., Emory University, Atlanta, Ga., 1969. The preparation of this thesis and the terminal research of R. M. G. were directed by Dr. Leon Mandell.

[2] (a) H. E. Zimmerman, B. R. Cowley, C-Y. Tseng, and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 947 (1964), and earlier reports; (b) H. Wehrli, C. Lehmann, P. Keller, J. Bonet, K. Schaffner, and O. Jeger, *Helv. Chem. Acta*, **49**, 2218 (1966), and earlier reports; (c) C. S. Markos and W. Reusch, *J. Amer. Chem. Soc.*, **89**, 3363 (1967), and earlier reports; (d) J. P. Pete and M. L. Villaume, *Tetrahedron Lett.*, 3753 (1969); (e) for an interesting vinylogous system, see M. Debono, R. M. Molloy, D. Bauer, T. Iizuka, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **92**, 420 (1970); (f) for a review, see A. Padwa in "Organic Photochemistry," Vol. I, Marcel Dekker, New York, N. Y., 1967, pp 93–100.

[3] A Hanovia 450-W medium-pressure Hg lamp was utilized together with a Corex filter ($\lambda > 280$ nm).

[4] L. F. Fieser and L. W. Newton, *J. Amer. Chem. Soc.*, **64**, 917 (1942).

[5] E. Ghigi, A. M. Drusiani, and L. Plessi, *Ann. Chim. (Rome)*, **53**, 266 (1963); *Chem. Abstr.*, **59**, 15225*a* (1963).

[6] K. Fleischer and E. Retze, *Chem. Ber.*, **55**, 3280 (1922).

[7] N. H. Cromwell and R. D. Campbell, *J. Org. Chem.*, **22**, 520 (1957).

[8] (a) The epoxy ketone was obtained crystalline, mp 35–38°; (b) experimental details will be presented in full report.