For the fast process, the difference spectrum suggests that the intermediate is relatively nonabsorbing in the near-uv region which allows us to estimate the second-order rate constants (at 20 ± 2°): $k_1 = (2 \pm 1) \times 10^9$ (THF), $(3 \pm 1) \times 10^9$ (acetonitrile), and $(5 \pm 1) \times 10^9\ M^{-1}\ \text{sec}^{-1}$ (cyclohexane). The values approach the estimated diffusion-controlled limits in the three solvents.[15] In THF, the rate of the fast process is unaffected by added inert electrolyte ($\text{N}(n\text{-C}_4\text{H}_9)^+\text{PF}_6^-$), ruling out reactions involving ions. The only reasonable interpretation is that light-induced cleavage of the Mo-Mo bond has occurred, followed by recombination of the monomeric fragments (eq 2).

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2 \xrightarrow{h\nu} 2(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3 \xrightarrow{k_1} [(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2 \quad (2)$$

This interpretation is consistent with: (1) the loss of absorbance in the $\sigma \rightarrow \sigma^*$ (Mo-Mo) region, (2) the nearly diffusion-controlled rates in the range found for radical recombination reactions in solution,[16] and (3) the chemical evidence obtained in other work for radical byproducts.[17]

For the slow process, an estimate of the *maximum* second-order rate constant can be made (at 20 ± 2°), $k_2 = 3 \times 10^7$ (acetonitrile), 5×10^7 (THF), and $1 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ (cyclohexane), and a lower limit can be set at one-tenth of these values. For purposes of comparison, the value for the recapture of CO by Cr(CO)_5 in cyclohexane has been reported to be $(3 \pm 1) \times 10^6\ M^{-1}\ \text{sec}^{-1}$.[18] In THF, the slow process is also unaffected by added inert electrolyte, again ruling out an ionic reaction. The slow process appears to involve recombination with CO (eq 3),[19]

$$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_5 + \text{CO} \rightarrow [(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2 \quad (3)$$

as shown by: (1) retention of the strong absorptivity in the uv, which implies the presence of a Mo-Mo bond in the intermediate, (2) the second-order kinetics with a rate constant in the range reported for the recapture of CO by Cr(CO)_5, and (3) the CO substitution behavior found for light-induced reactions between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ and neutral phosphine and phosphite ligands.[4,9]

The fact that *either* uv or visible photolysis gives *both* metal-metal bond cleavage and loss of CO implies that the two intermediates have a common origin, but it is not clear that the intermediate from which CO has been lost is a primary photoproduct. Metal-metal bond cleavage is expected following uv excitation into the $\sigma \rightarrow \sigma^*$ (Mo-Mo) band since the excited state should be antibonding with regard to the Mo-Mo bond, and, when thermally equilibrated, most likely consists of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3$ fragments in a solvent cage. Regardless of the detailed origin of the visible band, visible excitation could also lead to metal-metal bond cleavage. The energy of the thermally equilibrated $\sigma \rightarrow \sigma^*$ excited state can be estimated as <40 kcal/mol, since the metal-metal bond strength of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$ in organic solvents appears to be significantly less than 40 kcal/mol.[9] Photolysis in the visible band (λ ≥460 nm)[12] is sufficiently energetic to populate the thermally equilibrated $\sigma \rightarrow \sigma^*$ state. If there is an intersection between the $\sigma \rightarrow \sigma^*$ and $d \rightarrow d$ excited state surfaces, and if internal conversion and/or intersystem crossing efficiencies are high, efficient metal-metal bond cleavage is expected to occur, perhaps in competition with loss of CO.

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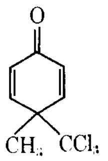
Light Intensity Effects on Ketone Photochemistry in Solution as a Consequence of Radical Quenching and Radical Chain Processes[1]

Sir:

We find that light intensity is a critical reaction variable in the photochemistry of cyclohexadienone (**1**) in 2-propanol (IPA) and other solvents and that intensity effects are related to unusual quenching behavior in this model system.[2] The fact that the role of light intensity (I^0) has been largely ignored by photochemists[3] may prove to have been a serious oversight, as demonstrated by the following observations.

The main products from irradiation of **1** in IPA are *p*-cresol (**2**), cyclopentenone ether (**3**), chloroform, and acetone. Compound **3** undergoes facile isomerization in the dark to **4** which is the material actually subjected to GLPC analysis. The ratio of **2** to **3** in preparative runs varied considerably using different light sources emitting over approximately the same wavelength range.[2j] Difficulty was also experienced in reproducing quantum yield measure-



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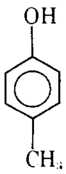

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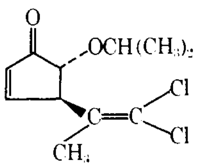

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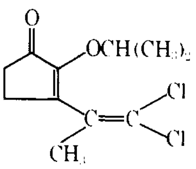

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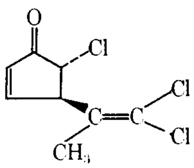

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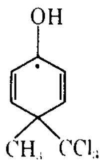

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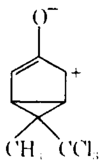

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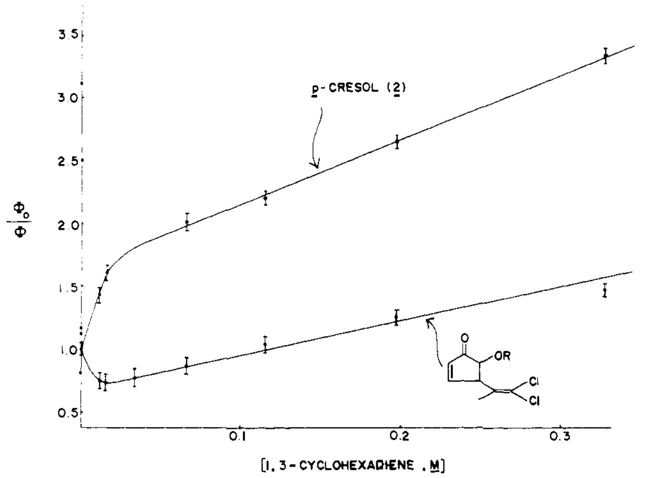

Figure 1. Effect of added 1,3-cyclohexadiene on product yields from photolysis of dienone **1** in 2-propanol.

ments for formation of **2** and **3**, even keeping in mind the previously established dependence of Φ on temperature and dienone **1** concentration.[2j] We therefore systematically varied all reaction conditions, including I^0, in this system. The observations pertinent to the present discussion are briefly summarized.

(1) The yield of **2** relative to **3** increases as the concentration of **1** is increased in nondegassed solution. (2) In nondegassed IPA solutions in closed tubes, the yield of **2** relative to **3** increases by a factor of six with a ninefold increase in I^0_{366}. Similar effects are seen in ethyl ether and cyclohexane. The data given in Table I illustrates the large effect of I^0 on Φ_2; there is a negligible effect on Φ_3. Conversions in these runs were kept below 2%. (3) Φ_2 was sharply reduced when the reaction cell contents were stirred, keeping the conditions otherwise as in (2). (4) On photolysis of IPA and ether solutions previously purged with nitrogen, values of Φ_2 greater than unity were obtained, and a decrease in Φ_2 was noticed when I^0 was increased. Hexachloroethane was a reaction product only at high I^0. (5) Plots of Φ^0/Φ for quenching by 1,3-cyclohexadiene (CHD) of formation of **2** and **3** in IPA are shown in Figure 1. These unusual quenching plots observed in degassed as well as nondegassed solutions have been reproduced by two different workers using completely different batches of purified reactants.[4] (6) The yield of CHD dimers, diagnostic of triplet energy transfer to CHD, increases linearly as [CHD] is increased. (7) As reported previously,[2i] **5** is formed at the expense of **3** when **1** is irradiated in IPA containing LiCl. Plots for quenching by CHD of formation of **2** and **5** in such solutions are analogous in all respects to those shown in Figure 1.[2j] (8) Di-*tert*-butyl nitroxide (DTBN) in IPA (0.01 *M*) totally quenches formation of **2** and slightly increases the yield of **3**. (9) Naphthalene inefficiently quenches formation of **2** (linear Stern-Volmer plot) but has no effect on **3**. (10) In agreement with an earlier report,[5] thermal decomposition of benzoyl peroxide in IPA containing dienone **1** gives high yields of **2**, chloroform, and acetone.

These results can be rationalized by the following scheme, which incorporates mechanistic features discussed previously[2e,i] and some new postulates.

$$\mathbf{1} + h\nu \rightarrow {}^1\mathbf{1}^* \rightarrow {}^3\mathbf{1}^* \tag{1}$$

$$^3\mathbf{1}^* + \mathrm{Me_2CHOH} \rightarrow \mathbf{6} + \mathrm{Me_2\dot{C}OH} \tag{2}$$

$$\mathbf{6} \rightarrow \mathbf{2} + \mathrm{Cl_3C\cdot} \tag{3}$$

$$\mathrm{Cl_3C\cdot} + \mathrm{Me_2CHOH} \rightarrow \mathrm{CHCl_3} + \mathrm{Me_2\dot{C}OH} \tag{4}$$

$$\mathrm{Me_2\dot{C}OH} + \mathbf{1} \rightarrow \mathbf{6} + \mathrm{Me_2C{=}O} \tag{5}$$

Table I. Effect of Light Intensity and Other Reaction Variables on the Quantum Yield of *p*-Cresol (**2**)[a]

Solvent	Deoxygenated	Light intensity 10^{16} photons $\mathrm{cm^{-2}\ min^{-1}}$ [b]	10^{18} Photons absorbed[c]	Φ_2[d]
IPA	No	6.89	6.08	0.02
IPA	No	12.4	5.58	0.05
IPA	No	27.7	6.29	0.06
IPA	No	106.5	6.23	0.12
IPA	No[e]	104.3	6.88	0.01
IPA	Yes	6.9	6.13	1.91
IPA	Yes	108.3	6.48	1.54
Ethyl ether	No	12.6	5.95	0.08
Ethyl ether	No	100.6	5.98	0.30
Ethyl ether	Yes	10.7	4.88	1.73
Ethyl ether	Yes	100.1	5.89	0.94
Cyclohexane	No	6.2	5.29	0.001
Cyclohexane	No	97.7	5.58	0.036

[a] Experiments made using a split-beam arrangement on an optical bench with an Osram 200-W super pressure mercury source and a Bausch and Lomb high intensity grating monochromator to isolate the 366-nm band. Wire screens were used to vary the light intensity, and jacketed holders were used to maintain solution temperatures at 28 ± 0.5°. [b] Ferrioxalate actinometry was used. [c] The total light absorbed was kept approximately constant by varying the time of irradiation. [d] Yields of **2** measured by GLPC relative to an internal standard (acenaphthene) on a 10-ft 10% OV-225 on Chrom Q column. [e] Solution magnetically stirred during irradiation.

$$2\mathrm{Me_2\dot{C}OH} \rightarrow \mathrm{Me_2C(OH)C(OH)Me_2} \tag{6}$$

$$2\mathrm{Me_2\dot{C}OH} \rightarrow \mathrm{Me_2CHOH} + \mathrm{CH_2{=}C(OH)CH_3} \rightarrow \mathrm{Me_2C{=}O} \tag{7}$$

$$2\mathrm{Cl_3C\cdot} \rightarrow \mathrm{C_2Cl_6} \tag{8}$$

$$^3\mathbf{1}^* + \mathrm{Q} \rightarrow {}^3\mathrm{Q}^* + \mathbf{1} \tag{9}$$

$$^3\mathbf{1}^* \rightarrow \mathbf{7} \tag{10}$$

$$\mathbf{7} + \mathrm{Me_2CHOH} \rightarrow \mathbf{3} + \mathrm{HCl} \tag{11}$$

$$\mathbf{7} + \mathrm{Cl^-} \rightarrow \mathbf{5} + \mathrm{Cl^-} \tag{12}$$

$$\mathbf{7} \rightarrow \mathbf{1} \tag{13}$$

We suggest that intermediate radicals are efficiently scavenged by low concentrations of CHD and DTBN and less efficiently by naphthalene.[6] Such radical trapping has ample precedent in the literature,[7] although it has frequently been overlooked by photochemists. Since these quenchers do not reduce the yields of **3** and **5**, derived from zwitterion **7**, it is evident that $^3\mathbf{1}^*$ is not quenched under these conditions, in agreement with earlier studies in benzene ($\tau_T \sim 10^{-8}$–10^{-9} sec).[2f] Thus, we propose that the steep portion of the quenching plot (Figure 1) for formation of **2** in IPA arises from trapping of intermediate radicals, interrupting the radical chain reaction, while the gentler slope is probably due to quenching of a triplet excited state.[8]

The data clearly establishes that O_2 is an efficient quencher of cresol formation in IPA, although earlier studies[2e] showed it had no effect on photoreactions of **1** proceeding via zwitterion **7** and its triplet precursor. At high light intensities, we suggest that oxygen in the business portion of the cell (the focused beam has a cross section of ~0.4 cm^2 and is largely absorbed within the first few millimeters of solution) is rapidly depleted by the intermediate radicals R· and the chain process (eq 3–5) proceeds. Stirring has a dramatic effect on Φ_2 indicating that diffusion of oxygen to the reaction site is critical. More efficient radical quenching occurs at low I^0, since the smaller steady state [R·] allows diffusion of O_2 to the reaction site to compete with O_2 consumption. In the absence of oxygen, [R·] increases with increasing I^0, enhancing the likelihood of radical-radical reactions (eq 6–8) which break the chain and reduce Φ_2.[9] For $\mathrm{Me_2\dot{C}OH}$ the most important of these reactions (eq 7) is disproportionation to IPA and acetone via the enol.[10]

The dip in the plot for CHD quenching of **3** and **5** in IPA (not seen in MeOH or CF_3CH_2OH) is tentatively attributed to scavenging by CHD (<0.05 *M*) of radicals which would otherwise react to some extent with **3** and **5**. At higher [CHD], triplet quenching becomes significant, and normal Stern–Volmer kinetic behavior is observed.

Several points of general significance emerge from this study. (1) Light intensity effects should be important in solution for photochemical reactions involving radical intermediates, especially when chain processes or induced decomposition of reactant is involved.[9] This may be quite general in IPA and related H-donor solvents. (2) Dienes acting as radical traps can efficiently quench photochemical reactions involving radical intermediates by processes other than triplet energy transfer.[8] Radical quenching may indeed be involved in systems where differential quenching of two or more products is observed, heretofore used as evidence for two reactive quenchable triplets.[2k,11] (3) There are increasingly frequent reports of dramatic changes in the course of a photochemical reaction as the wavelength of light is varied.[12] Since I^0 changes drastically as λ varied (often comparison is made between experiments at 254 and 366 nm using different lamps) it is frequently not possible without further study to unequivocally attribute such differences to one or the other factor.

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Direct Evidence for Reversal of Helicity in the Stereoisomerization Mechanism of Bis(β-diketonato)titanium(IV) Complexes

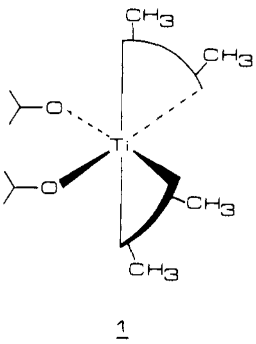
Sir:

In connection with our recent studies of isomerism and isomerization in propeller-like molecules[1] we became aware of a report[2] dealing with studies on static and dynamic stereochemistry of some *cis*-dialkoxybis(acetylacetonate)titanium compounds, in which prochiral groups were introduced as ligands. In particular, Bradley and Holloway[2] observed that "the kinetic parameters for methyl isopropyl group exchange (in **1**) were the same as for methyl (acac group) exchange" and that "at low temperature the α-protons of the neopentyl glycollate group in $Ti(acac)_2(OCH_2CMe_2CH_2O)$ broadened and split into an AB group".

The purpose of this communication is to note that such experiments provide *compelling evidence for reversal of helicity in the stereoisomerization mechanism of such molecules.* The relevance of such a conclusion is borne out in the following.

The cumulative weight of circumstantial evidence so far accumulated has pointed out that dialkoxybis(chelate)titanium compounds[2,3] as well as a large number of structurally related dihalogenobis(β-diketonato) derivatives of group 4 elements[4] adopt a cis octahedral structure. Such structure has C_2 skeletal symmetry point group and thus is chiral. It follows that **1** can be regarded[1d,e] as a two-bladed propeller-shaped molecule, and thus two enantiomeric forms are possible, which differ only in the sense of twist (helicity) of the chelate acetylacetonate rings.[5]

Therefore, when interconversion of the two enantiomeric forms is slow on the NMR time scale the methyl isopropoxy groups in **1**, as well the α-protons of the neopentyl glycol-



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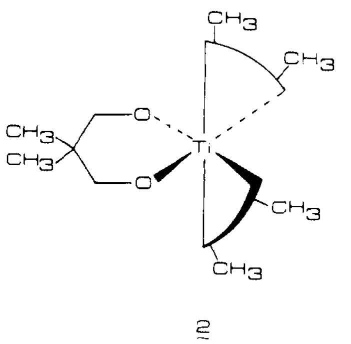

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