cis conformation, a chlorine atom, and N(7) of the theophylline anion. The bond lengths and angles in the complex cation are in good agreement with values found in the trans isomer[9] and will be described in detail elsewhere.[13] The presence of the interligand hydrogen bond system between the chelated ethylenediamine ligands and the carbonyl group at C(6) of the pyrimidine ring (Figure 2 and Table II) is in keeping with our

Table II. Distances (Å) and Angles (deg) in the Interligand Hydrogen Bonds, D–H···A

D	H	A	H···A	D···A	∠D–H···A
N(11)	H(8)	O(6)	2.1	2.942	153
N(13)	H(16)	O(6)	2.0	2.814	158

explanation of the electrophoretic results.

Our immediate objective was the understanding of the basic interaction of complexes with nucleic acid constituents. Our electrophoretic and structural studies indicate that high selectivity can be achieved by taking advantage of the hydrogen bonding and repulsive interactions between incoming nucleosides and coordinated ligands. The cis-β-[Co(trien)Cl₂]Cl reagent may have some utility in the types of studies suggested by Leonard.[8]

(14) (a) Department of Chemistry. (b) Department of Biophysics.

Luigi G. Marzilli,* [14a] Thomas J. Kistenmacher* [14a]
Paul E. Darcy,[14a] David J. Szalda,[14a] Michael Beer* [14b]

*Departments of Chemistry and Biophysics,
The Johns Hopkins University
Baltimore, Maryland 21218*
Received March 12, 1974

Photolysis of an α-Hydroperoxy Ketone. A Type-II Process Involving the Hydroperoxy Group and 1,2-Dioxetanes
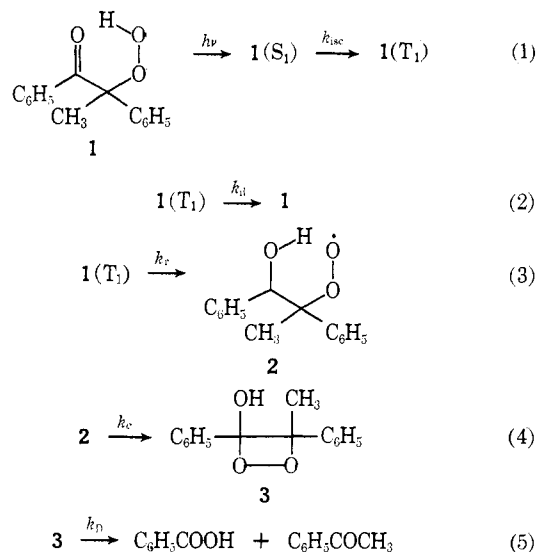
Sir:

Extensive studies of the type-II photolysis of ketones are reported.[1] It is now commonly accepted that C–H hydrogen atom abstraction occurs through a quasi-six-membered ring to give a 1,4-biradical. Considering the ease of hydrogen atom abstraction from hydroperoxides,[2] a facile type-II process might be expected from the photolysis of α-hydroperoxy ketones. In addition closure of the 1,4-biradical produced from an α-hydroperoxy ketone would lead to a 1,2-dioxetane, a unique peroxide that has generated considerable interest recently.[3] To test these proposals, the photolysis of 1,2-diphenyl-2-hydroperoxy-1-propanone (1)[4] in carbon

(1) Cf. P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).
(2) (a) K. U. Ingold, "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, p 80; (b) W. H. Richardson and H. E. O'Neal, "Comprehensive Chemical Kinetics," Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N. Y., 1972, p 539.
(3) Cf. W. H. Richardson, F. C. Montgomery, and M. B. Yelvington, *J. Amer. Chem. Soc.*, 94, 9277 (1972), and references therein.
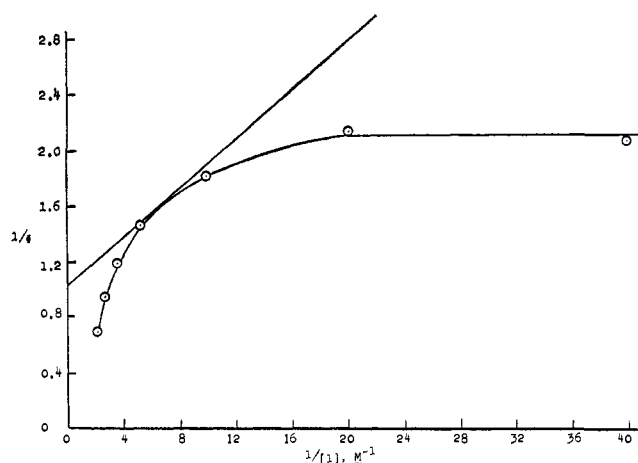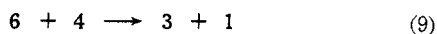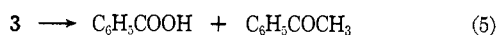(4) (a) Prepared by the method of H. R. Gersmann, H. J. W. Nieu-

tetrachloride solution was studied. The photolyses were carried out in degassed solutions on a merry-go-round[5] with a 100-W Hanovia high-pressure lamp. A potassium dichromate–potassium carbonate filter solution was used to isolate the 302.5–313.0-nm region.[6]

Benzoic acid and acetophenone are produced in quantitative chemical yield from the photolysis of 0.050–0.50 M solutions of **1**. The yield of the acid was determined by nmr, while the yield of acetophenone was obtained by nmr and glc. These products can be explained by the type-II scheme below (Scheme I). A search

Scheme I

$$1 \xrightarrow{h\nu} 1(S_1) \xrightarrow{k_{isc}} 1(T_1) \qquad (1)$$

$$1(T_1) \xrightarrow{k_{d}} 1 \qquad (2)$$

$$1(T_1) \xrightarrow{k_r} 2 \qquad (3)$$

$$2 \xrightarrow{k_c} 3 \qquad (4)$$

$$3 \xrightarrow{k_D} C_6H_5COOH + C_6H_5COCH_3 \qquad (5)$$

was made for oxygen and 1,2-diphenyl-1-propanone, the products expected from fragmentation of the biradical **2**. Neither of these products was observed where yields greater than 1% would be detected. In part, the lack of fragmentation of **2** could be due to substitution at the α-position in **1**. For example, 10% cyclization occurs with butyrophenone, while α-methyl and α-gem-dimethyl derivatives give 29 and 89% cyclization, respectively.[7] Alternatively, if the activation energies for cyclization and fragmentation of **2** parallel the heats of these reactions, cyclization ($\Delta H_r° \simeq -56$ kcal/mol)[8] would be favored over fragmentation ($\Delta H_r° \simeq -48$ kcal/mol).[8] Conceivably, the hydroperoxy ketone could undergo decomposition by a radical chain process, where an alcohol (1,2-diphenyl-2-hydroxy-1-propanone) and oxygen are among the expected products.[9] Neither of these products was detected. Lastly, energy transfer from **1** to carbon tetrachloride[10] appears unlikely. The expected products from such a process (chloroform, hexachloroethane, and hydrogen chloride) were not detected or produced in a chemical yield no greater than 2%.

wenhius, and A. F. Bickel, *Proc. Chem. Soc., London*, 279 (1962). (b) The nmr spectrum and the iodometric analysis is consistent with structure **1**.
(5) R. S. N. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, 87, 3406 (1965).
(6) P. J. Wagner, P. A. Kelso, and R. C. Zepp, *J. Amer. Chem. Soc.*, 94, 7480 (1972).
(7) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 92, 6672 (1970).
(8) Calculated by methods presented in S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.
(9) Ref 2b, p 540, and references therein.
(10) (a) J. O. Pavlik, P. I. Plooard, A. C. Somersall, and J. E. Guillet, *Can. J. Chem.*, 51, 1435 (1973); (b) J. E. Guillet, *Pure Appl. Chem.*, 36, 127 (1973).
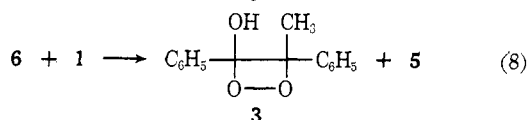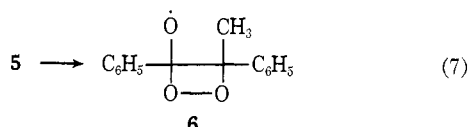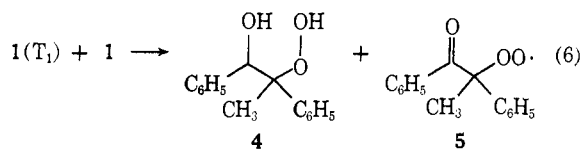
Figure 1. Quantum yields as a function of initial concentration in the photolysis of 1,2-diphenyl-2-hydroperoxy-1-propanone in degassed carbon tetrachloride.

Quantum yields for **1**, determined relative to a benzophenone–benzhydrol actinometer,[11] were found to be concentration dependent. The Φ values ranged from about 0.47 at 0.0250 M **1** to 1.44 at 0.480 M **1**. Kinetically higher order processes in Scheme II are

Scheme II

$$1(T_1) + 1 \longrightarrow \underset{4}{\underset{\underset{CH_3 \quad C_6H_5}{|}}{\underset{|}{C_6H_5}}} + \underset{5}{\underset{\underset{CH_3 \quad C_6H_5}{|}}{C_6H_5}} OO \cdot \quad (6)$$

$$5 \longrightarrow \underset{6}{C_6H_5-C_6H_5} \quad (7)$$

$$6 + 1 \longrightarrow \underset{3}{C_6H_5-C_6H_5} + 5 \quad (8)$$

$$3 \longrightarrow C_6H_5COOH + C_6H_5COCH_3 \quad (5)$$

$$6 + 4 \longrightarrow 3 + 1 \quad (9)$$

proposed to explain this result *in addition* to the unimolecular processes in Scheme I. Some steps in Scheme II are analogous to those proposed earlier by Walling and Gibian for the benzophenone sensitized decomposition of *tert*-butyl hydroperoxide.[12] A steady-state treatment on the combined Schemes I and II reveals that a reciprocal plot (Figure 1) is most informative. The data follow the curved line, while the straight line corresponds to the hypothetical result if Scheme II is solely operative but without the chain propagation step (eq 8). The actual data clearly deviate from this latter prediction, and, at concentrations of 0.05 M or less of **1**, the slope is zero which is indicative that only Scheme I is functional. Here, the limiting quantum yield is 0.47. Deviation from the hypothetical straight line at higher

(11) (a) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962); (b) T. R. Evans in "Technique of Organic Chemistry," Vol. 14, P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 331.
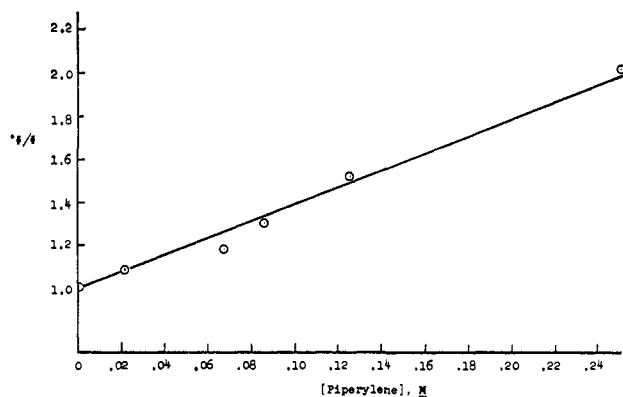(12) C. Walling and M. G. Gibian, *J. Amer. Chem. Soc.*, **87**, 3413 (1965).

Figure 2. Stern–Volmer plot for the piperylene quenching of 1,2-diphenyl-2-hydroperoxy-1-propanone in degassed carbon tetrachloride, where $^0\Phi/\Phi$ = (% reaction without piperylene)/(% reaction with piperylene) and the slope = $k_q \tau$ = 3.90 M^{-1}.

concentrations of **1** is then indicative of the importance of chain propagation (eq 8).

Quenching studies with piperylene were carried out at 0.050 M **1**, where only the unimolecular processes (Scheme I) are important and the results are shown in Figure 2. From the slope and a calculated[13] diffusion controlled rate coefficient (k_q) of 7.55 × 10^9 M^{-1} sec^{-1}, the lifetime of **1** (T$_1$) is then 5.2 × 10^{-10} sec. With the usual assumption that $k_r \gg k_d$ (Scheme I),[1] k_r = 1.9 × 10^9 sec^{-1}, a value which is two orders of magnitude greater than that reported for α,α-dimethylbutyrophenone.[7] This rate acceleration is in qualitative agreement with hydrogen atom abstraction by *tert*-butoxy radicals[1] from an OO–H *vs.* a C–H bond.[2a] Other aspects of the type-II reaction with α-hydroperoxy ketones are currently under investigation.

Acknowledgment. We thank the U. S. Army Research Office (Durham) for support of this research.

(13) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 95.

William H. Richardson,* Gregory Ranney, Frederick C. Montgomery

Department of Chemistry, San Diego State University
San Diego, California 92115

Electron Paramagnetic Resonance of Mononuclear Cobalt Oxygen Carriers Labeled with Oxygen-17

Sir:

The structure of oxygen carriers, both natural and synthetic, and in particular the nature of the metal–oxygen bond has been a subject of controversy ever since Pauling and Coryell[1] proposed that the M–O–O unit was linear in oxyhemoglobin. Subsequently Pauling[2] proposed a bent structure and Griffith[3] a π-bonded structure with equivalent oxygens equidistant from the metal atom. It is conceivable that for a given complex the energy difference between the two forms is small, and environmental factors may influence which of the forms is more stable. The crystal structure of a mononuclear

(1) L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci. U. S.*, **22**, 210 (1936).
(2) L. Pauling, "Haemoglobin," Butterworth, London, 1949.
(3) J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956).