Chemically Produced Excited States. Energy Transfer, Photochemical Reactions, and Light Emission

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Abstract: Electronically excited states formed in chemical reactions have been used to sensitize several photochemical reactions ("Photochemistry without Light"). The principal source of excited-state energy was trimethyl-1,2-dioxetane which cleaves thermally to acetone and acetaldehyde and yields excited-state products with reasonable efficiency. Photoreactive acceptors used were stilbene, acenaphthalene, 4,4-diphenyl-2,5-cyclohexadienone, and santonin. The results are discussed in terms of triplet–triplet energy transfer from the initially formed excited carbonyl compound to the reactive species. Variations in the apparent chemical yield of excited states observed with different acceptors are discussed with regard to possible quenching modes and energetics of the reactions. Chemiluminescence was observed from thermal decomposition of trimethyl-1,2-dioxetane in the presence of the fluorescent lanthanide complex, europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline. The formation of excited states in the reaction of oxalate esters with hydrogen peroxide was also examined. In contrast to previous reports, we found no evidence of a stable intermediate in the reaction of oxalate esters with hydrogen peroxide.

Electronically excited states of molecules are usually produced from ground states by light absorption. They possess not only an enhanced general reactivity (photochemistry) compared to the ground state, but also the ability to emit light (fluorescence and phosphorescence). Excited states can also be formed directly in chemical reactions. When prepared in this way they have usually been detected through their light emission properties (chemiluminescence and bioluminescence). We have recently shown that chemically produced excited states can also be detected through their chemical reactions (photochemistry without light);[1] the full account of these and related results is the subject of this paper. A lively interest in this area of research has led to several recent publications by other workers.[2]

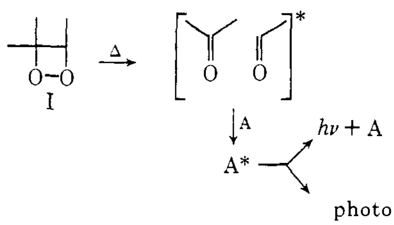
Although a large number of chemiluminescent reactions are known, in only a few cases have the reactions been demonstrated to be reasonably efficient in the production of excited states.[3] While the "photochemical" reactions of such excited states could be determined, the approach would not be general since X and Y would have to be "tailor-made" to generate the desired A* excited state.

$$X + Y \longrightarrow A^* \longrightarrow A + h\nu \qquad (1)$$

Generality can be introduced through the use of energy transfer.[1a]

$$Z + Y \longrightarrow D^* \xrightarrow{A} D + A^* \qquad (2)$$

In our work, trimethyl-1,2-dioxetane (I) was used as the source of excited states for the energy transfer.



(3)

As will be shown later, effectively only the triplet state is formed in the dioxetane decomposition. The method described above is a general one for any molecule A, provided sufficient energy is available to excite the acceptor A. The specific case of chemically produced singlet oxygen has been examined in detail recently by several authors.[4]

Results

Dioxetane Preparation. The principal dioxetane used in this study, trimethyl-1,2-dioxetane (I), was first reported by Kopecky and Mumford;[5a,b] it was prepared by the action of base on 3-bromo-2-methyl-2-butyl hydroperoxide. Because of the dioxetane's instability and explosive properties, the details of the preparation of pure I and of its solutions are given in the Experimental Section. In dilute solution (0.2 *M* in benzene) I decomposes (eq 3) with a first-order rate constant of 1×10^{-4} sec^{-1} at 50°. The rate is unaffected by the presence of 0.01 *M* diphenylanthracene. Similarly, Kopecky and Mumford[5b] reported a decomposition rate constant of 6×10^{-4} sec^{-1} for a 0.1 *M* solution of I in benzene at 60°. The rate increased only to 11×10^{-4} sec^{-1} in the presence of 0.2 *M* biacetyl.[5b] Thus the presence of a fluorescent acceptor does not affect the first-order decomposition of I. In a concentrated solution, however, the dioxetane is sub-

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[1] (a) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); (b) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970); (c) E. H. White and C. C. Wei, *Biochem. Biophys. Res. Commun.*, **39**, 1219 (1970).

[2] (a) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); (b) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970); (c) T. Wilson and A. P. Schaap, *ibid.*, **93**, 4126 (1971); (d) A. P. Schaap, *Tetrahedron Lett.*, 1757 (1971); (e) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972); (f) A. A. Lamola, *Biochem. Biophys. Res. Commun.*, **40**, 304 (1971); (g) H. Gusten and E. F. Ullman, *Chem. Commun.*, 28 (1970); (h) N. J. Turro and P. Lechtken, *Tetrahedron Lett.*, 565 (1973).

[3] (a) K. D. Gundermann, "Chemilumineszenz Organischer Verbindungen," Springer-Verlag, West Berlin, 1968; (b) E. H. White and D. F. Roswell, *Accounts Chem. Res.*, **3**, 54 (1970); (c) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970); (d) M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969).

[4] (a) C. S. Foote, *ibid.*, **1**, 104 (1968); (b) D. R. Kearns, *Chem. Rev.*, 71, 395 (1971).

[5] (a) K. R. Kopecky and C. Mumford, 51st Annual Conference of the Chemical Institute of Canada, Vancouver, B. C., June 1968, p 41; (b) *Can. J. Chem.*, **47**, 709 (1969); (c) K. R. Kopecky, J. H. van de Sande, and C. Mumford, *ibid.*, **46**, 25 (1968).

Table I. The Trans → Cis Isomerization of Stilbene[a]

Solvent	Temp, °C	Starting concn, *M*: Trimethyl-1,2-dioxetane	Starting concn, *M*: Stilbene	Final % cis isomer[b]	Apparent quantum yield Φ isom (× 10²)[c]
Benzene	95–100	0.3	0.25 trans	5	4
	95–100	0.3	0.05 trans	10	1.7
	95–100	3	0.05 trans	30	0.6
	95–100	*d*	0.05 trans	41	
	95–100	*d*	0.05 cis	41	
e	95–100	3	0.05 trans	2	0.04
Acetone	95–100	3	0.05 trans	26	0.4
f	80	3	0.05 trans	17	0.3
Methanol	23	3	0.05 trans	16	0.3
Piperylene[g]	95–100	3	0.05 trans	15	0.3

[a] Solution degassed (except where noted) and heated in sealed tubes. [d] By glpc (% cis found/% recovered olefin). [c] Mol of cis/mol of trimethyl-1,2-dioxetane (minimum value because of reversibility). [d] 50 molar equiv of I added slowly. [e] 0.4 *M* in cyclooctatetraene. [f] Saturated with air (effectively the same results degassed). [g] Mixture of cis and trans.

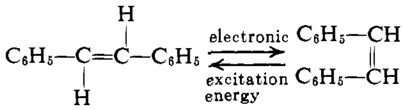
ject to an erratic and rapid decomposition;[2c,h,5] therefore, the neat substance or its concentrated solutions should be stored at low temperatures (< −20°).

A second procedure for the preparation of dioxetanes involves the low-temperature addition of singlet oxygen to olefins.[2a–c] The method results in good yields but the olefins must be activated by electron-releasing substituents and must not contain reactive allylic hydrogens.

A third general procedure for making dioxetanes—the ozonolysis of olefins in ketone or aldehyde solvents, as described recently by Story[6] and by Yang[7]—has now been challenged.[8]

A thermochemical approach to the stability of dioxetanes has resulted in the prediction that alkyl substitution results in increased stability.[9] Steric effects are apparently important variables in view of the high stability reported recently for the dioxetane prepared from diadamantylidene.[10]

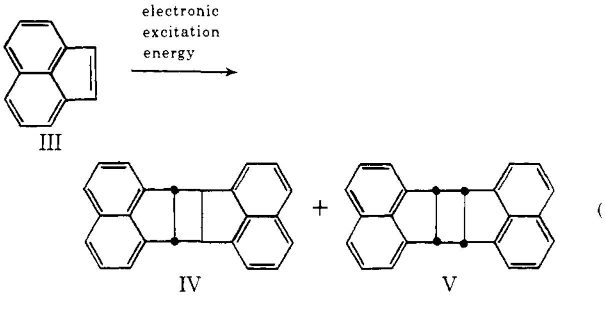
Trimethyl-1,2-dioxetane–Stilbene System. To achieve isomerization of *trans*-stilbene to the cis isomer (and *vice versa*) through the use of chemically produced excited states, it was necessary, merely, to heat a solution of the stilbene and I in an inert solvent. The results are listed in Table I. A "photostationary" state consisting of ~41% of the cis isomer and 59% trans was reached in a few minutes of heating. This final isomeric composition differs from the stationary state obtained photochemically. The sensitized and nonsensitized light-driven isomerization of *cis*- and *trans*-stilbenes has been studied by Hammond, *et al.*[11] These workers studied the influence of the triplet sensitizer energy on the point of the photostationary state. The highest energy sensitizers used were acetophenone (74 kcal) and benzophenone (68 kcal), and in both cases the photostationary state contained about 60% of the cis isomer. It is interesting that in our case the "photostationary" state favors the trans isomer (see Table I) despite the fact that the triplets apparently available are energetic to the extent of at least *ca.* 69 kcal (enough to excite 4,4-diphenylcyclohexadienone; see below). The influence of several factors on the isomerization efficiency was studied in this system. Quenching with cyclooctatetraene (Table I) results in a drastic reduction of the apparent quantum efficiency of the transformation, an expected result in view of the fact that the transfer of triplet energy is involved (see below). The apparent quantum efficiency of isomerization is somewhat lower in the polar solvents used (Table I), possibly because of specific interactions with the solvent. The effect of temperature can be expected to be complex since it affects not only the rate of the energy transfer but also the rate of decomposition of the dioxetane. The isomerization run at 50° compared to that run at 100° shows a decline in the apparent quantum efficiency of about 20%. The variable showing the most dramatic effect on efficiency is concentration. In general, low dioxetane concentrations and high stilbene concentrations increase the apparent quantum yield. Cutting the dioxetane concentration from 3 to 0.3 *M* triples the quantum yield; then quintupling the stilbene concentration triples it again, giving 4% efficiency with 0.3 *M* dioxetane and 0.25 *M* *trans*-stilbene (Table I).



$$C_6H_5{-}CH{=}CH{-}C_6H_5 \underset{\text{excitation energy}}{\overset{\text{electronic}}{\rightleftarrows}} C_6H_5{-}CH{=}CH{-}C_6H_5 \qquad (4)$$

II

Trimethyl-1,2-dioxetane–Acenaphthylene System. The dimerization of acenaphthylene has recently been studied by Cowan and Drisko,[12a–c] and by Hartmann, Hartmann, and Schenck.[12d] These workers found that acenaphthylene singlet leads to the cis dimer while the triplet, formed by the intersystem crossing of the singlet, leads to a mixture of the cis and trans dimers. Aerated runs result in nearly complete quenching of the triplets, and only the cis dimer appears. The same is true of runs conducted in the presence of other triplet quenchers. Sensitized runs, conducted in the presence of low-energy sensitizers, give a mixture of cis and



III

IV V (5)

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(6) P. R. Story, E. A. Whited, and J. A. Alford, *J. Amer. Chem. Soc.*, **94**, 2143 (1972).

(7) N. C. Yang and R. V. Carr, *Tetrahedron Lett.*, 5143 (1972).

(8) (a) P. S. Bailey, T. P. Carter, Jr., C. M. Fischer, and J. A. Thompson, *Can. J. Chem.*, **51**, 1298 (1973); (b) K. R. Kopecky, P. A. Lockwood, J. E. Filby, and R. W. Reid, *ibid.*, **51**, 468 (1973). (c) We thank Professor K. R. Kopecky for a preprint of his study. We have also been unable to successfully repeat the ozonolysis approach.

(9) H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970).

(10) J. H. Wieringa, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 169 (1972).

(11) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(12) (a) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); (b) R. L. Drisko, Ph.D. Thesis, The Johns Hopkins University, 1968; (c) D. O. Cowan and R. L. E. Drisko, *J. Amer. Chem. Soc.*, **92**, 6281, 6286 (1970); (d) I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967).

Table II. Dimerization of Acenaphthylene[a]

Solvent	Trimethyl-1,2-dioxetane, *M*	Acenaphthylene, *M*	Temp, °C	Ratio,[b] cis/trans dimers	Total yield of cis + trans wt %	Total apparent quantum yield Φ dim (× 10²)[c]
Benzene	2.0	0.9	95–100	0.2	6	1+
Benzene	1.8	0.7	95–100	0.3	8	1.5
Benzene[d]	1.8	0.7	95–100	0.3	7	1+
Benzene[e]	1.8	0.7	95–100	0.4	0.2	0.04
Methanol	1.3	0.6	40	0.7	2	0.4

[a] All solutions degassed, except where noted. [b] Determined by ultraviolet spectra of the products separated on a tlc plate (silica gel developed with cyclohexane at 40°). [c] Mol of dimer/mol of I. [d] Solution saturated with oxygen. [e] 0.16 *M* in cyclooctatetraene.

trans dimers that is solvent dependent. For example, values of 0.44–0.58 for the cis to trans ratio were found in methanol.

Our findings for the dioxetane driven dimerization of acenaphthylene are listed in Table II; they are consistent with the transfer of triplet energy from the excited carbonyl compound to acenaphthylene. The resulting dimerization gives rise to both the cis and the trans dimers in the ratio of 0.2–0.3 in benzene. The presence of cyclooctatetraene suppresses the dimerization almost completely, as expected,[12d] but the presence of oxygen has little effect, a surprising result in view of the observations of Cowan and Drisko.[12a–c] No quantum yields are available to date for the sensitized photochemical dimerization of acenaphthylene by which we could calculate the efficiency of the dioxetane–acenaphthylene reaction.

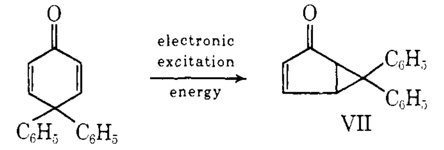
The usefulness of the concept of photochemistry through chemically produced excited states is exemplified by the following simple procedure. A solution of the dioxetane and acenaphthylene is heated on a steam bath for about 10 min; on cooling, crystals of the trans dimer separate. The apparent quantum yield is a simple function of the chemical yield.

Trimethyl-1,2-dioxetane–4,4-Diphenyl-2,5-cyclohexadienone System. The data on the two runs with this system are given in Table III. The dienone is known to rearrange *via* its triplet state into an isomeric photoketone.[13] The triplet energy of the dienone was reported to be 69 kcal/mol; thus quanta of at least approximately this energy are available from the decomposition of I.

Table III. Isomerization of 4,4-Diphenylcyclohexadienone[a]

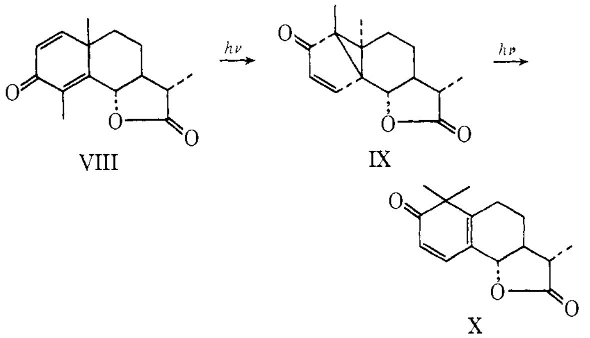
Solvent	Trimethyl-1,2-dioxetane, *M*	4,4-Diphenylcyclohexadienone, *M*	Temp, °C	Yield of photoketone, wt %[b]	Total apparent quantum yield Φ VI → VI (× 10²)[c]
Benzene	1	0.02	95–100	19	0.4
Benzene	0.5	0.01	95–100	11	0.25

[a] Solutions degassed. [b] Determined by weighing of the product separated on and eluted from a tlc plate (cellulose pretreated with dimethylformamide and developed with cyclohexane). [c] Mol of photoketone/mol of I.



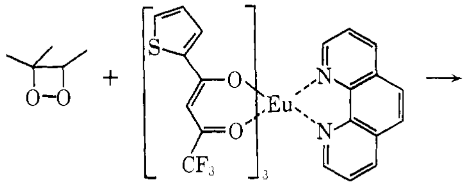
VI VII (6)

Trimethyl-1,2-dioxetane–Santonin System. Santonin (VIII) which has been isolated from several species of *Artemisia*[14] can be readily converted on irradiation into lumisantonin (IX),[15] which in turn on irradiation passes into an isomer (X).[16,17] We have achieved a similar conversion by heating benzene solutions containing sanotonin and I. The results are summarized in Table IV.

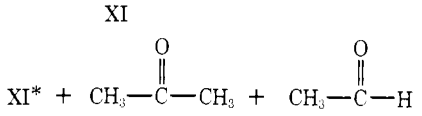


VIII IX X (7)

Trimethyl-1,2-dioxetane–Europium Tris(thenoyltrifluoroacetonate)-1,10-phenanthroline System. Heating solutions containing I and europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline (XI) results in narrow band europium ion emission (Figure 1).



XI



$$XI^* + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \quad (8)$$

In all cases, after constant temperature was established, the light intensity decreased exponentially with time with a rate constant of about 1.3 × 10^{-4} sec^{-1} at 50°, independent of the concentration of XI or the

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(13) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

(14) J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, The University Press, Cambridge, 1952, p 249.

(15) D. H. R. Barton, P. de Mayo, and M. Shafig, *J. Chem. Soc.*, 140 (1958).

(16) O. L. Chapman and L. F. Englert, *J. Amer. Chem. Soc.*, **85**, 3028 (1963).

(17) M. H. Frisch and J. H. Richards, *ibid.*, **85**, 3029 (1963). The authors showed that the triplet states of santonin and lumisantonin were involved in these conversions.

Table IV. Isomerization of Santonin

Sample no.[a]	Trimethyl-1,2-dioxetane added, ml[b]	% IX after reaction[c]	% X after reaction	Apparent quantum yield Φ VIII → IX (× 10^2)[d]
1	0.5	7		2.9
2	0.5	13		2.9
3	0.5	17		2.5
4	0.5	19		2.1
5	0.5	22		2.0
6	0.5	27	Trace	2.0
7	1.0	31	1.3	1.7
9	1.0	34	1.8	1.5

[a] Sample 1 was prepared by dissolving 16.5 mg (0.068 mmol) of santonin in 0.5 ml of 0.3 *M* I in benzene. The solution was degassed, heated 20 min at 100°, and then analyzed by glpc. The sample was then evaporated with a stream of dry nitrogen. Subsequent samples were prepared by adding the indicated volume of 0.3 *M* dioxetane solution to the residue and treating as above. [b] Dioxetane added as 0.3 *M* solution in benzene. [c] Reaction at 100° for 20 min. [d] Mol of IX/mol of I.

initial concentration of I.[18] The quantum yield of emission (Φ_{ch}, einsteins/mole of dioxetane decomposed) increased with increasing concentration of XI in the range 10^{-5}–10^{-3} *M* (Table V); Φ_{ch} was independent of initial dioxetane concentration in the range 0.001–0.02 *M*. Degassing the solution by three cycles of freeze–pump–thaw and sealing at 10^{-5} Torr resulted in a 1.5-fold increase in light yield (Table V).

Table V. Light Yields

Concn of XI,[a] *M* × 10^3	Φ_{ch}[b] × 10^2
0.01[c]	0.04
0.1	0.3
0.5	0.8
0.5[d]	1.2
1.0	1.1
1.0[d]	1.5

[a] Undegassed acetone solution containing an initial concentration of 0.001 *M* I except where otherwise noted. [b] Einsteins per mole of I decomposed. [c] Initial dioxetane concentration 0.004 *M*. [d] Degassed by three cycles of freeze–pump–thaw and sealed at ~10^{-5} Torr.

It has previously been shown that ion fluorescence from certain lanthanide ions such as Eu^{3+} and Tb^{3+} can be sensitized by energy transfer from triplet excited organic compounds.[19] In the case of lanthanide chelates the excitation path involves triplet–triplet energy transfer from the organic sensitizer to the chelating ligand (in the present case thenoyltrifluoroacetone) followed by intramolecular energy transfer from the triplet excited ligand to the lanthanide ion.[20]

Gas Phase Trimethyl-1,2-dioxetane Chemiluminescence. When trimethyl-1,2-dioxetane is warmed to >50° (5–15 Torr) in the gas phase, a dim blue chemiluminescence is observed. The emission consists of a broad structureless band extending from ~320 to 580 nm with a maximum at *ca.* 430 nm. Very similar emission was observed from heating other 1,2-dioxetanes (see Table VI). The low density of the emission necessitated the use of wide slit widths (40-nm band pass) in recording the spectrum so the absence of fine structure is uncertain. The intensity of emission increased with increasing dioxetane pressure in the range 2–15 Torr. Increasing the pressure with an inert gas such as argon had no effect on the emission intensity even at 1 atm. The emission was strongly quenched by air (oxygen), however. Increasing the pressure from 5 to 13 Torr by addition of air resulted in ~85% quenching of the emission.

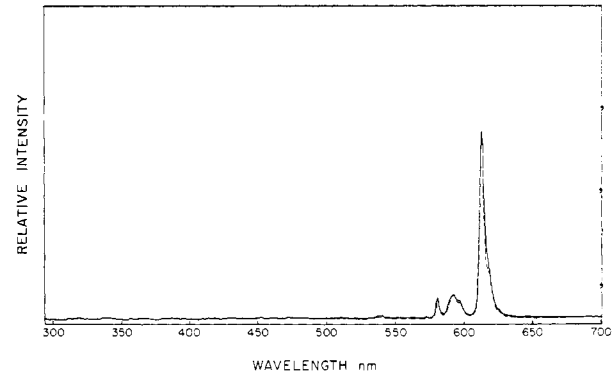

Figure 1. Chemiluminescent (—) and fluorescent (- - - - -) emission of XI in acetone recorded using a Hitachi MPF-2A spectrophotofluorometer: chemiluminescence solution, 5 × 10^{-3} *M* XI and 0.004 *M* I (initial concentration); $T = 50°$; fluorescence solution, 1 × 10^{-3} *M* XI, $\lambda_{excitation}$ 380 nm.

Both acetaldehyde and acetone are reported to give fluorescence and phosphorescence in the approximate range 340–500 nm in the gas phase on photoexcitation.[21] For acetone the emission is ~90% phosphorescence which is strongly quenched by oxygen, and 10% fluorescence which is not subject to oxygen quenching.[21b] The data available at present do not allow unambiguous assignment of the emission from the gas phase thermal decomposition of trimethyl-1,2-dioxetane, but the oxygen quenching suggests that a major portion of the emission is probably phosphorescence.

Attempts at Gas–Solid Energy Transfer. Several attempts were made to excite emission from a thin layer of solid fluorescent material by passing trimethyl-1,2-dioxetane vapor over the hot solid. Fluorescent substances used included 9,10-dibromoanthracene, pyrene, rubrene, and europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline.

Two general procedures were used. In the first, a thin layer of the fluorescer was deposited on the walls of a glass tube either by evaporation of a solution or by sublimation. The tube was evacuated and filled with trimethyl-1,2-dioxetane to a pressure of *ca.* 10 Torr, then immersed in an oil bath at 50–100°. Alternatively, the solid could be deposited on a coil of nichrome wire which was then sealed into the glass tube. After evacuating the tube and introducing trimethyl-1,2-dioxetane gas as before, the wire was heated by passing an electric current through it. In all cases the dim blue emission associated with trimethyl-1,2-dioxetane de-

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[18] Clean dry systems and pure solvents must be used for reproducible rates and yields.

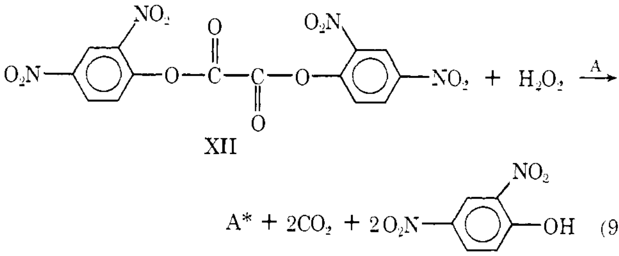
[19] N. Filepescu and G. W. Mushrush, *J. Phys. Chem.*, **72**, 3516 (1968).

[20] M. A. El-Sayed and M. L. Bhaumik, *J. Chem. Phys.*, **39**, 2391 (1963).

[21] (a) R. G. Shortridge, Jr., C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1863 (1971); (b) R. B. Cundall and G. S. Davies, *Progr. React. Kinet.*, **4**, 149 (1967); (c) J. Heicklen, *J. Amer. Chem. Soc.*, **81**, 3863 (1959).

composition was observed, but in no case could fluorescence from the solid material be detected. Perhaps the dioxetane decomposes only on contact with the hot glass or wire. Poor heat transfer in the solid fluorescer may preclude formation of the excited product while in contact with the fluorescer.

The Bis-2,4-dinitrophenyloxalate–Hydrogen Peroxide System. Chemiluminescence from the reaction of electronegatively substituted phenyl oxalates with hydrogen peroxide in the presence of fluorescent acceptors has been reported.[3d] Using bis-2,4-dinitrophenyl oxalate (XII) with rubrene as the fluorescer, chemiluminescence quantum efficiencies as high as 0.23 based on the oxalate have been observed.[3d]


XII

(9)

In contrast to the dioxetane decomposition discussed above, the XII + hydrogen peroxide reaction appears to generate primarily singlet excited state energy. Thus, for example, with XII + hydrogen peroxide, the use of rubrene or 9,10-diphenylanthracene as fluorescer results in more efficient chemiluminescence than is observed using 9,10-dibromoanthracene. When the dioxetanes are used as excited state energy generators, more efficient chemiluminescence is observed with 9,10-dibromoanthracene as acceptor, presumably because triplet–singlet energy transfer to a compound containing the heavy atom, bromine, is more sufficient.[2c] Reacting XII ($\sim$0.01 *M*) with hydrogen peroxide in glyme with $\sim 10^{-4}$ *M* europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline resulted in no europium fluorescence.

Several attempts were made to observe "photochemical" reactions by using photoreactive acceptors with XII and hydrogen peroxide. Reactive acceptors used were stilbene, β-carotene, 4-dimethylamino-4′-nitrostilbene, 2-(β-styryl)naphthalene (possible cis–trans isomerization), acenaphthylene, and anthracene (possible dimerization). In most cases changes observed were slight and the existence of excited state energy transfer is uncertain. With 4-dimethylamino-4′-nitrostilbene, the reaction is complicated by oxidation of the amino function under the reaction conditions. More recently, Gusten and Ullman have reported several successful photoreactions with this energy generating system.[2g]

When a gas, nitrogen or air, was passed through a solution of XII and hydrogen peroxide in glyme, some volatile chemiluminescent material was detected in the vapor leaving the reaction vessel.[3d] The volatile material was observed by passing the effluent gas over a filter paper which had been soaked in a rubrene solution. Approximate measurements of the light obtained from the vapor indicate, however, that the volatile material represents less than *ca.* 5% of the total light yield from the reaction. Numerous attempts to detect intermediates in reaction 9 by infrared spectroscopy gave negative results. Formation of carbon dioxide at about the same rate as the disappearance of the oxalate ester was the only observable result. The rate of disappearance of the oxalate absorbance in the ir was unaffected by the presence of rubrene. The rate was greatly increased by small amounts of base. Addition of 0.001 molar equiv of 2,6-lutidine to a glyme solution 0.01 *M* in XII in hydrogen peroxide increased the rate of the reaction by about a factor of 100. The intensity of light emission was increased in the presence of 2,6-lutidine, but the light yields were approximately the same with and without added base.

In contrast to previous reports, [3d] our results indicate that there is no stable intermediate in the reaction of XII with hydrogen peroxide. The existence of a stable intermediate was suggested by Rauhut[3d] on the basis of the following observations. When XII and hydrogen peroxide are mixed in solution, *e.g.*, in dimethoxyethane, the carbonyl absorbance in the ir disappears in a few minutes. In dimethyl phthalate solution, however, it was reported that substantial light yield could be obtained when a fluorescer such as 9,10-diphenylanthracene was added more than 1 hr after mixing the oxalate and hydrogen peroxide; the yield when fluorescer was added after 70 min was 50% of the yield obtained by adding the fluorescer at the beginning. We have been unable to duplicate these results. In fact, we find the light yield from delayed addition of fluorescer is just what one would expect from the rate of decay of light intensity in samples with fluorescer added initially. The rate of decay of chemiluminescence is strongly dependent on base, however, as noted above. Introduction of trace amounts of base with the fluorescer could have complicated Rauhut's results.

Discussion

Nature of the Excited States Formed from the Dioxetanes. The data indicate that the reactive species formed in our experiments with compound I are triplet excited states. The excitation of europium ion fluorescence is known to proceed *via* triplet energy transfer (see above). Cyclooctatetraene effectively quenched the stilbene isomerization (Table I) and the dimerization of acenaphthylene (Table II).[22] Further, the cis–trans isomer ratio formed in the dimerization of acenaphthylene (Table II) suggests that the triplet state of acenaphthylene is formed in the dioxetane driven reaction.

The singlet state of stilbene is reported to react with oxygen to yield phenanthrene.[23] In our stilbene runs in the presence of oxygen (Table I), no phenanthrene was formed.

Other workers have also concluded that thermal decomposition of dioxetanes leads predominately or exclusively to triplet excited carbonyl products. Wilson and Schaap[2c] studied chemiluminescence from the thermal decomposition of *cis*-3,4-diethoxydioxetane in solutions containing dibromoanthracene or diphenylanthracene, and concluded that the results were best explained by triplet–singlet energy transfer from triplet excited ethyl formate to the fluorescer.

Recently it was shown by Turro and Lechtken[2e] that tetramethyl-1,2-dioxetane not only carries out photo-

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[22] Similar quenching was reported by Schenck.[12d]

[23] F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

chemical reactions *via* the triplet state but also yields the triplets directly (rather than *via* the singlet excited state and intersystem crossing). The possibility of this was suggested on theoretical grounds by Kearns.[24]

Efficiency of Production of Excited States. The overall quantum efficiency Φ_{chem} for an excited-state reaction which follows eq 2 is defined as the number of molecules of A undergoing change per molecule of X (or Y) which react. This quantum yield is a product of three efficiencies: Φ_{es}, the efficiency of excited-state product formation by X (or Y), Φ_{tr}, the efficiency of energy transfer from the initially formed excited-state species to the acceptor molecule, and Φ_{photo}, the quantum yield of the photochemically analogous reaction.

$$\Phi_{\mathrm{chem}} = \Phi_{\mathrm{es}}\Phi_{\mathrm{tr}}\Phi_{\mathrm{photo}} \tag{10}$$

In general, Φ_{chem} and Φ_{photo} can be easily measured. By using high concentrations of the acceptor, Φ_{tr} can usually be made effectively equal to one, and therefore it is possible to calculate Φ_{es}.

The best estimate we have for Φ_{es} in the thermal decomposition of trimethyl-1,2-dioxetane is 0.14. This value was obtained from a study with europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline (XI). The results with the latter system, summarized in Table V, are consistent with the reaction scheme described by eq 11–15, where C = dioxetane decomposition product.

$$\mathrm{I} \xrightarrow{k_1} \Phi_{\mathrm{es}}\,\mathrm{C}^* + (1 - \Phi_{\mathrm{es}})\mathrm{C} \tag{11}$$

$$\mathrm{C}^* + \mathrm{XI} \xrightarrow{k_2} \mathrm{C} + \mathrm{XI}^* \tag{12}$$

$$\mathrm{C}^* \xrightarrow{k_3} \mathrm{C} \tag{13}$$

$$\mathrm{XI}^* \xrightarrow{k_4} \mathrm{XI} + h\nu \tag{14}$$

$$\mathrm{XI}^* \xrightarrow{k_5} \mathrm{XI} \tag{15}$$

From eq 11–15

$$\Phi_{\mathrm{ch}} = \Phi_{\mathrm{fl}}\Phi_{\mathrm{es}}\Phi_{\mathrm{tr}} = \Phi_{\mathrm{fl}}\Phi_{\mathrm{es}}\{k_2[\mathrm{XI}]/(k_2[\mathrm{XI}] + k_3)\} \tag{16}$$

and

$$\frac{1}{\Phi_{\mathrm{ch}}} = \frac{1}{\Phi_{\mathrm{es}}\Phi_{\mathrm{fl}}}\left(1 + \frac{k_3}{k_2}\frac{1}{[\mathrm{XI}]}\right) \tag{17}$$

(Φ_{fl} = quantum yield of fluorescence of XI = Φ_{photo} in eq 10, Φ_{ch} = photons emitted per molecule of I = Φ_{chem} in eq 10). A plot of $1/\Phi_{\mathrm{ch}}$ *vs.* 1/[XI] should therefore give a straight line with slope = $k_3/k_2\Phi_{\mathrm{es}}\Phi_{\mathrm{fl}}$, intercept = $1/\Phi_{\mathrm{cs}}\Phi_{\mathrm{fl}}$ and slope/intercept = k_3/k_2. A plot of $1/\Phi_{\mathrm{ch}}$ *vs.* 1/[XI] does give a good straight line with slope ~0.03 and intercept ~65; thus the maximum emission yield, $\Phi_{\mathrm{es}}\Phi_{\mathrm{fl}}$, ~ 0.015. The quantum yield of fluorescence of XI is approximately 0.11 in acetone solution;[25] therefore, about 14% of the dioxetane molecules which decompose yield an excited product C* which leads *via* energy transfer to excitation of the europium complex to its fluorescent excited state.

The value for Φ_{es} obtained in the experiments with XI is the best estimate we have for the yield of excited states from thermal decomposition of I.[1b] However, we cannot rigorously rule out the possibility that Φ_{es} may actually be higher. Other authors[2c,e] have reported results with similar 1,2-dioxetanes which were interpreted as indicating values of Φ_{es} between 0.5 and 1.0. Possible complications include quenching of C* by XI without energy transfer and induced decomposition of the dioxetane by XI. The latter possibility is probably unimportant since at the concentrations used in our work the rate of decomposition of I did not depend on the concentration of XI. We have no evidence regarding the possibility of unproductive quenching.

Values of Φ_{chem} were also calculated for the photoreactive acceptors. The observed efficiencies for the stilbene isomerization (Table I), the acenaphthylene dimerization (Table II), the isomerization of the diphenylcyclohexadienone (Table III), and the isomerization of the diphenylcyclohexadienone (Table III), and the isomerization of santonin have not been corrected for triplet quenching nor have they been optimized; they are undoubtedly not the maximum possible yields. In the experiments with these photoreactive acceptors, relatively high concentrations of the reactive energy acceptor were used (0.01–0.25 *M*) in an attempt to make Φ_{tr} equal to 1. The evidence indicates, however, that the efficiency of energy transfer to the reactive acceptors is much lower than was supposed. In the diphenylcyclohexadienone case, an increase in acceptor concentration from 0.01 to 0.02 *M* increased Φ_{chem} from 0.0025 to 0.004 (Table III). In the stilbene isomerization an increase in stilbene concentration from 0.05 to 0.25 *M* increased Φ_{chem} from 0.017 to 0.04 (Table I); thus apparently even at acceptor concentrations above 0.01 *M* energy transfer does not occur with unit efficiency.

The increase in Φ_{chem} for stilbene isomerization with *decreasing* initial dioxetane concentration as well as the higher yields at higher temperature suggest the possibility of triplet quenching by unreacted I.[2c] Other authors have reported reactions between dioxetanes and triplet excited organic compounds resulting in quenching of the excited compound and decomposition of the dioxetane.[2a,c,h] Quenching of stilbene triplets by unreacted I may also help explain the preponderance of the trans isomer at the "photostationary" state (see above). If I is capable of acting as a low energy triplet acceptor[2h] it may exert an effect on the excited-state isomerization of stilbene similar to that observed with azulene;[11] such low energy acceptors lead preferentially to the trans isomer.

The reasonably efficient dioxetane sensitized isomerization of stilbene in piperylene as solvent (Table I) seemed surprising since piperylene has been widely used as a triplet quencher.[26,27] Recent studies have shown, however, that in high concentration piperylene can act as a triplet sensitizer.[28] Indeed, we found that irradiation of a piperylene solution 0.05 *M* in *trans*-stilbene and 0.05 *M* in benzophenone with 366-nm light[29]

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[24] D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

[25] (a) M. L. Bhaumik and C. L. Telk, *J. Opt. Soc. Amer.*, **54**, 1211 (1964); (b) N. Filepescu and G. W. Mushrush, *Nature (London)*, **211**, 960 (1966); (c) W. R. Dawson, J. L. Kropp, and M. W. Windsor, *J. Chem. Phys.*, **45**, 2410 (1966).

[26] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[27] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

[28] (a) R. A. Caldwell, *J. Amer. Chem. Soc.*, **92**, 3229 (1970); (b) A. M. Braun, W. B. Hammond, and H. G. Cassidy, *ibid.*, **91**, 6196 (1969); (c) R. Hurley and A. C. Testa, *ibid.*, **92**, 211 (1970).

[29] The sample, 2 ml of solution in a 60 × 12 mm Pyrex test tube, was degassed by three cycles of freeze–pump–thaw and sealed. Irradiation was done with a Bausch and Lomb high-pressure mercury lamp and a Bausch and Lomb high-intensity grating monochromator.

resulted in 11% isomerization to the cis isomer in 4 hr. Isomerization to ca. 64% *cis*-stilbene was achieved in 44 hr.

Experimental Section

Infrared spectra were obtained on Perkin-Elmer spectrometers, Models 337 and 521. Nmr spectra were determined on a Varian A-60 instrument, using $CDCl_3$ as solvent and tetramethylsilane as internal standard. A Cary 14M spectrophotometer was employed for ultraviolet spectral determination. Thin-layer chromatography (tlc) was performed according to Stahl, using Eastman flexible plates, coated with silica gel GF_{254} or alumina F_{254}. Developed spots were visualized at either 25 or −196° with a 254-nm ultraviolet lamp. Vapor phase chromatography separations were performed on a Varian Model 1200 instrument equipped with 6 ft × $^1/_8$ in. stainless steel columns and a flame ionization detector. Helium was employed as carrier gas. Melting points were obtained using either a Kofler hot stage or a Thomas-Hoover bath and are uncorrected.

All solvents were reagent (distilled before use) or Spectroquality grade. Dimethoxyethane, ether, and tetrahydrofuran were freshly distilled from lithium aluminum hydride. Hydrogen peroxide solutions were freshly prepared from 98% reagent (Becco Chemical Division, FMC Corp.). *trans*-Stilbene and rubrene were used as obtained from commercial sources. Acenaphthylene was recrystallized from methanol and then sublimed at 25° (0.01 Torr). 9,10-Diphenylanthracene was recrystallized from ethanol–chloroform. 2,4-Dinitrophenol was sublimed twice at 45–105° (0.01 Torr).

3-Bromo-2-methyl-2-butyl Hydroperoxide. This compound was prepared in the manner described by Kopecky, *et al.*[5c] The crude hydroperoxide prepared in this way showed the following nmr spectrum (CCl_4):[5c] τ 1.40 (s, 1 H), 5.56 (q, $J = 7$ Hz, 1 H), 8.32 (d, $J = 7$ Hz, 3 H), 8.63 (br s, 6 H); in addition impurity peaks appeared at τ 8.07 and 8.19. This impurity was more volatile than the hydroperoxide and could be removed by oil-pump vacuum applied to the stirred crude product. The hydroperoxide could also be purified on a smaller scale by bulb-to-bulb distillation. The hydroperoxide, whether crude or purified, is unstable and yellows rapidly at room temperature, but can be stored for several weeks at −15°.

Trimethyl-1,2-dioxetane. 3-Bromo-2-methyl-2-butyl hydroperoxide (10 g, 0.055 mol) was added dropwise to a cooled solution of sodium hydroxide (20 g, 0.5 mol) in 120 ml of water–methanol (1:1) at −10°. The mixture was stirred magnetically and allowed to warm to 5°. It was maintained at that temperature for 10 min and then poured into 200 ml of precooled (0°) saturated aqueous sodium chloride in a separatory funnel. The mixture was extracted five times with 5 ml of benzene, and each extract was stored in a separate vial at −15°.

Examination of the extract solution by nmr indicated the presence of trimethyl-1,2-dioxetane showing absorptions at τ 5.03 (q, $J = 6$ Hz, 1 H), 8.82 (s, 3 H), 8.84 (s, 3 H), and 9.05 (d, $J = 6$ Hz, 3 H); in addition impurity absorptions were visible in the τ 6.85–6.96 area (the region of methanol and water absorption), and in the methyl region ranging from τ 8.25 (acetone, acetaldehyde) to 9.5. The total yield of dioxetane isolated in the five extracts was about 70% (based on the nmr integration), with the total recovery of organic matter higher than this value, though not determined. The second, third, and fourth extracts contained the highest concentrations of dioxetane and lower concentrations of impurities than the first and fifth extracts. These three extracts were combined and subjected to further purification. Repeated washing with water removed most of methanol, acetone, and acetaldehyde even though it caused considerable loss of dioxetane itself. Bulb-to-bulb distillation using vacuum transfer at ~0.01 Torr in a closed system permitted the removal of involatile impurities (sodium hydroxide, the starting hydroperoxide).

Trimethyl-1,2-dioxetane could be prepared as a nearly pure liquid by a modification of the procedure described above. 3-Bromo-2-methyl-2-butyl hydroperoxide (10 g, 0.055 mol) was added dropwise over a period of 5 min into a stirred solution containing 5 g (0.125 mol) of sodium hydroxide in 25 ml of methanol–water mixture (1:1) at −10°. The solution was then taken out of the cooling vessel and stirred until its temperature reached 0°. It was then stirred for another 15 min with intermittent cooling so as not to allow the temperature to go above 5°. The solution was then poured into a separatory funnel containing 48 ml of saturated aqueous sodium chloride solution (precooled to 0°), and the funnel was swirled gently. A yellow oil separated as the light phase; it was separated and stored at −20° (crude yield 1.9 g, 0.019 mol, 34%). The aqueous layer was extracted with benzene to yield additional material.

The crude dioxetane, examined by nmr (CCl_4), showed the presence of unchanged hydroperoxide (presence of the characteristic quartet centered at τ 5.56). It was then distilled at 0° and 0.01 Torr (caution). The distillate was cooled to −20°, at which temperature crystals separated; the oily phase was removed with a pipet. Further purification was not achieved because of the explosive nature of the compound; traces of acetone were seen in the ir and nmr spectra.

Anal. Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.49; H, 10.35.

Trimethyl-1,2-dioxetane is a mobile yellow oil with a penetrating smell and lachrymatory properties. It freezes into a yellow crystalline mass at about −15°: ir (CCl_4) 1393, 1380, 1156, 1069, 884 cm^{-1}; nmr (CCl_4) τ 4.78 (q, $J = 6.5$ Hz, 1 H), 8.47 (s, 3 H), 8.53 (s, 3 H), 8.65 (d, $J = 6.5$ Hz, 3 H); mol wt 100 (freezing point depression of C_6H_6).

3-Bromo-2-phenyl-2-propyl Hydroperoxide. The modified procedure of Kopecky, *et al.*,[5c] was used, as described for the case of 3-bromo-2-methyl-2-butyl hydroperoxide above. 3-Bromo-2-phenyl-2-propyl hydroperoxide was prepared from 5.9 g (0.05 mol) of 2-methylstyrene, 7.1 g (0.025 mol) of 1,3-dibromo-5,5-dimethylhydantoin, and 8.5 g (0.25 mol) of 98% hydrogen peroxide. The yield of the hydroperoxide, after evaporating the solvent, was 9 g (0.039 mol, 78%). The hydroperoxide was a very viscous, unstable oil (it was stored at −20°): nmr (CCl_4) τ 2.65 (m, 5 H), 6.24 (s, 2 H), and 8.36 (s, 3 H). Impurity peaks (not eliminated by pumping) were observed at τ 5.70, 6.37, 7.31, 8.21, and 8.30.

3-Methyl-3-phenyl-1,2-dioxetane. The crude 3-bromo-2-phenyl-2-propyl hydroperoxide prepared above (1 g, 4.3 mmol) was dropped into a stirred solution of 6 g of sodium hydroxide in 55 ml of methanol (precooled to −45°). The stirred solution was warmed to −10°, cooled down again to −45°, and stirred at that temperature for 45 min. The cold solution was then poured into a separatory funnel containing saturated aqueous sodium chloride solution (160 ml) cooled to 0°. The funnel was shaken and the contents was then extracted with 6-ml and 4-ml portions of benzene. The first extract, markedly yellow, when examined by nmr showed absorptions at τ 6.32, 6.39, 6.47, and 6.55 (2 H), and a singlet at τ 9.55 (3 H) (phenyl absorption obscured by the solvent). These absorptions were assigned to 3-methyl-3-phenyldioxetane, since they disappeared after the benzene extract had been heated for 5 min in steam and, after heating, the solution no longer emitted luminescence on heating with 9,10-dibromoanthracene. The nmr spectrum also showed impurity peaks at τ 9.07 (acetophenone), 8.11 (methanol), and 9.65 (methyl peak of the hydroperoxide) in addition to unidentified impurity absorptions at τ 7.62, 8.02, and 9.77.

Other Hydroperoxides. The following hydroperoxides were prepared following the method of Kopecky:[5c] *threo*-3-bromo-2-butyl hydroperoxide, nmr (CCl_4) τ 5.3–5.9 (m, 2 H), 8.35 (d, $J = 6.5$ Hz, 3 H), 8.75 (d, $J = 6.8$ Hz, 3 H), and 0.78 (s, 0.82 H); *erythro*-3-bromo-2-butyl hydroperoxide, nmr (CCl_4) τ 8.75 (d, $J = 6$ Hz, 3 H), 8.3 (d, $J = 7$ Hz, 3 H), 6.1 (m, 1 H), 5.5 (m, 1 H), and 1.1 (s, 0.7 H); *erythro*-2-bromo-3-methyl-3-pentyl hydroperoxide, nmr (CCl_4) τ 8.34 (d, $J = 7.0$ Hz, 3 H), 8.66 (s, 3 H), 8.33 (q, $J = 7.0$ Hz, 2 H), 9.03 (t, $J = 7$ Hz, 3 H), 5.48 (q, $J = 7.0$ Hz, 1 H), and 2.0 (s, 1 H); *threo*-2-bromo-3-methyl-3-pentyl hydroperoxide, nmr (CCl_4) τ 8.3 (d, $J = 6.5$ Hz, 3 H), 8.78 (s, 3 H), 8.24 (q, $J = 7.0$ Hz, 2 H), 9.05 (t, $J = 7.0$ Hz, 3 H), 5.50 (q, $J = 6.5$ Hz, 1 H), and 2.0 (s, 1 H).

Other Dioxetanes. The following dioxetanes were prepared by cyclization of the corresponding hydroperoxides in basic solution, as described above for the case of 3,3,4-trimethyl-1,2-dioxetane: *cis*-3,4-dimethyl-1,2-dioxetane, nmr (CCl_4) τ 8.8 (d, $J = 6$ Hz, 6 H), and 4.7 (br q, 2 H); *trans*-3,4-dimethyl-1,2-dioxetane, nmr (benzene) τ 9.0 (d, $J = 4.5$ Hz, 6 H), and 5.1–5.2 (m, 2 H); 3-ethyl-*trans*-3,4-dimethyl-1,2-dioxetane, nmr (benzene) τ 9.35 (t, $J = 7.0$ Hz, 3 H), 9.02 (d, $J = 6.3$ Hz, 3 H), 8.86 (s, 3 H), and 5.04 (q, $J = 6.3$ Hz, 1 H); 3-ethyl-*cis*-3,4-dimethyl-1,2-dioxetane, nmr (benzene) τ 9.36 (t, $J = 7$ Hz, 3 H), 9.0 (d, $J = 6.2$ Hz, 3 H), 8.45 (m), 8.8 (s, 3 H), and 5.0 (q, $J = 6.2$ Hz, 1 H).

Europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline was prepared by the method of Bauer, Blanc, and Ross,[30] and recrystal-

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(30) H. Bauer, J. Blanc, and D. L. Ross *J. Amer. Chem. Soc.*, **86**, 5125 (1964).

lized from acetonitrile: mp 246–248°; uv (95% ethanol) 340 nm (log ϵ 4.73), 265 (4.63), 230 (4.65).

Anal. Calcd: C, 43.42; H, 2.02. Found: C, 43.68; H, 2.06.

Measurement of Chemiluminescent Light Intensities and Yields from the Europium Complex. Solutions of the dioxetane and the europium chelate were mixed at 0°, then injected into a Pyrex cell held in an aluminum holder immersed in a constant-temperature bath at 50°. The light emitted was detected by an EMI 9558 B photomultiplier, the output from which was amplified and recorded as a function of time. Total emission was calculated by graphical integration of the intensity *vs.* time curve. Alternatively, in some cases the photomultiplier output was used to charge a capacitor. The total charge recorded was proportional to the total light emitted. Absolute light yields were determined by comparison with the reaction of luminol with hydrogen peroxide and hemin in aqueous base.[31]

Emission Spectra of 1,2-Dioxetanes. The chemiluminescent spectra were measured on a Hitachi-Perkin-Elmer MPF-2A spectrophotofluorimeter with a R106 photomultiplier detector. For the emission spectrum in the gas phase, a very small amount of dioxetane was introduced into a quartz cell which was then degassed and sealed. Wide slits (up to 40-nm band pass) were necessary because of the low level of light emission.

Table VI. Light Emission from the Dioxetanes

Compound	Solvent	Temp, °C	λ_{max}, nm
I	(Gas phase)[a]	80	429
I	Benzene	80	430–440[b]
cis-3,4-Dimethyl-1,2-dioxetane (0.1 *M*)	Cyclohexane	50	418
trans-3,4-Dimethyl-1,2-dioxetane (0.1 *M*)	Cyclohexane	50	424
3-Methyl-3-phenyl-1,2-dioxetane	Cyclohexane	50	431
3-Ethyl-*trans*-3,4-dimethyl-1,2-dioxetane	Benzene	46	425
3-Ethyl-*cis*-3,4-dimethyl-1,2-dioxetane	Benzene	46	425

[a] p = 1–10 Torr. [b] See ref 5b.

***trans*-Stilbene–Trimethyldioxetane System.** A solution containing 20 mg (0.11 mmol) of *trans*-stilbene and 0.5 g (5 mmol) of trimethyldioxetane in 10 ml of benzene was degassed, sealed under vacuum, and heated on a steam bath for 10 min. The solution was chromatographed on a silicic acid coated tlc plate with cyclohexane as the developing solvent. A band with a R_f value identical with that of authentic *cis*-stilbene was present, in addition to unchanged *trans*-stilbene and a small amount of slower moving material. The *cis*-stilbene band was eluted with methanol; the uv spectrum of the resulting solution was identical with that of authentic *cis*-stilbene (maxima at 223 and 276 nm with the relative intensities in the ratio of 2:1).

A number of quantitative runs were performed to measure the extent of *trans*- and *cis*-stilbene conversion under a variety of conditions, with the details given in Table I. Unless otherwise specified, the reactions were run in sealed glass tubes and the resulting solutions were analyzed using the 2% NPGS on 80–100 Chromosorb Q glpc column. The ratio of *cis*-stilbene to the total olefin recovered gave a measure of the degree of trans to cis conversion. The yield of the cis isomer obtained in a typical quantitative run ranged between 5 and 25%. A blank run was performed with the dioxetane solution in benzene preheated on a steam bath for 10 min; *trans*-stilbene was added and the heating was repeated. No *cis*-stilbene was detected in this mixture by glpc. As little as 0.1% would have been detected.

Acenaphthylene–Trimethyldioxetane System. The quantitative results obtained in the acenaphthylene–trimethyldioxetane runs are given in Table II. The following is the description of a typical quantitative run, and the method of analysis. A degassed, sealed tube containing 71 mg (0.47 mmol) of sublimed acenaphthylene, and 0.1 g (1 mmol) of trimethyldioxetane in 0.5 ml of benzene was heated on a steam bath for 10 min. After cooling to room temperature a deposit of crystals was formed. These were filtered off and proved to be the pure trans dimer by its uv spectrum,[32] comparison of its ir spectrum with that of the authentic trans dimer,[33] and its melting point behavior (the sample was found to sublime at 300°, lit.[32] mp 304°). The mother liquor was taken to dryness in a sublimer cavity. Sublimation at room temperature, with liquid nitrogen cooling on the cold finger, removed the unreacted acenapthylene. The unsublimed residue was taken up in benzene and chromatographed on a silica gel tlc plate using cyclohexane–benzene (20:1) or cyclohexane at 40°. The bands corresponding to the cis and trans dimers were scraped off and eluted with hot benzene–methanol (1:1). The extracts were then taken to dryness. The trans dimer obtained in this way was dissolved in hot cyclohexane; this solution gave a uv spectrum identical with the reported one.[32]

The cis dimer eluted from the silica gel was found to melt at 225–232° (lit.[32] mp 230–234°); it gave ir and uv spectra identical with those of the authentic cis dimer.[33]

The total trans dimer (the crystalline precipitate and the material eluted from the tlc plate and determined quantitatively by uv) amounted to 3.2 mg (0.0105 mmol, 4.5%). The yield of the cis dimer, determined by uv, was 0.7 mg (0.0023 mmol, 1%). In addition, 63 mg (89%) of unreacted acenaphthylene was recovered. The cis to trans dimer ratio was 0.22 and the apparent quantum efficiency of this reaction (based on moles of the dimer formed) was 0.013.

A blank run was performed as described above using the same amounts and concentrations of the reagents except that the dioxetane solution was preheated for 10 min on a steam bath in a sealed tube before the acenaphthylene was introduced. After the addition of acenaphthylene, the heating was repeated. The solution was evaporated to dryness and sublimed to remove acenaphthylene. The deposit left in the sublimer cavity (4.6 mg) contained no detectable amounts of the cis or trans dimers (as shown by tlc).

4,4-Diphenyl-2,5-cyclohexadienone–Trimethyldioxetane System. 4,4-Diphenylcyclohexadienone[34] (100 mg, 0.4 mmol) was dissolved in 18 ml of benzene containing 1.8 g (18 mmol) of trimethyldioxetane. The benzene solution of dioxetane used here had been bulb-to-bulb distilled using the low temperature vacuum transfer technique, thus ensuring complete removal of traces of sodium hydroxide. The dienone–dioxetane solution was degassed three times and sealed under vacuum. It was then heated for 10 min at 100° on steam. The resulting solution was chromatographed on cellulose tlc plates, using cyclohexane as the developing solvent. The plates were preconditioned before application and development by being totally immersed in a dimethylformamide-ether mixture (2:7) and exposed briefly to air to let the ether evaporate. Two main bands were observed under 254-nm ultraviolet light, with the top band corresponding to the starting dienone. Other bands of lower R_f values (higher polarity) were observed, but were not investigated. The two main bands were scraped from the plates and eluted with a methanol–ether mixture (1:1). The extracts were evaporated to near dryness, dissolved in ether, washed two times with water and once with saturated aqueous sodium chloride, and then were taken to dryness. The recovery of starting dienone was 40 mg (0.16 mmol, 40%). The weight of the photoketone recovered was 18.7 mg (0.076 mmol, 18.7%).

Another run involving 17.3 mg (0.07 mmol) of 4,4-diphenylcyclohexadienone and 0.3 g (3 mmol) of trimethyldioxetane in 6.5 ml of benzene was performed as described above. The photoketone was isolated as described above (1.9 mg, 0.0073 mmol, 11%) and identified from the ir and nmr spectra.

Trimethyl-1,2-dioxetane–Santonin System. The method of the dioxetane sensitized isomerization of santonin (VIII) to compounds IX and X is described in the text. Compounds IX and X were identified by their glpc retention times compared with authentic material from Eguchi.[35] Compound IX was also isolated by preparative tlc on silica gel with hexane–ethyl acetate (1:1). The band corresponding to IX was scraped off and eluted with benzene. The extract was evaporated to dryness and crystallized from acetone–hexane (1:1) to give colorless crystals, mp 153.5–155° (lit.[36]

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mp 156–157°). The ir spectrum (KBr) was identical with authentic material prepared by Eguchi.[35]

Bis-2,4-dinitrophenyl Oxalate–Hydrogen Peroxide Plus Substrates. A. Acenaphthylene. A solution of 69.4 mg (2 mmol) of hydrogen peroxide (98%) in 1 ml of dimethoxyethane was added to a suspension of 844 mg (2 mmol) of DNPO and 1.54 g (10 mmol) of acenaphthylene in 16 ml of the same solvent. After 3.5 hr, no further light was obtained when aliquots were treated with rubrene. Chloroform was added and the mixture was treated with saturated sodium bicarbonate. Evaporation, chromatography of the residue on Woelm acidic alumina, and recrystallization of the material eluted after acenaphthylene (benzene–pentane, 1:9) yielded 1.6 mg (0.01 mmol, 0.5% based on the DNPO) of the trans dimer, mp 303–305° (sealed tube) (lit.[32] mp 305°, sealed tube). Only traces of the cis isomer were seen.

B. Anthracene. Treatment of anthracene similar to that outlined above yielded anthraquinone (14%); anthracene 9,10-endoperoxide may also have been formed (identified by tlc).

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Photochemistry of Alkenes. Direct Irradiation in Hydroxylic Media[1]

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Abstract: The photochemical behavior of a series of alkenes and cycloalkenes on direct irradiation in hydroxylic media has been studied and compared with the sensitized behavior of these same olefins under similar conditions. On irradiation in methanol 1-methylcyclohexene, -heptene, and -octene (**1b–d**) underwent photoprotonation, in complete analogy with their behavior on sensitized irradiation. In the case of 1-methylcyclohexene (**1b**) the photoproducts **3b** and **4b** were obtained in identical ratios on direct and sensitized irradiation, and labeling studies involving irradiation of **1b** in methanol-*O-d* showed that **3b** and **4b** were formed with extensive incorporation of deuterium, as observed earlier on sensitized irradiation. This parallel behavior between direct and photosensitized irradiation is consistent with the involvement of a *trans*-cycloalkene intermediate for the photoprotonation process, as previously proposed. By contrast, 1-methylcyclopentene (**1a**) did not undergo photoprotonation on irradiation in methanol. Comparison of the cycloalkenyl alcohols **6a** and **b** showed that the cyclohexenyl alcohol **6b**, but not the cyclopentenyl homolog **6a**, underwent fragmentation to **3** on either direct or sensitized irradiation, in concert with our earlier proposal that the photofragmentation process involves an initial protonation of the cycloalkene. A novel photochemical process was observed for tetralkyl-substituted olefins on direct irradiation in hydroxylic media. Thus 1,2-dimethylcyclopentene (**14**) afforded a mixture of the photoproducts **15–18** on irradiation in methanol; 2,3-dimethyl-2-butene (**20**) yielded the products **24–27**, and bicyclohexylidene (**32**) gave the products **33–35**. The trisubstituted analog 2-methyl-2-butene (**36**) underwent much slower reaction but provided the analogous products **37–43**. 1,2-Dimethylcyclohexene (**8**) exhibited mixed behavior, affording the products **9–11** *via* photoprotonation and the mixture of products **9–13** *via* the new pathway. More extensive studies with 2,3-dimethyl-2-butene (**20**) showed that the rate of reaction is dependent upon the medium, decreasing in the order aqueous $CH_3CN \sim CH_3OH > C_2H_5OH > n\text{-}C_4H_9OH$. In less reactive media, competing isomerization of **20** to the protoproducts **24**, **28**, and **29** occurred; in nonhydroxylic media these were the principal photoproducts. Deuterium labeling studies involving irradiation of **20** in methanol-*O-d* revealed that the ethers **26** and **27** were formed without significant deuterium incorporation, whereas formation of the hydrocarbon products **24** and **25** was accompanied by extensive deuterium incorporation. These results are interpreted in terms of nucleophilic trapping of the Rydberg excited state **21a** or the radical-cation intermediate **21b**. The mechanistic ramifications of this interpretation are discussed.

Previous studies in these laboratories[4] and others[5] have shown that on sensitized irradiation in hydroxylic media cyclohexanes, -heptenes, and -octenes afford a mixture of photoproducts which result from an initial light-induced protonation of the olefin (*cf.* **1b–d** → **2b–d**). In striking contrast, cyclopentenes and other highly constrained cyclic olefins exhibit radical behavior on irradiation under similar conditions,[4b,6] whereas large-ring cyclic and acyclic olefins exhibit only cis $\rightleftarrows$ trans isomerization. Exocyclic olefins, such as the methylenecycloalkanes **3**, exhibit no observable photobehavior, although they probably also undergo an undetected cis $\rightleftarrows$ trans isomerization under these conditions. The unique behavior of cyclohexenes, -heptenes, and -octenes leading to photoprotonation has been attributed[4,5] to initial cis $\rightleftarrows$ trans isomeri-

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