twice with water by thorough intermixing, then centrifuged, and the aqueous layer was removed by pipet. The carbon disulfide layer was decanted and its infrared spectrum recorded between 900 and 1100 cm^{-1} (C–D band at 920 cm^{-1}; C–H band at 1050 cm^{-1}), and the deuterium content was obtained by comparison with the infrared spectra of standard mixtures. In phenyl cyclopropyl sulfone the relevant absorption bands were situated at 820 (C–D) and 920 cm^{-1} (C–H).

A Color Test for the Selection of Compounds Having Short-Lived Triplet States[1]

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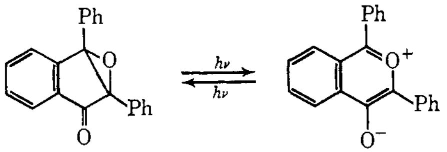
Abstract: 2,3-Diphenylindenone oxide (I) can be used as a color indicator for the selection of compounds with exceptionally short-lived spectroscopic triplet states. The method is simple and requires no instrumentation or degassing of solutions. The maximum lifetimes for the spectroscopic triplets of molecules that are active in the test are less than about 2.2 × 10^{-7} sec. Longer lived triplets cannot be detected. Rough estimates of the effective triplet energies have been made for a number of compounds with short-lived triplet states. The data suggest that triplet energy transfer for sensitizer triplets to diphenylacetylene, *cis*-stilbene, and *trans*-stilbene, and possibly other quenchers, may involve concerted geometrical changes (nonvertical excitation). The chemical processes involved in the color test are described.

In the course of our work on the mechanism of the photochemical valence tautomerization of 2,3-diphenylindenone oxide (I) to the bright red diphenylbenzopyrylium oxide II,[3] a simple color test was discovered for the identification of compounds having exceptionally short-lived triplets. Since conventional techniques for studying triplet excited states such as phosphorescence,[4a,b] triplet–triplet absorption,[4c,d] and singlet–triplet absorption induced by oxygen or heavy atom perturbation[4e,f] frequently fail when very short-lived triplet states are encountered, the method provides in some cases the only readily accessible information concerning such triplets. The color test provides a means for establishing limits on triplet lifetimes and can be used to estimate roughly both the triplet energies of conventional sensitizers and the effective triplet energies of certain quenchers.



I II

Description of the Color Test.

The indenone oxide I is known to give II both by direct absorption of light and by the use of sensitizers.[3] Only sensitizers with triplet energies greater than 64 kcal effect the reaction. The product pyrylium oxide II is intensely colored [$\lambda_{\max}^{C_6H_6}$ 544 mμ (ϵ 26,750)] and is converted by direct but not by sensitized excitation back to I.[3] On prolonged irradiation of degassed solutions of the indenone oxide I with or without sensitizers ($E_T > 64$ kcal), a steady-state concentration of II is attained. When the solutions are not degassed the concentrations of II that are reached are considerably reduced.

When nondegassed benzene solutions of I that contained sensitizers having $E_T < 64$ kcal were irradiated with 3650-A light no color was formed at all unless the concentration of the sensitizer was insufficient to absorb all the light. However, if the indenone oxide I was allowed to absorb some of the light, the intensity of color due to II rapidly reached a maximum, and then faded gradually as the reservoir of I became depleted by photo- and thermal oxidation of II (*vide infra*). By adjusting the relative concentrations of I and sensitizer the maximum concentration of II that was attained could be reduced to any desired level. In the test to be described, ratios of sensitizer to I were selected so as to obtain just visually observable maximum concentrations of II ([II] ≈ 2-4 × 10^{-6} *M*). Generally solutions about 0.5–1.0 × 10^{-2} *M* in I were used, and small quantities of the sensitizer were added to the solution until, by trial and error, the desired color intensity was reached. Since on irradiation of a portion (0.5–1.0 ml) of these solutions the maximum color was generally reached within 15 sec, little time was required for this procedure. Continued irradiation of solutions having these low maximum color intensities produced nearly steady-state concentrations of II.

When a compound known to have a short-lived triplet state such as *trans*-stilbene[5] was added to several

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(1) A preliminary account of this work has been published: E. F. Ullman, *J. Am. Chem. Soc.*, **86**, 5357 (1964).

(2) To whom inquiries may be addressed: Synvar Research Institute, Palo Alto, Calif.

(3) E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **86**, 5050 (1964); **88**, 4942 (1966).

(4) See, *inter alia*: (a) A. Jablonski, *Z. Physik.*, **94**, 38 (1935); (b) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); (c) G. N. Lewis, D. Lipkin, and T. T. Magel, *ibid.*, **63**, 3005 (1941); (d) G. Porter and M. W. Windsor, *J. Chem. Phys.*, **21**, 2088 (1953); (e) M. Kasha, *ibid.*, 20, 71 (1952); (f) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

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

such solutions, each containing a different sensitizer, the rate of appearance of color (II) and the steady-state color intensities were found to increase with solutions containing certain sensitizers but not others. In these experiments about 0.5 ml of the solution was added to each of two Pyrex glass test tubes, one of which contained 1–10 mg of the test compound to be studied ($\sim 10^{-2}$–10^{-1} M). The two tubes were then irradiated simultaneously for up to 30 sec with a 3650-A light source (100-w U-shaped Hanovia mercury lamp equipped with Corning No. 5860 and 7380 filters), and the relative color intensities were periodically compared visually. Depending on the sensitizer used, the solutions containing the test compound usually reached either the same or a more highly colored photostationary state than the blank.

It was found that the ability of many of the test compounds studied to increase the photostationary concentration of II was a function of the triplet energy of the sensitizer. Generally, when sensitizers with decreasing energies were employed, an energy was reached for a given test compound below which there was no visually detectible color difference between the test solution and the blank. An illustration of the results obtained is given for *trans*-stilbene in Table I. Similar results have been obtained for other compounds, and the critical data are presented in Table II.

Table I. Quenching of Sensitizer Triplet by *trans*-Stilbene

Sensitizer[a]	E_T, kcal[a]	Visually observable increase in [II]
Fluoranthene	52.8	+
1,2,3,4-Dibenzanthracene	50.9	+
Pyrene	48.7	+
1,2-Benzanthracene	47.3	+
Acridine	45.4	+
Phenazine	44.6	+
Anthracene	42.4	–
9,10-Dichloroanthracene	40.2	–
Perylene	35.6	–
Naphthacene	29.3	–

[a] Other sensitizers that were studied had E_T from 53.3 to 62.0 kcal and all caused increases in [II]. See Experimental Section for complete list.

Interpretation of these results requires knowledge of all the processes taking place in these solutions. It could readily be shown that the steady-state concentrations of II that were obtained in these experiments were dependent on the relative rates of the following reactions.

$$\mathrm{I} \xrightarrow{h\nu\ \text{(direct)}} \mathrm{II} \tag{1}$$

$$\mathrm{II} \xrightarrow{h\nu\ \text{(direct)}} \mathrm{I} \tag{2}$$

$$\mathrm{II} \xrightarrow{h\nu\ \text{(sensitized)}} \text{oxidation product} \tag{3}$$

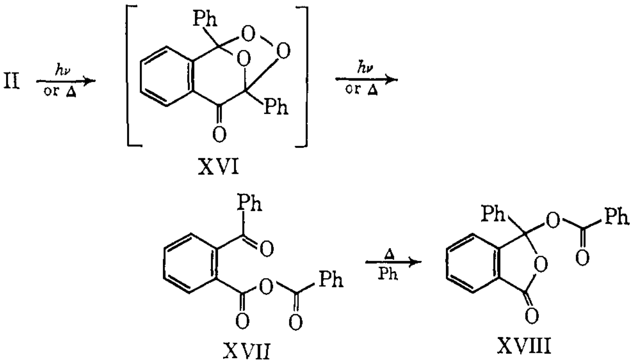
$$\mathrm{II} \xrightarrow{\text{thermal}} \text{oxidation product} \tag{4}$$

The existence of only direct, and not sensitized, interconversions of I and II (namely eq 1 and 2) is assured because the sensitizers all had triplet energies of <64 kcal.[3] The probable existence of the photooxidation reaction 3 was demonstrated by the isolation of good yields of XVII on irradiation of benzene solutions of I with or without sensitization with benzophenone (E_T = 68.5 kcal).[6] Thus the formation of XVII can be rationalized by assuming that oxygen adds to II in analogy to the known dipolar additions of reactive olefins and acetylenes to this compound.[7] The expected ozonide XVI has previously been prepared by ozonization of 2,3-diphenylindenone,[8] and we have found that it readily undergoes photorearrangement to give the observed photooxidation product XVII. The pyrylium oxide II appears to add oxygen

Table II. Effective Quencher Triplet Energies

	Quencher	E_T, kcal Effective[a]	Spectroscopic
III	$(C_6H_5)_2C{=}C{=}C(C_6H_5)_2$	54.5 (53.3)	57.4[b]
IV	$(C_6H_5)_2C{=}CH_2$	54.5 (53.3)	*c*
V	$(C_6H_5)_2C{=}CCl_2$	54.5 (53.3)	*c*
VI	$(p\text{-}CH_3OC_6H_4)_2C{=}CCl_2$	52.8 (50.9)	*c*
VII	$C_6H_5N{=}CHC_6H_5$	$\leqslant$ 50.9 (48.7)[d]	*c*
VIII	$C_6H_5C{\equiv}CC_6H_5$	50.9 (48.7)	62.5[e]
IX	$(C_6H_5)_2C{=}C(C_6H_5)_2$	$\leqslant$ 47.3 (45.4)[d]	*c*
X	*trans*-$C_6H_5CH{=}CHC_6H_5$	44.6 (42.4)	50[f]
XI	$(C_6H_5)_2C{=}CHC_6H_5$	42.4 (40.2)	*c*
XII	*cis*-$C_6H_5CH{=}CHC_6H_5$	40.2 (35.6)	57[g]
XIII	$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$	$\leqslant$ 29.3[h,i,m]	*c*
XIV	1,3-Cyclohexadiene	$\leqslant$ 29.3[i,m]	53[j]
XV	$C_6H_5C(CH_3){=}CH_2$	$\leqslant$ 59.3[l]	*k*

[a] Lowest sensitizer triplet energy where color increase was observed, and, in parentheses, highest sensitizer triplet energy where color increase was not observed. See Experimental Section for list of sensitizers studied. [b] S–T absorption measured under O_2 pressure in $CHCl_3$; this work. [c] Not observable by phosphorescence or oxygen pertubation. [d] Possible error due to partial light absorption by quencher; *cf.* ref 12. [e] See ref 4f and 19. [f] See ref 4f and R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962). [g] See ref 5. [h] Color decrease observed with anthraquinone (E_T = 62.4 kcal) due to formation of charge-transfer complex which absorbed light. [i] Lowest energy sensitizer studied. [j] D. F. Evans, *J. Chem. Soc.*, 2566 (1961). [k] Not studied. [l] Studied only with α-acetonaphthone as sensitizer at 6°. Observation difficult due to rapid reaction with II. [m] Energy not meaningful due to probable reaction with oxygen singlet; see text.



in a similar fashion in a thermal reaction (eq 4) since on heating I in the presence of oxygen the principal product was the thermal rearrangement product XVIII of the anhydride XVII.

It was possible to confirm experimentally that XVII was formed principally or exclusively from the pyrylium

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(6) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(7) E. F. Ullman and J. E. Milks, *ibid.*, **84**, 1315 (1962); **86**, 3814 (1964).

(8) R. Criegee, P. deBruyn, and G. Lohaus, *Ann.*, **583**, 19 (1953).

oxide II and not by a direct reaction of the indenone oxide I. Thus when oxygenated solutions of I were irradiated with ultraviolet light, the rate of oxidation could be greatly reduced by simultaneous irradiation with very intense visible light (>4350 A). Since the visible light is absorbed exclusively by II and converts II back to I (eq 2),[3] the observed low rate of oxidation demonstrated that direct absorption of light by I or II is alone insufficient to cause photooxidation, and that for the reaction to occur II must be present in appreciable concentrations. The oxidation is, therefore, a reaction of II which required sensitization by some substance other than II (eq 3).

We need then only consider reactions 1–4 in the color test. The test compounds III–XV might affect these reactions by behaving as sensitizers, quenchers, or reactants. The effect of these compounds to increase the steady-state concentration of II requires that they either effect an increase in the relative efficiency of reaction 1 or a decrease in the efficiency of reactions 2, 3, or 4. An increased efficiency of reaction 1 through sensitized excitation of I by the test compounds can be excluded since only VII and IX absorbed significantly at 3650 A, and even these compounds were found to inhibit the formation of II if they were used in sufficient concentrations to behave as sensitizers. Moreover, reaction 2 cannot be quenched,[3] and it was easily demonstrated that the test compounds did not inhibit the thermal oxidation process 4. Thus the test compounds must inhibit the photooxidation process 3.

Discussion

The above data show that the new color test provides a means of detecting compounds which inhibit the sensitized photooxidation of an indicator, the pyrylium oxide II. Two mechanisms for the photooxidation can be envisaged: reactions 5–7 or 5, 8, and 9. Inhibition of the over-all reaction by a test compound must, therefore, involve either quenching of triplet sensitizer, triplet pyrylium oxide II or singlet oxygen, or

$$S \xrightarrow{h\nu} {}^1S \longrightarrow {}^3S \qquad (5)$$

$${}^3O_2 + {}^3S \longrightarrow S + {}^1O_2 \qquad (6)$$

$${}^1O_2 + II \longrightarrow III \xrightarrow{h\nu} IV \qquad (7)$$

$${}^3S + II \longrightarrow S + {}^3II \qquad (8)$$

$${}^3O_2 + {}^3II \longrightarrow III \xrightarrow{h\nu} IV \qquad (9)$$

trapping of singlet oxygen.[9] Since compounds III–XII had effects on the photooxidation which were demonstrably a function of the sensitizer triplet energies (Table II), at least these compounds must inhibit the photooxidation by acting as quenchers of sensitizer triplets.

Having established that the behavior of these quenchers (III–XII) in the color test is directly related to the triplet energies of the sensitizers, it becomes clear that a rapid means is at hand for estimating at least roughly the triplet energies of new sensitizers merely by comparison against each of the quenchers III–XII. Conversely, the color test provides a measure of the *effective* triplet energy of these and other quenchers. However, the significance of these *effective* triplet energies and the identification of the property of compounds III–XII that permits them to act as quenchers require further consideration of the processes occurring in the test.

The quenching process may involve the intermediacy of quencher triplets (reactions 10 and 11), or conceivably the quenchers may catalyze crossing of sensitizer triplets to the ground state without themselves becoming excited (reaction 12). In order to establish whether

$${}^3S + Q \longrightarrow {}^3Q + S \qquad (10)$$

$${}^3Q \longrightarrow Q \qquad (11)$$

$${}^3S + Q \longrightarrow Q + S \qquad (12)$$

quencher triplets were actually formed as intermediates, color tests were carried out using benzophenone as sensitizer in sufficient quantity to absorb all the light. Under these conditions I gave II exclusively by a sensitized process and II was simultaneously destroyed by a photosensitized oxidation. After irradiation of such a solution until a near steady-state concentration of II was obtained, one of the quenchers III–XII was added, and the solution was irradiated again. If quenching of sensitizer triplets occurred only by process 12 in these experiments, the rate of all photochemical reactions should have been greatly reduced on adding the quenchers, and only a slow disappearance of II should have occurred due to the thermal oxidation process 4. In point of fact, however, irradiation produced a rapid reduction in the concentration of II. This behavior strongly suggests that quencher triplets were formed (eq 10 and 11) and that they were of sufficiently low energy (<64 kcal) that they could sensitize only the photooxidation reaction 3 and not the conversion I to II.

Since quencher triplets are formed in the color test and are able to sensitize the photooxidation of II, the ability of the quenchers III–XII to inhibit the sensitized oxidation must be due to their triplets being less efficient as energy donors than are sensitizer triplets. This inefficiency is probably an intrinsic property of the quencher molecule and is not associated with the energy of the acceptor, for the acceptor appears to be oxygen (*vide infra*), which has a low singlet energy of only 22.5 kcal.[10a] In principle, the low efficiency of energy transfer from quencher triplets might be due to either an exceptionally low energy transfer rate constant k_{13} or an exceptionally high rate of intersystem crossing of the quencher triplet to the ground state (k_{11}) as compared to the equivalent processes involving sensitizer triplets. Although we cannot distinguish between these possibilities we can lump them together and compare the over-

$${}^3Q + {}^3O_2 \longrightarrow {}^1O_2 + Q \qquad (13)$$

all donor ability of quencher triplets with that of conventional sensitizer triplets. For this purpose we define the *effective* lifetime of quencher triplets, τ_{eff}, by eq 14.

$$\tau_{\text{eff}} = (1/k_{11})(k_{13}/k_6) \qquad (14)$$

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(9) The intermediacy of singlet oxygen in numerous photooxidation reactions has been amply demonstrated: (a) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879, 3880 (1964); (b) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters*, 4111 (1965); (c) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, 43, (1965); (d) T. Wilson, *J. Am. Chem. Soc.*, **88**, 2898 (1966).

(10) (a) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 560. (b) Estimated from the atmospheric pressure of oxygen and its absorption coefficient in benzene of 0.163 atm^{-1} at 20°: S. Glasstone, "Textbook of Physical Chemistry," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1946, p 695.

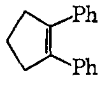
An upper limit on τ_{eff} for the quencher triplets may then be estimated from the experimental requirement that it must be less than the actual lifetime of the sensitizer triplets under the reaction conditions. The lifetime of the sensitizer triplets in the absence of added quencher is dependent principally on the rate of quenching by oxygen (eq 6). The concentration of oxygen in aerated benzene is 1.5×10^{-3} *M*,[10b] and the rate constant for diffusion-controlled energy transfer to oxygen (k_6) is about 3×10^9 sec^{-1}.[11] The sensitizer triplet lifetime is, therefore, $1/k_6[O_2] \approx 2.2 \times 10^{-7}$ sec. This demonstrates that those compounds which behave as quenchers in the color test must have effective triplet lifetimes of $\tau_{\mathrm{eff}} < 2.2 \times 10^{-7}$ sec. This is in agreement with the previously estimated minimum effective lifetime of *trans*-stilbene triplet of $<7.7 \times 10^{-8}$ sec.[5]

The significance of the *effective* triplet energies of the quenchers III–XII can now be considered. For the color differences to be observable in the color test we estimate that the quencher must reduce the efficiency of the photooxidation reaction by at least 10%. To achieve this reduction in efficiency $\geqslant 10\%$ of the sensitizer triplets must transfer energy to the quencher (eq 10) rather than to oxygen (eq 6); that is, $k_{10}[Q] \geqslant 0.1k_6[O_2] \approx 4.5 \times 10^5$ sec^{-1}. Since the quencher concentrations used did not exceed 10^{-1} *M*, the rate constant for quenching sensitizer triplets, k_{10}, must be $>4.5 \times 10^6$ sec^{-1} for color differences to be observable. The *effective* triplet energies of the quenchers are, therefore, the energies of the least energetic sensitizer triplets from which quenchers can accept energy with a rate constant of $>4.5 \times 10^6$ sec^{-1}.[12]

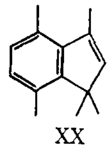
In simple triplet energy transfer processes in which a spectroscopic triplet of the acceptor is formed, the rate is diffusion controlled when the process is exothermic, and it is expected to drop below 4.5×10^6 sec^{-1} only when the process becomes endothermic in excess of 5 kcal.[13] If one assumes only simple energy transfer in the quenching process, 0–5 kcal must then be added to the observed *effective* quencher triplet energies (Table II) to obtain their true spectroscopic triplet energies. However, energy transfer to diphenylacetylene (VIII), *trans*-stilbene (X), and *cis*-stilbene (XII) seems to be more endothermic than 5 kcal (Table II), indicating that at least these quenchers and probably the others as well are not being excited to their spectroscopic triplets. Rather the energy transfer process appears to give directly lower energy quencher triplets that presumably have suffered some geometrical change. Unlike conventional energy transfer, this previously described non-Franck–Condon process, called nonvertical energy transfer,[5,14] has been shown to proceed at less than diffusion-controlled rates and to fall off further in rate as the energy transfer process increases in apparent endothermicity.

This ability of quencher triplets VIII, X, and XII to undergo geometrical changes is almost certainly responsible for their short effective lifetimes. Such rearranged triplets would be expected to behave as very inefficient energy donors since energy transfer from them would involve their deactivation by a slow nonvertical process.[15] By inference, the short effective triplet lifetimes of the other quenchers III–VII, IX, XI, and XV suggest that these compounds probably also undergo rearrangement in their triplet states and that nonvertical energy transfer is an available pathway for their excitation.

Direct confirmation that geometrical changes were in fact responsible for the short effective triplet lifetimes of the phenyl-substituted ethylenes was obtained from the two geometrically constrained derivatives XIX and XX.[16] It was found that in the color test these compounds produced no increase in color intensity with any of the sensitizers despite the fact that the related compounds, *cis*-stilbene (XII) and α-methylstyrene (XV), were excellent quenchers. *The short effective triplet lifetimes of the phenyl-substituted ethylenes must, therefore, be directly dependent on the ability of these compounds to undergo rotation about their carbon–carbon double bonds.*



XIX



XX

A similar conclusion may be reached by considering further the significance of the effective triplet energies of the stilbenes. We have shown that experimentally these effective triplet energies are simply the energies of the least energetic sensitizer triplets from which the quenchers can accept energy with a rate constant $k_{10} \geqslant 4.5 \times 10^6$ sec^{-1}. However, comparison of the experimentally determined ranges for the effective triplet energies of *cis*- and *trans*-stilbene (Table II) with the known thermal activation energies for rearrangement of *cis*- to *trans*- (36.7 kcal)[17] and *trans*- to *cis*-stilbene (42.4 kcal)[17,18] reveals a striking coincidence of numbers. Accordingly, it seems likely that at least among the experimentally uncomplicated examples of phenyl-substituted ethylenes (III–VI, VIII, and X–XII), the *effective triplet energies of the quenchers given in Table II may represent the energies of the rearranged triplets, and the rearranged triplets may be similar in geometry and energy to the transition state of the thermal reactions.*

Unfortunately, no direct evidence concerning the geometry of the triplets of the other quenchers is available. Nevertheless in the case of diphenylacetylene (VIII) few alternatives are available. While this compound has a measurable triplet lifetime (0.3 sec) at 77°K,[19] the color test indicates that its triplet has an effective lifetime of $<2.2 \times 10^{-7}$ sec at room temperature. Since this compound can undergo a rapid apparently

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(11) (a) R. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958); (b) G. Porter and M. W. Windsor, *Proc. Roy. Soc.* (London), **A245**, 238 (1958).

(12) Possible errors in the effective triplet energies given in Table II would not invalidate this statement since all conceivable errors would arise from failure to observe a color increase, and too high an effective triplet energy would then result. Possible sources of error included (1) the increased importance of the thermal process 4 with sensitizers having very low intersystem crossing ratios, and (2) the absorption of light by the quencher.

(13) (a) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964); (b) K. Sandros and H. L. J. Backstrom, *ibid.*, **16**, 958 (1962).

(14) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

(15) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

(16) We wish to thank Professor Frank B. Mallory for the donation of a sample of 1,2-diphenylcyclopentene.

(17) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).

(18) R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942).

(19) M. Beer, *J. Chem. Phys.*, **25**, 745 (1956).

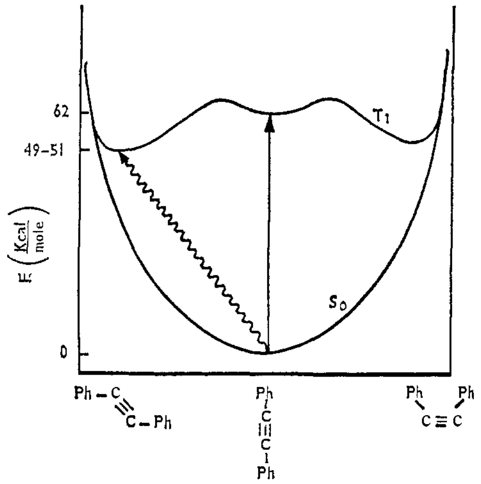

Figure 1. Possible potential function for bending of the ground and triplet states of diphenylacetylene: vertical excitation, →; nonvertical excitation, ⇝.

endothermic energy transfer of 11–14 kcal, nonvertical energy transfer and rearrangement of its triplet must take place. We therefore conclude that triplet diphenylacetylene must undergo an exothermic geometric change to a nonlinear geometry, although possibly an activation energy is associated with this change to account for the long lifetime of the triplet at 77°K (*cf.* Figure 1). Interestingly, similar geometrical changes in the lowest excited states of acetylene have been suggested by spectroscopic data and theoretical calculations.[20]

The observed short lifetime of tetraphenylallene (III) triplet likewise suggests a geometrical change, perhaps to a planar triplet. It might, therefore, be predicted that optically active derivatives of this compound should undergo photoracemization. Since little apparent endothermic energy transfer was obtained with this compound the energy of the planar species may not lie far below the spectroscopic triplet level.

There remain for consideration those compounds XIII–XIV which appeared to act as quenchers with all sensitizers that were tried. While it is possible that the effective triplet energies of these compounds are actually below 29 kcal, the lowest sensitizer energy tried, it appears more probable that they inhibit the photooxidation of II either by trapping singlet oxygen or by quenching pyrylium oxide triplets (E_T < 49 kcal).[3] In order to distinguish between these possibilities, furan, a compound calculated to have a high triplet energy (101 kcal)[21] that reacts readily with singlet oxygen,[10,22] was employed as a "quencher." It was found that this compound not only caused an increase in color with all the sensitizers used in the color test (E_T = 29–62 kcal) but also caused a color increase when benzophenone (E_T = 68.5 kcal) was used as sensitizer. Since only sensitized photochemical reactions were possible under these latter conditions, quenching of benzophenone triplets by furan would be expected to reduce the color as did legitimate quenchers. Since in fact the color intensity increased, furan must trap singlet oxygen. Thus the photooxidation proceeds by the reaction sequence 5–7, and the compounds XIII–XIV may inhibit oxidation in a manner similar to furan. However, since these compounds produced no color increase when benzophenone was used as a sensitizer, they may also be acting as quenchers and have short-lived triplet states.

Experimental Section

All sensitizers and quenchers and the indenone oxide I were purified by crystallization to constant melting point or by distillation. The sensitizers that were studied included benzophenone (E_T = 68.5 kcal),[6] anthraquinone (E_T = 62.4 kcal),[6] flavone (E_T = 62.0 kcal),[6] β-acetonaphthone (E_T = 59.3 kcal),[6] α-naphthaldehyde (E_T = 56.3 kcal),[6] coronene (E_T = 54.5 kcal),[13b] fluorenone (E_T = 53.3 kcal),[6] fluoranthene (E_T = 52.8 kcal),[4f] 1,2,3,4-dibenzanthracene (E_T = 50.9 kcal),[4f] pyrene (E_T = 48.7 kcal),[4f] 1,2-benzanthracene (E_T = 47.3 kcal),[13b] acridine (E_T = 45.4 kcal),[4f] phenazine (E_T = 44.6 kcal),[4h] anthracene (E_T = 42.4 kcal),[4f] 9,10-dichloroanthracene (E_T = 40.2 kcal),[23] perylene (E_T = 35.6 kcal),[24] and naphthacene (E_T = 29.3 kcal)[23]

The color tests were carried out using 3-in. Pyrex test tubes and an Hanovia 100-w U-shaped mercury lamp equipped with Corning No. 5860 and 7380 filters. Benzene was employed as solvent.

Photooxidation of 2,3-Diphenylindenone Oxide. A solution of 500 mg of the indenone oxide I in 50 ml of benzene was stirred at 10° under oxygen and irradiated for 4 hr with 3100–4000-A light (GE B-H6 1000-w, high-pressure Hg lamp with Hanovia No. 16223A and 6541 filters). A total of 0.98 equiv of oxygen was consumed. The solvent was removed *in vacuo* to leave a yellow oil which crystallized on trituration with petroleum ether (bp 30–60°). Recrystallization from benzene–petroleum ether gave 380 mg (76%) of the anhydride XVII,[8] mp and mmp 88–90°.

Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.25. Found: C, 76.06; H, 4.05.

In a similar experiment using 3650-A light (Hanovia 100-w Hg lamp with Corning No. 5860 and 7380 filters) and benzophenone as sensitizer, 51% of the anhydride was obtained.

Benzoic *o*-Benzoylbenzoic Mixed Anhydride. A mixture of 6.2 g of benzoyl chloride, 10.2 g of *o*-benzoylbenzoic acid, and 4.6 g of triethylamine in 150 ml of toluene was allowed to stand at room temperature for 1 hr. The mixture was then filtered, and the solvent was removed *in vacuo*. The resulting oil crystallized on trituration with petroleum ether. Recrystallization from benzene–petroleum ether gave 9.1 g of the anhydride XVII which was identical with the above described photochemical product. The infrared spectrum (chloroform) showed carbonyl bands at 1810 and 1740 cm^{-1} (linear anhydride) and 1680 cm^{-1} (aromatic ketone). On heating in toluene or chlorobenzene above 100°, the anhydride was slowly converted to the phthalide XVIII.

Thermal Oxidation of 2,3-Diphenylindenone Oxide. A solution of 1.57 g of the indenone oxide I in 25 ml of chlorobenzene was heated at 100° with stirring in a oxygen atmosphere for 6 days, during which time 0.86 equiv of oxygen was consumed. The solvent was removed *in vacuo*, and the resultant oil was found by infrared analysis to be a mixture of the anhydride XVII (20%) and the phthalide XVIII (80%). Crystallization of this product from ether gave 1.01 g (58%) of the phthalide XVIII, mp and mmp 115–117°.

3-Hydroxy-3-phenylphthalide Benzoate Ester (XVIII). A mixture of 2.44 g of 3-chloro-3-phenylphthalide[25,26] and 2.29 g of silver benzoate in 50 ml of ether was stirred at reflux for 16 hr. The mixture was filtered and concentrated. The crystalline precipitate was recrystallized from ether to give 2.46 g (74%) of the phthalide XVIII, mp 115–117°, $\lambda_{max}^{CHCl_3}$ 1795 (lactone) and 1735 cm^{-1} (benzoate ester).

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Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.18; H, 3.88.

2,3-Diphenylindenone Ozonide (XVI). The crystalline ozonide XVI was prepared by the method of Criegee.[8] On standing at 10° in benzene solution, it was completely converted to the anhydride XVII in 24 hr. In a similar solution irradiated with 3100–4000-A light the reaction was greatly accelerated and XVII was formed in quantitative yield after 1.5 hr.

Colligative Property Measurements on Oxygen- and Moisture-Sensitive Compounds. I. Organolithium Reagents in Donor Solvents at 25°

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Abstract: The differential vapor-pressure technique used to study solution colligative properties of oxygen- and moisture-sensitive compounds is described. Colligative measurements on organolithium reagents in tetrahydrofuran and diethyl ether at 25° are reported. Deviations from ideality are accounted for in terms of solute aggregation and solute–solvent interactions. The findings are that organolithium reagents may or may not be aggregated in these donor solvents at 25°. The data indicate a predominance of tetrameric methyllithium, dimeric phenyllithium, and monomeric benzyllithium, these species being representative of alkyl, sp^2 hybridized, and charge-delocalized reagents. These aggregate sizes agree with postulations of organolithium aggregation in tetrahydrofuran based on kinetic studies.

Kinetic studies of metalation[1-4] and olefin addition[5,6] by organolithium reagents in tetrahydrofuran (THF) solution at 22° revealed fractional reaction orders for certain of the organolithium species. These reaction orders of less than unity were interpreted to be a consequence of organolithium aggregation in THF solution,[2-6] a surprising result in view of the good solvating power of THF for such species.

No accounts are reported of colligative studies of organolithium compounds in THF solution. This report describes colligative property measurements made on organolithium solutions in pure donor solvents THF and diethyl ether.[6]

Previous colligative studies have established that alkyllithiums are aggregated in hydrocarbon solution.[7-9] Nevertheless, in the presence of basic solvents it was logical to expect that aggregation would be disrupted in favor of strong solvation by the basic solvents.[10] Pioneering ebullioscopic measurements on organolithiums in diethyl ether,[11] on the other hand, indicated methyllithium to be approximately trimeric and *n*-butyllithium pentameric, whereas both benzyllithium and phenyllithium were indicated to be dimeric. Later ebullioscopic experiments[12] also indicated phenyllithium to be dimeric in diethyl ether and *n*-butyllithium to be hexameric in this solvent. Ebulliometrically determined degrees of organolithium aggregation in ether solvents are, however, open to criticism[13] because of the possible reaction of the organolithiums with solvent at elevated temperatures.[14] Another point of view, deduced from freezing-point measurements of *n*-butyllithium in cyclohexane solution containing a small amount of diethyl ether[15] and ethyllithium in benzene–triethylamine mixtures,[16] is that alkyllithiums are dimeric in the respective donor solvents. These experiments in mixed solvents are, however, subject to alternative explanations.[2] Interpretation of recent low-temperature nmr studies on concentrated ($\sim$1 *M*) mixtures of methyllithium and ethyllithium in diethyl ether invoked tetrameric structures for alkyllithium species at −80°,[17] although it was not possible to rule out an alternative model based on trimeric species. Low-temperature findings may not reflect the behavior at room temperature.

The experiments reported here illustrate that certain organolithium species are aggregated in diethyl ether and THF at 25° in spite of the opportunity for solvent coordination. With other structure types more extensive solvation is apparently favored and the species are found to be monomeric in these solvents. The

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