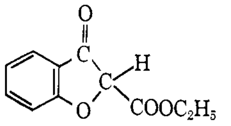
97% yield of the pure tertiary sulfide (III, A = SC_6H_5) is obtained. An even more compelling argument against the carbanion mechanism is the fact that the pure tertiary sulfide is isolated in 97% yield when the reaction is conducted in absolute ethanol.

The reaction of II with sodiomalonic ester is also extraordinarily clean; in DMF, at 25°, after 1 day a 95% yield of the alkylated malonic ester III, A = $CH(COOC_2H_5)_2$, is produced. Treatment of II with the lithium salt of 2-nitropropane at 25° in DMSO gives the carbon alkylate III, A = $C(CH_3)_2NO_2$, in 71% yield. Furthermore, the reaction of II with the sodium salt of β-keto ester VI also follows eq 2, the yield of carbon alkylate being about 70%.

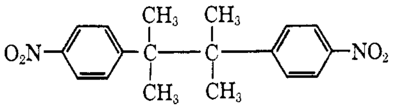


VI

Sodium phenoxide in DMSO at 25° displaces the nitro group of II according to eq 2, giving the tertiary ether III, A = OC_6H_5, in 66% yield; the sodium salt of 1-methyl-2-naphthol reacts with II in a strictly analogous way, giving the tertiary ether (64% yield). Finally, treatment of II with methanolic sodium methoxide at 60° results in the formation of the methyl ether III, A = OCH_3, in 56% yield.

In no instance does α-nitrocumene (IV) undergo any significant amount of reaction when exposed to the various anions under conditions which result in complete reaction according to eq 2 when α,p-dinitrocumene (II) is employed.

It seems very likely that the reactions of eq 2 are radical anion processes.[1,3] This view is supported by a number of observations, including the fact that various of these reactions show some of the following characteristics: light speeds up the reaction whereas oxygen retards it, and small amounts of the dimer VII are isolated.[4]



VII

Acknowledgment. We thank the Petroleum Research Fund and the Explosives Department of Du Pont for generous support.

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(3) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966).

(4) All reactions were conducted under nitrogen or argon.

(5) X-R Fellow of the Purdue Research Foundation, 1965–1967.

(6) National Science Foundation Cooperative Fellow, 1965–1967.

(7) National Science Foundation Cooperative Fellow, 1964–1966; Standard Oil of Ohio Fellow, 1966–1967.

(8) Union Carbide Fellow, 1965–1966.

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Received August 14, 1967

Nearest Neighbor Triplet Quenching at High Quencher Concentrations[1]

Sir:

The purpose of this communication is to point out a feature of triplet energy transfer which has not, to my knowledge, been elaborated previously. It is widely assumed that *exothermic* triplet energy transfer is intrinsically so efficient that the rate at which it occurs in solution is limited by and equals the rate at which the excited donor and the quenching acceptor can diffuse together.

In the absence of transient effects,[2] the ability of low concentrations of a particular compound to quench excited-state photoreactions of another compound is adequately expressed by the Stern–Volmer expression

$$\phi_0/\phi_q = 1 + k_q[Q]\tau_0 \qquad (1)$$

where k_q is the bimolecular rate constant for quenching, [Q] is the concentration of quencher, and τ_0 is the lifetime of the excited state being quenched. However, if quenching is so efficient that it occurs at the diffusion-limited rate, the simple Stern–Volmer expression above is no longer accurate at high quencher concentrations.

Let us consider as a typical case the quenching of some triplet-state photoreaction of a ketone. At quencher concentrations greater than 0.1 *M*, a significant percentage of the ketone molecules will have a quencher molecule as nearest neighbor at the moment of excitation. This percentage increases rapidly with quencher concentration. If exothermic energy transfer from the ketone triplet to the quencher is 100% efficient, that portion of the excited ketone molecules "born" with quencher molecules as nearest neighbors will be quenched immediately and will never be able to enter into the normal competition between photoreaction and diffusional quenching. Consequently, high concentrations of quenchers should be much more efficient at quenching a photoreaction than might be extrapolated from Stern–Volmer plots at low quencher concentrations. Such behavior is conceptually similar to the "static" fluorescence quenching postulated long ago by Bowen and Metcalf,[3] except that no special interactions between ground-state ketone and quencher need be invoked. Weller has developed and applied the kinetics of static quenching to fluorescence studies.[4]

Simple statistical considerations yield the following expression for the quantum yield of triplet-state reaction, where u is the fraction of ketone molecules which have at least one quencher molecule as a nearest neighbor, k_r is the unimolecular rate constant for reaction of the ketone triplet, and k_{et} is the rate at which energy transfer occurs once excited ketone and quencher molecules are nearest neighbors.

$$\Phi = \frac{(1-u)k_r}{1/\tau_0 + k_q[Q]} + \frac{uk_r}{1/\tau_0 + k_{et}} \qquad (2)$$

Division of the above equation into $k_r\tau_0$ yields the following modification of the Stern–Volmer equation,

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(1) Triplet Energy Transfer. II. Part I is P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820 (1967). This work was supported by the Office of Naval Research and the National Science Foundation.

(2) R. M. Noyes, *Progr. Reaction Kinetics*, **1**, 131 (1961).

(3) E. J. Bowen and W. S. Metcalf, *Proc. Roy Soc.* (London), **A206**, 437 (1951).

(4) A. Weller, *Discussions Faraday Soc.*, 27, **28** (1959); *Progr. Reaction Kinetics*, 1, 187 (1961).

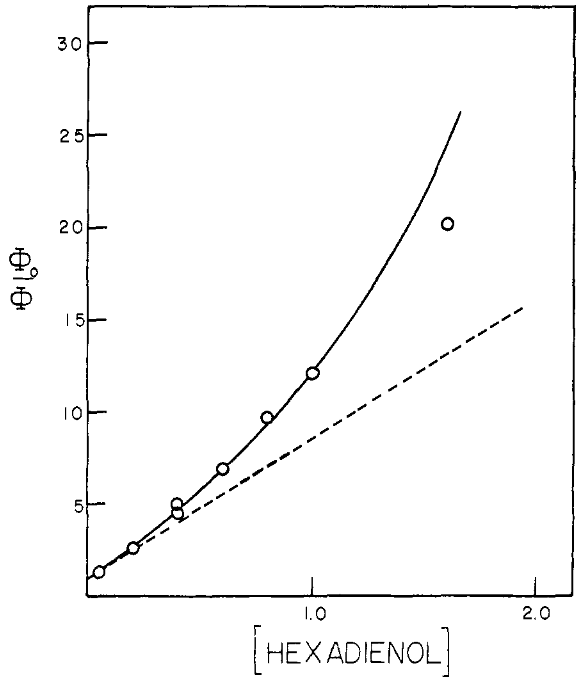

Figure 1. Stern–Volmer plot of the quenching of γ-methylvalerophenone by high concentrations of 2,4-hexadien-1-ol in *t*-butyl alcohol at 25°. Dotted line is linear extrapolation of low concentration data.

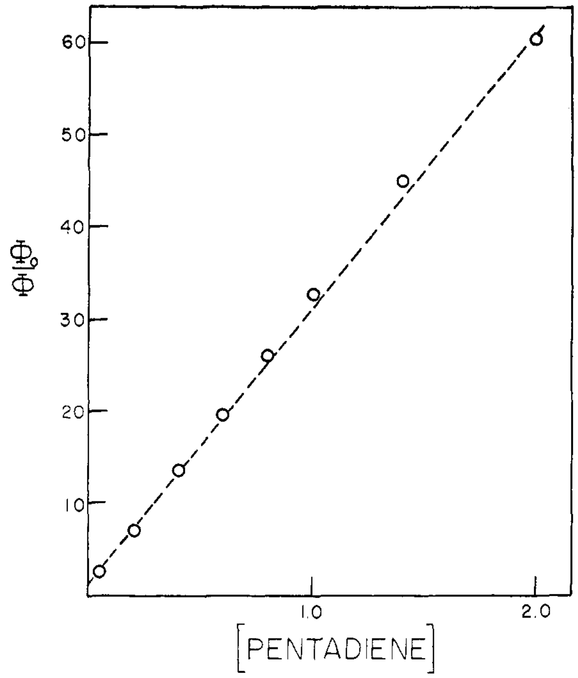

Figure 2. Stern–Volmer plot of the quenching of γ-phenylbutyrophenone by high concentrations of pentadiene in pentane at 25°. Dotted line is linear extrapolation of low concentration data.

where α is the probability that energy will be transferred from triplet ketone to quencher during the lifetime of a solution encounter.

$$\frac{\Phi_0}{\Phi} = \frac{1 + k_q[Q]\tau_0}{1 - \alpha u} \tag{3}$$

When triplet energy transfer is truly diffusion controlled, $\alpha = 1$. Under such conditions, Stern–Volmer plots should curve upward at moderate values of u and at $u \sim 1$ attain the limiting value indicated by the following expression. When every excited ketone molecule is continually surrounded by quencher molecules, the only reaction possible is from direct competition of k_r with k_{et}, *i.e.*, from the second term of eq 2.

$$\frac{\Phi_0}{\Phi} = 1 + k_{et}\tau_0 \tag{4}$$

In tertiary alcohols, rate constants for quenching of triplet valerophenone by conjugated dienes are inversely proportional to viscosity, which behavior indicates diffusion-controlled quenching ($\alpha \sim 1$).[5] Figure 1 is a Stern–Volmer plot of the quenching of acetophenone formation from γ-methylvalerophenone by 2,4-hexadien-1-ol in *t*-butyl alcohol solutions.[6] The dotted line is the extrapolation of the linear Stern–Volmer slope obtained at dienol concentrations below 0.05 *M* ($k_q\tau_0 = 7.6\ M^{-1}$). It is obvious that the experimental points fall increasingly above the extrapolated line at higher dienol concentrations, in excellent agreement with the statistical treatment outlined above. The curved solid line is that predicted by eq 3 for $\alpha = 1$ and values of u calculated on the assumption of random distribution of molecules in solution.[7] It is offered merely as an approximate example of what kind of deviation from linearity might be expected.

Figure 2 depicts the efficiency with which *cis*-1,3-pentadiene quenches acetophenone formation from γ-phenylbutyrophenone in pentane solution. In contrast to the behavior noted in the fairly viscous alcohol solvent, here there is little, if any, deviation from linearity in the Stern–Volmer slope, which straightness persists out to 10 *M* diene. This behavior is very good evidence for the suggestion[8] that in low viscosity alkane solvents triplet energy transfer is only partially diffusion controlled (here, $\alpha \sim 0.3$), since eq 3 collapses to eq 1 quite rapidly as α becomes less than unity.

It should be noted that the transient terms in the full solution of Fisk's diffusion equations would predict the same behavior attributed here to static quenching.[2,9] However, if transient effects were very important, the curvature in Figure 1 should have begun at even lower dienol concentrations.

Ware has reported that the efficiency with which carbon tetrabromide quenches anthracene fluorescence in isobutyl alcohol solutions is greater at high quencher concentrations than would be predicted from low concentration results.[9] It is possible that nearest neighbor static quenching such as suggested here may be responsible.

Knowledge of quenching rates is highly desirable because quenching studies can then yield fairly accurate estimates of the lifetimes of excited states. Several cases have been reported of ketones which have such short triplet lifetimes that quite high quencher concentrations must of necessity be employed to pro-

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(5) P. J. Wagner and I. Kochevar, manuscript in preparation.

(6) Dilution of *t*-butyl alcohol with the hexadienol produces only a slight change in viscosity, so that k_q should remain constant.

(7) H. P. Waits and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1911 (1964).

(8) P. J. Wagner, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967, R118.

(9) W. R. Ware and J. S. Novros, *J. Phys. Chem.*, **70**, 3246 (1966).

duce measurable quenching.[10] If accurate values of rate constants are to be obtained in such systems, Stern–Volmer quenching studies will have to be interpreted very carefully.

[10] (a) E. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967); (b) H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967); (c) D. J. Patel and D. I. Schuster, *ibid.*, **89**, 184 (1967); (d) P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5672 (1966).

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Optically Active Aromatic Chromophores. VII.[1] Evidence for the Optically Active ^1L_a Transition

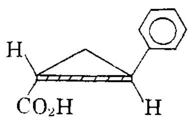
Sir:

Monosubstituted benzene rings exhibit three major transitions in the accessible isotropic absorption region: a weak band termed ^1L_b in the Platt notation[2] in the 255–275-nm region corresponding to a symmetry-forbidden π–π^* transition, and two stronger bands near 210 and 185 nm. The 210-nm band, classified ^1L_a, is also forbidden but probably involves a contribution from the first allowed π–π^* transition which overlaps it at shorter wavelength.[3] Upon appropriate ring substitution both of these latter bands may shift to longer wavelength.

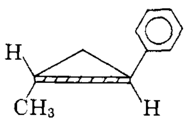
Although the question of whether the ^1L_b transition of a monosubstituted benzene ring is optically active has been answered,[4] conflicting reports exist in the recent literature concerning the origin of a Cotton effect found in the 215–225-nm region of several benzene derivatives. For example, a band in this region which we have observed[5] in the CD spectra of several α-amino and α-hydroxy aromatic acids has been stated[6] to be due to the carboxyl chromophore and not to a transition involving the phenyl ring. In contrast to this, Rosenberg[7] concluded on the basis of ORD comparisons of phenylalaninol and tyrosinol with the corresponding amino acids that the ^1L_a transition of the phenyl ring is indeed optically active.

In this communication we present evidence for the direct observation of the optically active ^1L_a transition.

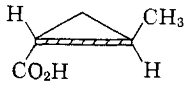
The compounds chosen for this ultraviolet and CD investigation were a series of structurally related cyclopropane derivatives of established absolute configuration:[8] (−)-(1*R*,2*R*)-*trans*-2-phenylcyclopropanecarboxylic acid, (−)-**1**; (−)-(1*R*,2*R*)-*trans*-1-methyl-2-phenylcyclopropane, (−)-**2**, and (−)-(1*R*,2*R*)-*trans*-2-methylcyclopropanecarboxylic acid, (−)-**3**. This series possesses the advantage that the substituents vary in such a way that the electronic effect of the three-membered ring should be a constant factor.



(−)-**1**



(−)-**2**



(−)-**3**

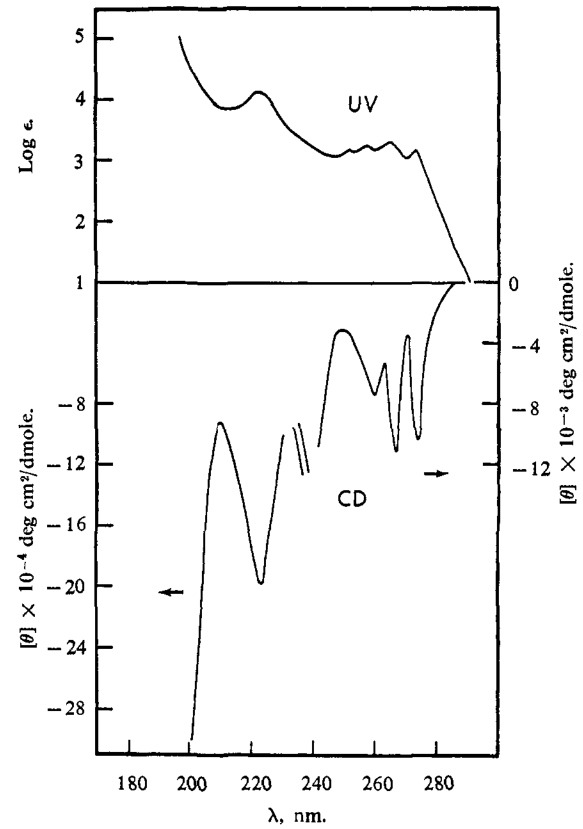


Figure 1. Ultraviolet and CD spectra of (−)-(1*R*,2*R*)-*trans*-2-phenylcyclopropanecarboxylic acid, (−)-**1**, in methanol solution. See ref 9 for explanation of the ordinate scales.

The ultraviolet and CD spectra of (−)-**1** in methanol solution are shown in Figure 1.[9,10] The isotropic absorption spectrum (upper curve) exhibits the typical vibrational structure of the ^1L_b band in the 250–275-nm region as well as a peak at 222 nm. The CD spectrum (lower curve) of (−)-**1** possesses negative Cotton effects corresponding to these peaks. The presence of the optically active carboxyl group makes the assignment of the 222-nm Cotton effect to the ^1L_a transition of the phenyl ring equivocal since the absorption band of the carboxyl chromophore occurs in a spectral region (206 nm for cyclopropanecarboxylic acid) close to that of the ^1L_a transition. It is well established that two overlapping Cotton effects give a resultant

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[1] Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1967, Abstract S86; part VI: L. Verbit, E. Pfeil, and W. Becker, *Tetrahedron Letters*, 2169 (1967).

[2] J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

[3] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p 129.

[4] A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Am. Chem. Soc.*, **87**, 1813 (1965); L. Verbit, *ibid.*, **87**, 1617 (1965); **88**, 5340 (1966).

[5] L. Verbit and P. J. Heffron, *Tetrahedron*, in press.

[6] M. Legrand and R. Viennet, *Bull. Soc. Chim. France*, 2798 (1966).

[7] A. Rosenberg, *J. Biol. Chem.*, **241**, 5119 (1966).

[8] T. Sugita and Y. Inouye, *Bull. Chem. Soc. Japan*, **39**, 1075 (1966); Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964).

[9] Because of the relative weakness of the Cotton effect in the 260-nm region, the CD curve (*which is continuous*) was divided into two parts: the right-hand ordinate refers to the longer wavelength Cotton effect and the left-hand ordinate refers to the bands below *ca.* 240 nm. The log ε scale refers to the isotropic absorption spectrum.

[10] The CD spectra were measured using a JASCO Model ORD/UV/CD-5 spectropolarimeter with CD recorder operating under the conditions described in L. Verbit, *J. Am. Chem. Soc.*, **89**, 167 (1967).