

they indicate that interaction between two groups can be greatly enhanced by appropriately modifying the chromophores. The *p*-methoxybenzoate chromophore in **10** would be expected to interact much more efficiently with the naphthalenoid chromophore because its band at 256 nm ( $\epsilon \sim 18,000$ ) is located closer to the corresponding naphthalenoid band, and according to the molecular exciton model the chromophoric interaction would be favored by similar excitation energies. As shown in Figure 3, this expectation is verified, and the apparent amplitudes of the ORD Cotton effects are enhanced about three times ( $a = -3326$ ); the CD curve also consists of two strongly interacting Cotton effects at 272 ( $\Delta\epsilon - 61.1$ ) and 250 nm ( $\Delta\epsilon + 39.9$ ).

Since the Cotton effects associated with dipole-dipole interaction between two aromatic chromophores are extremely strong<sup>1,7</sup> and only the directions of transition moments need be considered, the present method should be widely applicable to the determination of the chiralities between benzoate groups and/or other aromatic chromophores.<sup>20</sup>

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## Quenching of Acylnitrile Singlets by Piperylene

Sir:

Singlet quenching of aromatic compounds by conjugated dienes is well documented and apparently proceeds by an electronic-vibrational energy-transfer mechanism.<sup>1</sup> A purely electronic mechanism is ruled out on energetic grounds. The corresponding quenching of the singlet states of carbonyl compounds has not been observed,<sup>2-4</sup> although the rates of intersystem crossing (the major mode of deactivation of the singlet state) are not prohibitive for diffusional quenching of alkyl ketone<sup>5</sup> and diketone<sup>6</sup> singlet states. In the present communication we note and stress that *singlet quenching by dienes is not restricted to aromatic systems*.

(1) (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966); (b) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968); (c) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968); (d) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); (e) R. S. Cooke and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 2958 (1968).

(2) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(3) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

(4) R. E. Rebbert and P. Ausloss, *ibid.*, **87**, 5569 (1965).

(5) For calculations concerning the rate of intersystem crossing of acetone from its fluorescence spectrum, see R. F. Borkmann and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966). However, recent results indicate that there may be complications with regard to the normally observed fluorescence emission of alkyl ketones: M. O. Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, **90**, 6245 (1968).

(6) N. J. Turro and R. Engel, *ibid.*, **90**, 2989 (1968).

In the course of an investigation of the photoreactions of acylnitriles, we have found that in the several solvents employed the "apparent" intersystem crossing yield,<sup>7</sup> ( $\varphi_{ic}$ )<sub>a</sub>, for pyruvonnitrile (CH<sub>3</sub>COCN) varies with the concentration of *cis*-1,3-pentadiene, better known as *cis*-piperylene (Figure 1 and Table I).<sup>8</sup> Analytical monitoring involves only the *cis* → *trans* isomerization of piperylene. The results clearly show that the olefin is capturing the precursor to the state responsible for photo-

**Table I.** Determinations of the "Apparent" Intersystem Crossing Yields ( $\varphi_{ic}$ )<sub>a</sub>

Solvent	Piperylene concn, <i>M</i>	( $\varphi_{ic}$ ) <sub>a</sub>	( $\varphi_{ic}$ ) <sub>a</sub> <sup>-1</sup>
Acetic acid	0.0186	0.376	2.66
	0.0419	0.33	3.03
	0.0910	0.40	2.50
	0.0964	0.42	2.38
	0.258	0.255	3.92
	0.473	0.195	5.14
	0.950	0.12	8.3
	1.55	0.09	11.1
Acetonitrile	0.138	0.162	6.16
	0.190	0.0765	13.1
	0.278	0.0565	17.7
	0.478	0.039	25.6
Carbon tetrachloride	0.0967	0.157	6.36
	0.345	0.126	7.94
	0.619	0.0855	11.7
Isopentane	0.209	0.086-0.103	11.6-9.7
	0.198	0.0382	26.2
	0.408	0.0298	33.6

sensitization leading to acceptor isomerization (*i.e.*, the lowest triplet state). Furthermore, this precursor does not itself cause chemical change of piperylene.<sup>9</sup> Formation of oxetanes and/or piperylene cyclodimers is of minor, if any, significance since such products would have been observed.<sup>9</sup> All of the above observations indicate that the precursor being captured is the singlet state of pyruvonnitrile and are in agreement with the observations on singlet quenching of aromatic compounds.<sup>1d</sup> A simple, purely electronic singlet-singlet energy transfer mechanism for the system under consideration is ruled out on the same basis as it is by Hammond and Stephenson<sup>1d</sup> for the aromatic systems. The absorption maximum for the first singlet of pyruvonnitrile is at 310 nm in cyclohexane, the 0-0 band being 40-50 nm to the red of this. For *cis*-piperylene  $\lambda_{max}$  (cyclohexane) is near 230 nm, the 0-0 band lying about 20 nm to the red, at about 250 nm. Pyruvonnitrile emits relatively strong phosphorescence (at 77°K in an EPA glass), indicating a triplet energy of  $72 \pm 2$  kcal/mol. No fluorescence was detectable either at 77°K or at ambient temperatures. In many respects acylnitriles are spectroscopically very much like aliphatic ketones and  $\alpha$ -keto acids and esters—a fact of some consequence

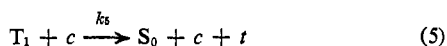
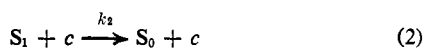
(7) As measured by the method of A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(8) All photoreactions were performed at ambient temperatures (28°) using a Hanovia medium-pressure mercury lamp surrounded by a 3100-Å filter (K<sub>2</sub>CrO<sub>4</sub>, 0.2 g/l.; K<sub>2</sub>CO<sub>3</sub>, 10 g/l.). The samples were degassed, sealed in Pyrex tubes, and held in a Southern New England Ultraviolet MGR-500 merry-go-round apparatus. Pyruvonnitrile concentration was invariably 0.10 *M*.

(9) The photostationary state ( $pss = [c]/[t]$ ) is independent of olefin concentration; *no measurable loss of piperylene or pyruvonnitrile has been found*.

with respect to the behavior of the latter compounds toward as yet unreported singlet quenching.

A mechanism consistent with the experimental observations is given in eq 1–5, where  $S_0$ ,  $S_1$ , and  $T_1$  refer to



the ground, first singlet, and first triplet states of pyruvitrile, and  $c$  and  $t$  refer to *cis*- and *trans*-piperylene. The kinetic expression relating  $(\varphi_{ic})_a$ , the "apparent" intersystem crossing yield, with the concentration of piperylene is given in eq 6, which follows from eq 7,

$$\frac{1}{(\varphi_{ic})_a} = \frac{1}{(\varphi_{ic})_0} + \frac{1}{\varphi_{ic0}} \left[ \frac{k_4}{k_3[c]} \right] + \frac{k_2[c]}{k_3} + \frac{k_2 k_4}{k_3 k_5} \quad (6)$$

$$(\varphi_{ic})_a = \left[ \frac{k_3}{k_3 + k_1 + k_2[Q]} \right] \left[ \frac{k_3[Q]}{k_3[Q] + k_4} \right] \quad (7)$$

where  $Q$  is quencher, for both singlets and triplets, specifically *cis*-piperylene ( $c$ ). The first bracketed term is the fraction of singlets crossing to triplets, the second is the fraction of triplets "counted" (by measuring conversion to *trans*);<sup>7</sup>  $(\varphi_{ic})_0$  is the "true" intersystem crossing yield,  $k_3/(k_3 + k_1)$ . Simple algebraic manipulation yields eq 6, which at high ( $>0.1 M$ ) piperylene concentrations can be approximated by eq 8. A plot

$$\frac{1}{(\varphi_{ic})_a} = \frac{1}{(\varphi_{ic})_0} + \frac{k_2 k_4}{k_3 k_5} + \frac{k_2[c]}{k_3} \quad (8)$$

of  $1/(\varphi_{ic})_a$  vs.  $[c]$  should give a straight line with a slope equal to  $k_2/k_3$  (Figure 1). (At relatively low diene concentrations the second term in the right side of eq 6 will begin to dominate, so that the initial slopes in Figure 1 (not indicated except for acetic acid solvent) should in fact be negative.)

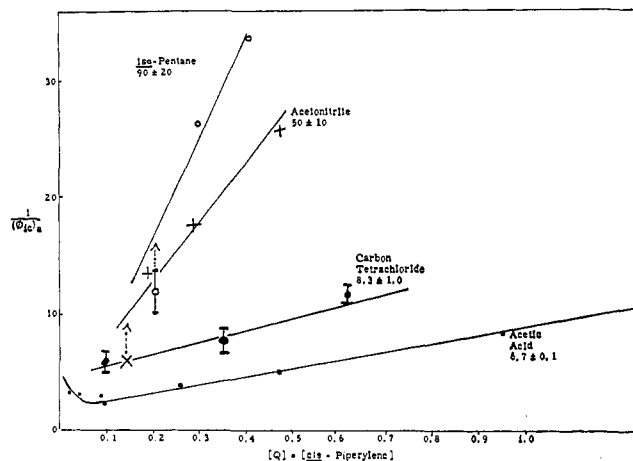
Focusing on eq 8 and Figure 1, we offer the following comments. If the rate of quenching of the singlet state is essentially diffusion controlled, then the slope should be inversely proportional to the viscosity of the solvent. Within a factor of approximately two, this expectation is realized (Table II). Equating  $k_2$  with  $k_{diff}$  allows  $k_3$ ,

**Table II.** Relation of Reciprocal Solvent Viscosity at 30° to Values of  $k_2/k_3$  (the Slopes in Figure 1)

Solvent	Slope ( $k_2/k_3$ )	Rel slope	Rel $1/\eta$
Acetic acid	$6.7 \pm 0.1$	1.00	1.00
Carbon tetrachloride	$8.3 \pm 1.0$	1.2	1.24
Acetonitrile	$50 \pm 10$	7.4	3.16
Isopentane	$90 \pm 20$	13	5.20

the rate of intersystem crossing, to be calculated.<sup>10</sup>

(10) The extrapolated intercept,  $1/(\varphi_{ic})_0 + (k_2 k_4/k_3 k_5)$ , can be approximated to  $1/(\varphi_{ic})_0 + k_4/k_3$  since  $k_2 \cong k_3 \cong k_{diff}$  (a general assumption with respect to  $k_3$ ). This last fraction should be relatively small since triplet deactivation should be slower than intersystem crossing. Knowledge of  $k_3$  does not, however, permit knowledge of  $k_4$  and thus  $(\varphi_{ic})_0$ , although other chemical experiments are in progress to determine  $(\varphi_{ic})_0$  values in various solvents.



**Figure 1.** Plot of reciprocal "apparent" intersystem crossing yield of pyruvitrile (0.10  $M$ ) vs. *cis*-piperylene concentration. Solvents and slopes are indicated on the figure. An additional point for acetic acid solvent where  $[c] = 1.55$ ,  $(\varphi_{ic})_a = 0.09$  does not appear on the figure, but fits well on the extrapolated line.

The rate of intersystem crossing ( $k_3$ ) calculated in this manner is  $7 \pm 2 \times 10^8 \text{ sec}^{-1}$ , an order of magnitude faster than the reported value for acetone,<sup>5</sup> which is, however, reasonable since pyruvitrile shows no detectable fluorescence. At this point we should like to add an additional consideration: that the intersystem-crossing rate constant ( $k_3$ ) and the "true"  $\varphi_{ic}$ , i.e.,  $(\varphi_{ic})_0$ , may well be variable with solvent, since the state of aggregation of the acyl nitrile (monomer, dimer, even pentamer) varies with solvent (unpublished results from these laboratories). This in no way dilutes the essential arguments for singlet quenching.<sup>11</sup> The error limits for calculated  $k_3$  represent limits that are essentially due to solvent variation, not experimental scatter for individual solvents. Additionally, reasonable scrutiny of the "high quencher concentration" extrapolated intercepts in Figure 1 indicates that these intercepts are not common, due either to solvent-dependent variations in the  $k_4/k_3$  ratio or to variations in  $(\varphi_{ic})_0$ , or, most likely, both (see footnote 10).

In summary, then, our evidence indicates that *piperylene quenches pyruvitrile* (and presumably other aliphatic acyl nitrile, and even perhaps other ketone) *singlets*, without apparent chemical change of either reagent, by a mechanism that cannot involve electronic energy transfer. Presumably the mechanism involves the formation of some species analogous to Hammond's<sup>1</sup> "exciplex" quenching of polynuclear aromatic systems.

**Acknowledgments.** We are indebted to D. R. Van-Alstine for technical assistance and to the National Institutes of Health (Grant GM 13592) and the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Partial support by the Alfred P. Sloan Foundation, the National

(11) A referee has pointed out that a mechanism involving self-quenching by piperylene would also, at high quencher concentration, give rise to an equation analogous to eq 8 in which  $(\varphi_{ic})_a^{-1}$  would be a linear function of  $[c]$  with slope equal to  $k(\text{self-quenching})$  divided by  $k(\text{cis triplet} \rightarrow \text{trans ground state})$ . The latter constant for electronic relaxation of dienes is well established, of the order of  $10^6 \text{ sec}^{-1}$  [cf. P. A. Leermakers, *et al.*, *Mol. Photochem.*, **1**, 57 (1969)], so that  $k(\text{self-quenching})$  would be of the order of  $10^8 \text{ M}^{-1} \text{ sec}^{-1}$ . This argument cannot be rigorously ruled out, but it is inconsistent with the viscosity data (which precludes appreciable activation energy) and with the absence of piperylene dimer formation.

Science Foundation, and the Connecticut Research Commission is also gratefully acknowledged.

(12) Alfred P. Sloan Fellow.

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## Hydrocarbon Degenerate Thermal Rearrangements.

### III. Characterization of the Methylallene Dimers.








#### Stereochemistry of the 1,2-Dimethylenecyclobutane Ring Opening

Sir:

Tetramethyleneethane (TME), or the 2,2'-bisallyl diradical, was indicated as being responsible for the thermally induced hydrogen-deuterium scrambling of 1,2-bis(dideuteriomethylene)cyclobutane.<sup>1a</sup> Degradative

subjected to vapor phase pyrolysis in a well-conditioned static reactor at partial pressures less than 10 Torr. Extended pyrolyses at 260° revealed that the hydrogen-shifted materials, trienes **8** and **9**, especially the former, constituted major portions of the product. However, at lower temperatures and shorter reaction times it was possible to observe interconversion of the nongeminal dimethyl-1,2-dimethylenecyclobutanes. The data of Table II indicate the product distribution from the pyrolysis of **1** and **2** at 237.8° and 254.7° for the lengths of time indicated. It was possible to isolate and pyrolyze **3** which gave mostly **8**, and **5** and **6** which gave mostly **9** (90% in each case). The approximate relative rates of disappearance of **1**, **2**, **3**, **5**, and **6** at 254.7° are 1.5:1.2:11:5.6:3.9, respectively. These data indicate that a substantial portion of the hydrogen-shifted product, **8**, formed in pyrolysis of **2** was derived from **3** but that **9** probably did not have **5** or **6** as precursors in these short-term pyrolyses.

Table I. Percentage of Dimer Products<sup>a</sup> from Methylallene at 170°

Reaction time, <sup>d</sup> hr							
	1	2	3	4	5	6 <sup>b</sup>	7 <sup>b</sup>
1	25	4	37	18	13	3	~0.5
13 <sup>c</sup>	10	2	32	14	29	11	2
20	4	0.6	25	7	46	15	2.5

<sup>a</sup> All new compounds had satisfactory exact masses. <sup>b</sup> **6** and **7** are identical with the two 1,2-diethylidene-cyclobutanes (1:1 mixture) obtained from base-catalyzed isomerization of *cis*-1,2-divinylcyclobutane: P. Heimbach and R. Schimpf, *Angew. Chem. Intern. Ed. Engl.*, **8**, 206 (1969). We thank Dr. Heimbach for a generous sample of this mixture. <sup>c</sup> Recovered methylallene, 32% (minimum); dimer, 29%; less volatile material, 8%; nonvolatile material, 31%. <sup>d</sup> All dimerizations were conducted with 450  $\mu$ l of the allene in 5-ml Pyrex tubes.

Table II. Product Distribution from Vapor Phase Pyrolyses of **1** and **2**

Compd	Temp, °C	Time, sec	1 ( <i>t</i> ) <sup>a</sup>	2 ( <i>c</i> )	3 ( <i>s</i> )	4 ( <i>a</i> )	5 ( <i>ss</i> )	6 ( <i>sa</i> )	7 ( <i>aa</i> )	8 <sup>2a</sup>	9 <sup>2a</sup>
<b>1</b>	237.8	3600	86.0	0	0.05	13.2	0	0	0.7	<0.05	0.09
<b>1</b>	254.7	3600	60.0	0	0.4	37.4	0	Trace	1.7	0.8	Trace
<b>2</b>	237.8	3600	1.6	90	3.6	1.0	0	1.0	<0.1	2.8	<0.1
<b>2</b>	254.7	3600	Trace	70	7.6	1.5	0	2.0	0	15.2	3.0

<sup>a</sup> Letters in parentheses are the first letters of the stereochemical designations of the dimethyldimethylenecyclobutanes.

experiments indicated that this species, if involved, had effectively or, in fact, mutually perpendicular allyl radical residues.<sup>1a</sup> It was our intention to provide further proof that a thermally induced skeletal rearrangement occurred with rotation about the central bond in the TME species and to provide information on the mode of opening of the cyclobutane ring.

*trans*- and *cis*-3,4-Dimethyl-1,2-dimethylenecyclobutanes, **1** and **2**, respectively, were isolated from dimerization of methylallene (Table I).<sup>2</sup> These materials were

The fact that **1** and **2** gave the other nongeminal dimethyl-1,2-dimethylenecyclobutanes renders unlikely the hypothesis that reversible hydrogen shifts were responsible for the 1,2-dimethylenecyclobutane thermally induced self-interconversion,<sup>1</sup> since methyl groups are not known to transfer as efficiently as hydrogen.<sup>3</sup> The data of Table II also confirm the fact that rotation about the central bond in the TME species occurs to give the single inversion<sup>4</sup> Cope type products, **3** and **4**, in addition

(1) (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) see also W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967).

(2) (a) Only seven dimers were found in the reaction; all were *cisoid* conjugated dienes (uv  $\lambda$  245–252  $m\mu$ ); nmr could easily distinguish between the sets (1, 2), (3, 4), and (5, 6, 7), and indeed between all of them; **6** is unique in the nmr; **2** was synthesized from the 2-butyne-maleic anhydride photoadduct<sup>2b</sup> in a manner that would ensure a *cis*-dimethyl relationship; the inside vinyl hydrogens of **4**, **6**, and **7** were at  $\delta$  5.35–5.63 ppm while the outside hydrogens of **3**, **5**, and **6** were at  $\delta$  4.98–5.18 ppm; ultimate proof of the stereochemistry about the double bonds rests on the fact that **3** underwent a rapid 1,5-hydrogen shift<sup>2c</sup> at 260° to give ultimately 3-methylene-4-methyl-*trans*-1,4-hexadiene (**8**),<sup>2d</sup> while **4** did so much slower; **5** and **6** gave 2-ethyl-3-methylene-1,4-

pentadiene (**9**), also *via* the hydrogen shift at 260°, while **7** was relatively inert.<sup>2f,g</sup> (b) R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freud, *Chem. Ber.*, **97**, 2942 (1964). (c) J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, **84**, 2775 (1962). (d) The *trans* stereochemistry was assigned in analogy to Frey's results with the thermal polymerization of 1,4-dimethylcyclobutene.<sup>2e</sup> (e) H. M. Frey, D. C. Marshall, and R. F. Skinner, *Trans. Faraday Soc.*, **61**, 861 (1965). (f) See E. F. Kiefer and J. Y. Fukunaga, *Tetrahedron Lett.*, 933 (1969), and E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969), for analogous reactions. (g) The significance of these and similar results will be discussed in a forthcoming publication.

(3) See, for example, J. W. De Haan and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1594 (1965).

(4) J. A. Berson and M. Jones, Jr., *J. Amer. Chem. Soc.*, **86**, 5019 (1964), and references contained therein.