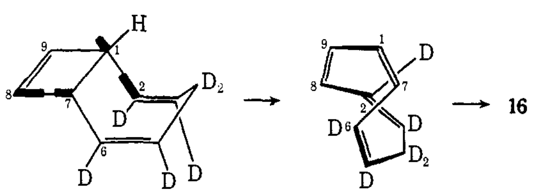
the bicyclo[5.2.0]nona-2,5,8-triene form of the labeled substrate (**19** → **20** → **16**).



19 **20**

Further labeling studies to distinguish between these two distinctly different types of mechanism are underway.[10]

Acknowledgment. This work was supported by the Cities Service Oil Co., the Du Pont Co., and the National Science Foundation.

[10] 3,6-Dideuteriobicyclo[6.1.0]nona-2,4,6-triene rearranges to 3a,6-dideuteriodihydroindene. This qualitative finding by R. K. Pinschmidt, Jr., is now being placed on a firm quantitative basis.

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On the Quenching of Photochemical Reactions and of Fluorescence of Alkanones by 1,3-Cyclohexadiene and *cis*-1,3-Pentadiene

Sir:

One of the most powerful techniques in investigating the mechanism of photochemical reactions of carbonyl compounds is the study on the energy transfer from excited states of carbonyl compounds to conjugated dienes which was developed in Hammond's laboratory.[1] The singlet energy level of dienes is above that of carbonyl compounds. However, the energy spacing between the singlet and the triplet states of carbonyl compounds is relatively small, while that between dienes is large. The triplet energy level of dienes is thus lower than that of carbonyl compounds. Therefore, dienes may readily accept energy from the triplet state of carbonyl compounds thus quenching it, while they have little effect on the behavior of the singlet state of carbonyl compounds. However, Hammond and coworkers found that dienes quenched the fluorescence of aromatic hydrocarbons.[2] Recently, Wettack, Turro, and their coworkers demonstrated that dienes also quenched the fluorescence of aliphatic and alicyclic ketones, but the quenching efficiency for fluorescence was much lower than that for the $^3n,\pi^*$ of ketones.[3] Many conjugated dienes have been used in the investigation on the mechanism of photochemical reactions and 1,3-pentadienes and 1,3-cyclohexadiene are among the most commonly used. This communication demonstrates that 1,3-cyclohexadiene is more efficient than *cis*-1,3-pentadiene in quenching the fluorescence and photochemical processes of alkanones.

Pinacolone (0.80 *M* in *n*-hexane) was used for the study on the type I process (reaction 1), and the reaction was followed by the consumption of pinacolone by gas chromatography using *n*-undecane as the internal standard.[4] 2-Hexanone (0.83 *M* in *n*-hexane) was used for the study on the type II process (reaction 2), and the reaction was followed by the formation of acetone.[5,6] The quenching studies were carried out with various concentrations of either diene at 313 nm using an apparatus previously described.[6] The data for quenching of pinacolone were taken from our earlier work and verified at a few selected diene concentrations.[4] The Stern–Volmer plots are presented in Figures 1 and 2. The plots were analyzed on the basis of two reactive states, the $^1n,\pi^*$ and the $^3n,\pi^*$, and the results are presented in Table I.[3,7] The quenching of fluorescence of alkanones was carried out in a conventional spectrofluorimeter using exciting light at 313 nm and *n*-hexane as the solvent. The results are also summarized in Table I.

$$CH_3COC(CH_3)_3 \xrightarrow{h\nu} CH_3CO\cdot + (CH_3)_3C\cdot \qquad (1)$$

$$CH_3CO(CH_2)_3CH_3 \xrightarrow{h\nu} CH_3C(OH){=}CH_2 + CH_3CH{=}CH_2 \qquad (2)$$

Our results clearly indicated that 1,3-cyclohexadiene is a more efficient quencher than *cis*-1,3-pentadiene for both the fluorescence and the photochemical reactions of alkanones. Since the photochemical reactions studied occur from both the $^1n,\pi^*$ and the $^3n,\pi^*$,[4,5] while the fluorescence occurs only from the $^1n,\pi^*$, *the higher quenching efficiency of cyclohexadiene may be attributed to its enhanced ability in quenching the $^1n,\pi^*$ of alkanones.* However, a minor discrepancy remains in the experimental results that *cis*-1,3-pentadiene appears to be a more efficient quencher than 1,3-cyclohexadiene at low concentrations for the type II process of 2-hexanone. Since the E_T (triplet energy) for both dienes are appreciably lower than the E_T for 2-hexanone, both quenching rates for the $^3n,\pi^*$ should approach that of a diffusion-controlled process. However, 1,3-cyclohexadiene is known to undergo sensitized dimerization at a very high quantum efficiency whereas 1,3-pentadienes do not.[2b,8] The concentration of 1,3-cyclohexadiene will decrease as the quenching proceeds, and the effective quencher concentration during the irradiation will be less than the starting quencher concentration. We suggest that the apparent lower efficiency of 1,3-cyclohexadiene in this case may be due to its consumption during the irradiation.

Hammond and his coworkers showed that 1,3-cyclohexadiene quenched the fluorescence of aromatic hydrocarbons more efficiently than do most acyclic dienes, and they also suggested that an exciplex between the excited state of the aromatic hydrocarbon and the diene was involved in the deactivation of the excited state.[2] Evans suggested that the initial complex formed underwent electron transfer from the diene as the donor to give an electron-transfer complex which subsequently deactivated to the ground state.[9] Recently Barltrop and Carless reported that dienes reacted with the $^1n,\pi^*$ of alkanones to form oxetanes.[10] The mechanism of

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[1] For a review on energy transfer to 1,3-dienes, see A. A. Lamola in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Interscience, New York, N. Y., 1969, p 96.

[2] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966); L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

[3] F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1794 (1970).

[4] N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).

[5] P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

[6] D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[7] J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

[8] D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5022 (1964).

[9] T. R. Evans, *ibid.*, **93**, 2081 (1971).

Table I

	$k_q{}^s\tau_s$, M^{-1}							
	cis-1,3-Pentadiene		1,3-Cyclohexadiene					
	Fluorescence	Chemical	Fluorescence	Chemical	τ_s, nsec	$\phi_s{}^\circ$	$\phi_t{}^\circ$	$k_q{}^t\tau_t$, M^{-1}
Acetone	0.19[a]		1.45		1.8–2.0[a]			
2-Pentanone	0.08[a]		0.88		1.8–2.0[a]			
2-Hexanone	0.064	0.06	0.44	0.40	0.73[b]	0.13	0.13	50 ± 15[c]
Pinacolone	0.08,[a] 0.075	0.10	0.49	0.47	3.2–4.2[d]	0.22	0.31	1.5

[a] Reference 3. [b] N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969). [c] This represents the range of values obtained in our laboratory by several different coworkers. [d] N. C. Yang, M. H. Hui, E. D. Feit, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 6974 (1970).

photocycloaddition of carbonyl compounds to olefins to form oxetanes has been a subject of extensive investigations. It has been reported that (a) an electron-transfer complex between the excited carbonyl compound and the ground state of the olefin may be the precursor of a biradical intermediate,[11] and (b) the biradical intermediate may cyclize to give the oxetane or dissociate to give its components in their ground state.[12] The following scheme (eq 3–8), which encompasses the existing concepts of photochemistry, is proposed for the quenching of ^{1}n,π^* of carbonyl compounds by dienes.

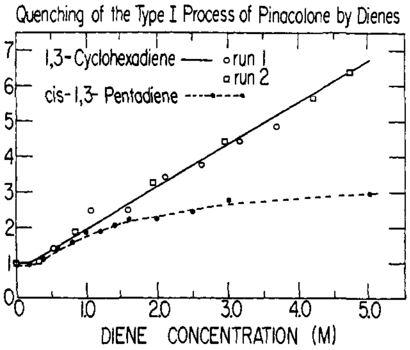


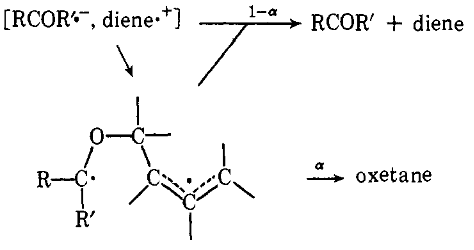
Figure 1.

$$\mathrm{RCOR'} \xrightarrow{h\nu} {}^1\mathrm{n},\pi^* \qquad (3)$$

$${}^1\mathrm{n},\pi^* \xrightarrow{{}^1\tau_s} {}^3\mathrm{n},\pi^*,\ \mathrm{RCOR'} + h\nu',\mathrm{etc.} \qquad (4)$$

$${}^1\mathrm{n},\pi^* + \mathrm{diene} \underset{k_{-q'}}{\overset{k_{\mathrm{dif}}}{\rightleftharpoons}} [\mathrm{exciplex}] \qquad (5)$$

$$[\mathrm{exciplex}] \xrightarrow{k_{q'}} [\mathrm{RCOR'}^{\cdot-},\ \mathrm{diene}^{\cdot+}] \qquad (6)$$



$$[\mathrm{RCOR'}^{\cdot-},\ \mathrm{diene}^{\cdot+}] \xrightarrow{1-\alpha} \mathrm{RCOR'} + \mathrm{diene} \qquad (7)$$

$$\xrightarrow{\alpha} \mathrm{oxetane} \qquad (8)$$

Experimentally we found that there was a direct correlation between the quenching efficiencies of various acyclic olefins and dienes on the fluorescence of acetone with their ionization potentials (Table II).[13] The result may be expressed as ln ($k_q/k_{\mathrm{dif}} - k_q$) = (21.39 ± 1.69) − (3.007 ± 0.187)IP assuming the k_{dif} to be 1 × 10^{10} l. mol^{-1} sec^{-1} which provides an excellent fit for the first two steps of quenching in the kinetic scheme as proposed by Evans (eq 5 and 6).[9,14] Subsequently, we isolated and characterized an oxetane formed from acetone and 1,3-cyclohexadiene, and then determined the quantum yield of oxetane formation (ϕ_{ox}) at various diene concentrations. We may assume the rate for the electron-transfer complex formation to be k_q ($k_q = k_{q'}k_{\mathrm{dif}}/k_{q'} + k_{-q'}$), the portion of the complex which will form the oxethane to be α, and the remaining portion which will decay back to acetone and the diene to be 1 − α. Therefore, the quantum yield of oxetane

Table II

Olefin	$k_q\tau_s$, M^{-1}	IP, eV
2,5-Dimethyl-2,4-hexadiene	2.07	7.91[a]
2,3-Dimethyl-2-butene	0.23	8.53[b]
cis-1,3-Pentadiene	0.19	8.68[b]
trans-1,3-Pentadiene	0.16	8.68[b]
2-Methyl-2-butene	0.082	8.85[b]
cis-3-Hexene	0.063	9.14[b,c]
1-Hexene	0.012	9.59[b]
1,3-Cyclohexadiene	1.45	8.25[d]

[a] J. L. Franklin and A. Morgenis, *J. Phys. Chem.*, **71**, 2820 (1967). [b] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Bedvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold, Ltd., London, 1966, pp 155–157. [c] The value is for *trans*-3-hexene, but values for all geometric olefins are all very similar. [d] D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970).

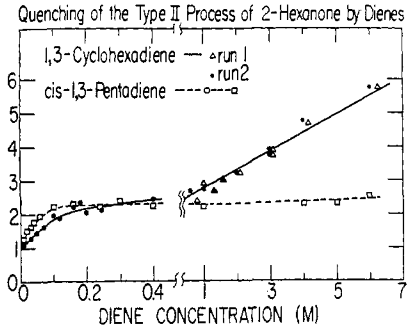


Figure 2.

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(10) J. A. Barltrop and H. A. J. Carless, *Chem. Commun.*, 1637 (1970).

(11) R. A. Caldwell, *J. Amer. Chem. Soc.*, **92**, 1439 (1970).

(12) N. C. Yang, J. I. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968); J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969); N. C. Yang and W. Eisenhardt, *ibid.*, **93**, 1277 (1971).

(13) Similar observations have been made by N. J. Turro and coworkers: N. J. Turro, unpublished results.

(14) 1,3-Cyclohexadiene being a cyclic diene has a substantially different molecular geometry from acyclic dienes. Since molecular complex formation will depend also on the geometry of its components, it is not surprising that 1,3-cyclohexadiene deviates somewhat from this correlation. However, its value still falls within the limit of standard deviation.

formation is

$$\phi_{ox} = \frac{\alpha k_q[\text{diene}]}{k_q[\text{diene}] + 1/\tau_s}$$

and

$$1/\phi_{ox} = 1/\alpha + 1/\alpha k_q[\text{diene}]\tau_s$$

By plotting $1/\phi_{ox}$ against 1/[diene], we will obtain a straight line with $1/\alpha$ as the intercept and $1/\alpha k_q\tau_s$ as the slope. We found experimentally the intercept to be 19.7 ± 1.9 and the slope to be 14.2 ± 1.2 *M*. Therefore, $k_q\tau_s$ is 1.39 ± 0.14 M^{-1} which is in good agreement with the value of $k_q\tau_s$ obtained from the quenching of fluorescence of acetone by 1,3-cyclohexadiene, 1.45 ± 0.15 M^{-1} (Table I). The results indicate that the fluorescence quenching and oxetane formation by dienes proceed *via* the same intermediate and offer experimental support to the kinetic scheme proposed above. However, the data do not exclude a number of alternative pathways, and the detailed discussion will be elaborated in a later publication.

An incidental finding in our investigation is that the Stern–Volmer plot from the quenching of the type I process of pinacolone by 1,3-cyclohexadiene has the appearance of a straight line in spite of the fact that the reaction may take place from both excited states. Dalton and Turro analyzed that the Stern–Volmer plot of a photochemical reaction involving a singlet and a triplet state would have the appearance of a straight line when $k_q{}^s\tau_s[1 + (\phi_0{}^t/\phi_0{}^s)]$ approached $k_q{}^t\tau_t$.[7] This is apparently the first such case found.

The higher efficiency of 1,3-cyclohexadiene than acyclic dienes as a quencher in photochemical reactions of unsaturated ketones has been reported in several instances,[15] but the nature of these quenching processes is not yet clearly understood.[16]

Acknowledgment. The authors wish to thank the National Science Foundation for the support of this work under Grants GP-16347 and GY-7232, the UniRoyal Company for a fellowship to one of us (M. H. H.), and Professor Nicholas J. Turro for the exchange of some unpublished information.

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[15] For recent examples of this phenomenon, see D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970); D. I. Schuster and N. K. Lau, *Mol. Photochem.*, **1**, 415 (1969); D. I. Schuster, *et al.*, *J. Amer. Chem. Soc.*, **90**, 5027 (1968); D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1302 (1968).

[16] T. S. Cantrell, *Chem. Commun.*, 1656 (1970).

[17] UniRoyal Fellow, 1970–1971.

[18] National Science Foundation Undergraduate Research Participant, 1970.

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A Simple Method for Determining the Chirality of Cyclic α-Glycols with $Pr(DPM)_3$ and $Eu(DPM)_3$

Sir:

We report an extremely simple method which enables one to determine the chirality of cyclic α-glycols. It involves no derivatization, only a minute amount of the glycol is required, and it is, moreover, applicable to α-glycols containing *tert*-hydroxyl groups.

The so-called nmr shift reagents, *e.g.*, $Pr(DPM)_3$ and $Eu(DPM)_3$, have been widely used[1] for analyzing nmr spectra of compounds containing hydroxyl, amine, and other functional groups. The present method utilizing these complexes is formally an extension of the "aromatic chirality method"[2] (or in a narrower sense the "dibenzoate chirality method"[3]), and merely involves measurement of CD spectra of 1:1 solute and complex mixtures in carbon tetrachloride or chloroform.

A typical CD Cotton effect curve is depicted in Figure 1. The chirality of the glycol moiety is defined as being negative (Figure 1) or positive, respectively, when the Newman projection represents an anticlockwise (left-handedness) or clockwise (right-handedness) rotation from one hydroxyl group to the other.[3] Mixtures of the glycol and complex result in CD curves having two Cotton effects of *opposite* signs at *ca.* 310 and *ca.* 290 nm. Although the amplitudes of these Cotton effects have been found to be dependent on several factors, invariably *the sign of the longer wavelength Cotton effect (first Cotton effect) is in agreement with the chirality of the cyclic α-glycol.* Superficially this observation is exactly what was encountered in the dibenzoate chirality method.[3]

Basic studies pertaining to various factors which influence the CD curves were carried out using 5-cholestene-3β,4β-diol as the substrate and $Pr(DPM)_3$[4] as the complex.

Some factors which influence the twin Cotton effects are the following. (a) The presence of water or alcohol reduces or annihilates the Cotton effects. (b) The $\Delta\epsilon$ is concentration dependent (Figure 2). (c) The $\Delta\epsilon$ is time dependent, *e.g.*, in carbon tetrachloride it almost doubles for a period up to 5–10 hr and then slowly decreases (measurements were made in a stoppered CD cuvette). It should be pointed out that in spite of variations in $\Delta\epsilon$ values, the signs do not change.

On the basis of these studies, the following procedure is recommended for actual measurements. An approximately 1:1 mixture of the glycol and complex is made in dry carbon tetrachloride (or ethanol-free chloroform)[5] so that the solutes are *ca.* 2×10^{-4} *M*. The CD is then measured after 30–60 min. It is preferable to mix the solutions in a drybox in order to obtain larger $\Delta\epsilon$ values; however, this is not mandatory, as the $\Delta\epsilon$ values are already quite strong.

As shown in Table I, measurements of a variety of known glycols under these conditions clearly show that signs of the first Cotton effects agree with the glycol chirality, and hence enable one to establish configurations or conformations of glycol-containing natural products in a straightforward manner. Entry 4 (Table I) shows the application of this method to a compound already possessing strong CD Cotton effects, *i.e.*, at 327 ($\Delta\epsilon$ +1.8) and 248 nm ($\Delta\epsilon$ −3.9) (in ethanol). Similarities in the values of entries 5 and 6 indicate that the distant 3-OH is playing a minor role, if any. It is to be noted that the 5-OH is tertiary,

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[1] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971), and references therein.

[2] N. Harada and K. Nakanishi, submitted for publication.

[3] N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 3989 (1969).

[4] The effect of $Eu(DPM)_3$ is similar to that of $Pr(DPM)_3$ (e.g., a solution of $Eu(DPM)_3$ and 5-cholestene-3β,4β-diol gives the same sign of the Cotton effect and λ_{max} as a solution of $Pr(DPM)_3$ with the glycol).

[5] Solvents were dried over molecular sieves prior to preparation of solutions.