

resonances, contrary to observation. Scheme 2 involves a twist of the diene about an axis normal to the plane containing the double bonds. However, these nmr results cannot distinguish this twist process from the pseudorotation mechanism, because the intermediate configuration III has the same (C_s) symmetry as that found in the process IIa \rightarrow IIb.²⁰ Experiments designed to distinguish unambiguously between these two mechanisms are currently in progress.

Finally, it was suggested²¹ that the equilibration of the diene resonances observed during the intermolecular exchange of $P(C_6H_5)_3$ with $Ir(COD)P(C_6H_5)_3Cl$ resulted from an angular twist of the diene in the proposed intermediate, $Ir(COD)P(C_6H_5)_3Cl$. Our observations on the closely related but stable pentacoordinate complexes afford a more detailed description of the intramolecular rearrangement occurring during the lifetime of such an intermediate. Studies underway are aimed at integrating a mechanistic picture of this type into a more general understanding of exchange reactions of planar four-coordinate d^8 metal complexes.²²

(20) The observed dependence on phosphine ($P(C_6H_5)(CH_3)_2 > P(C_6H_5)_2CH_3 > P(C_6H_5)_3$) suggests steric compression and/or metal-phosphine bonding changes in the rate limiting transition state. This favors scheme 1 over scheme 2.

(21) K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 109 (1969), and references therein.

(22) Cf. P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 4996 (1970).

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Quenching of the Fluorescence of Norcamphor and Its Derivatives by *trans*-1,2-Dicyanoethylene and *cis*-1,2-Diethoxyethylene. Evidence for Two Distinct Quenching Mechanisms¹

Sir:

Available evidence² indicates that the n, π^* states of alkyl ketones possess an excited carbonyl function which is simultaneously an electrophilic reagent (specifically reactive in the volume of space near the carbonyl plane and close to the oxygen atom) and a nucleophilic reagent (specifically reactive in the volume of space above and below the carbonyl plane). We report here that the utility of this simple model is nicely demonstrated in the fluorescence quenching of norcamphor, and a series of its methylated derivatives, by *trans*-1,2-dicyanoethylene (*t*-DCE) and *cis*-1,2-diethoxyethylene³ (*c*-DEE).

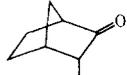
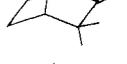
Slopes of the Stern-Volmer plots for fluorescence quenching by *t*-DCE and *c*-DEE are given in Table I. Linear slopes were observed in all cases, which indicates

(1) Molecular Photochemistry. XXV. Paper XXXIV: N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, **92**, 5727 (1970). The authors thank the Air Force Office of Scientific Research for their generous support of this research.

(2) (a) For example, see J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 138 (1970), and references therein; (b) M. Kasha, "Light and Life," W. N. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 31; H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(3) W. M. McElvain and C. H. Stammer, *J. Amer. Chem. Soc.*, **73**, 915 (1951).

Table I. Quenching of Ketone Fluorescence

Ketone ^a	No.	$k_q^f \tau_f^b$		$k_q^f(\text{DCE})/k_q^f(\text{DEE})$
		<i>t</i> -DCE	<i>c</i> -DEE	
	1	29	7.1	4.1
	2	21	2.6	8.1
	3	14	5.1	2.8
	4	14	2.7	5.2
	5	4.7	0.6	7.9
	6	5.0	7.3	0.69
	7	5.2	0.4	13.0
	8	5.6	2.6	2.1
	9	1.5	<0.1	>15
	10	34	8.1	4.2

^a 0.1 M in acetonitrile. ^b Slopes of Stern-Volmer plots of *t*-DCE and *c*-DEE quenching of ketone fluorescence. Error limits $\pm 10\%$.

that eq 1 (ϕ_f^0 = ketone fluorescence in the absence of quencher, ϕ_f = ketone fluorescence in the presence of quencher, k_q^f = the bimolecular rate constant for ketone fluorescence quenching, τ_f = the ketone singlet lifetime, and (Q) is the concentration of quencher) is valid for the systems studied. The measured fluores-

$$\frac{\phi_f^0}{\phi_f} = 1 + k_q^f \tau_f (Q) \quad (1)$$

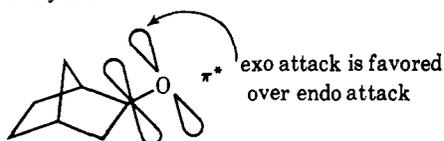
cence lifetimes of **1**, **4**, and **8** were found to be 5.2, 4.4, and 4.1 nsec, respectively. The relative fluorescence quantum yields of **1-8** were found to vary $\pm 20\%$ from an average value (ϕ_f^{rel} of **8** = 1.00)⁴ with the sole exception of **5** which was about 50% lower than the average value. Thus, it seems safe to conclude that the trends in $k_q^f \tau_f$ will reflect trends in k_q^f for the compounds listed in the table. Furthermore, the ratio $k_q^f(\text{DCE})/k_q^f(\text{DEE})$, which removes the problems of knowledge of τ_f , shows a wide variation, thus providing further evidence for a dichotomy of mechanism.

From the data listed in the table it can be seen that the response of k_q^f to ketone structure, while quite different for *t*-DCE relative to *c*-DEE, is easily understandable on the basis of the expected reactivity pattern of a

(4) Ketone solutions were approximately 0.1 M in acetonitrile. Measurements made on an Aminco-Bowman spectrophotofluorimeter.

singlet ketone possessing the characteristics of the simple model, mentioned above, for an n, π^* state. There are, of course, two choices for attack on the faces of the carbonyl group by *t*-DCE. On the basis of ground-state nucleophilic additions to the carbonyl group,⁵ exo attack by *t*-DCE should be favored for **1**, while endo attack by *t*-DCE should be favored for **6**; however, endo attack for **6** should occur at a slower rate than unhindered exo attack. Similar reasoning leads to the conclusion that "steric approach" controls the reactivity of molecules **1**–**10** toward nucleophilic attack by *t*-DCE on the excited carbonyl group, and the reactivity pattern **1** > **2** > **3** ~ **4** > **5** ~ **6** ~ **7** ~ **8** > **9** corresponds well to the expected accessibility of the faces of the excited carbonyl group's half-filled π^* orbital to *t*-DCE (Scheme I). The close agreement between

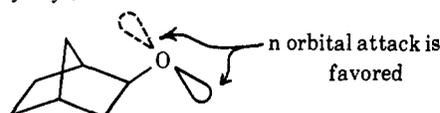
Scheme I. Quenching of Alkanone Fluorescence by 1,2-Dicyanoethylene



the $k_q^f \tau_f$ values for **1** and **10** provides strong support for the preference of exo over endo attack for *t*-DCE on alkanone singlets.

In striking contrast to the correlation of the fluorescence quenching of **1**–**10** by *t*-DCE with the ground-state model for nucleophilic attack on the π face of the carbonyl group,⁵ the quenching of the fluorescence of **1**–**10** by *c*-DEE displays a totally different response to ketone structure. It appears that quenching by *c*-DEE is most efficient when interaction from the sides of the carbonyl function are sterically accessible (Scheme II).

Scheme II. Quenching of Alkanone Fluorescence by 1,2-Diethoxyethylene



Thus, the reactivity pattern **1** ~ **6** ~ **10** > **3** > **2** ~ **4** ~ **8** > **5** ~ **7** > **9** nicely parallels the expected accessibility of the excited carbonyl's n orbital to *c*-DEE and electrophilic attack. The slightly higher $k_q^f \tau_f$ value for **3** over **2** may reflect a difference in lifetimes or result from puckering of the excited carbonyl⁶ in a fashion so as to favor quenching of **3** over **2** by *c*-DEE.

Since preliminary measurements of the quantum yields for oxetane formation for **1**, **4**, and **8** (0.12, 0.048, and 0.032, respectively)⁷ parallel the quenching reactivity of *t*-DCE toward these ketones, we feel that the quenching mechanism is intimately connected to oxetane formation. Further studies are presently in progress to substantiate this proposal.

In summary, quantitative study of the variation of fluorescence quenching reactivities of *t*-DCE and *c*-DEE

(5) For example, see H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966), and references therein. See also E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970).

(6) Cases of both photochemical and spectroscopic results which can be interpreted in terms of a nonplanar n, π^* carbonyl function are known: O. Jeger and K. Schaffner, *Pure Appl. Chem.*, **21**, 247 (1970); C. A. Emeis and L. J. Oosterhoff, *Chem. Phys. Lett.*, **1**, 129 (1967); W. D. Chandler and L. Goodman, *J. Mol. Spectrosc.*, **35**, 232 (1970).

(7) Quantum yields for oxetane formation were determined for acetonitrile solutions of ketone (0.5 *M*) and *t*-DCE (0.1 *M*) employing benzophenone-benzhydrol actinometry.

as a function of ketone structure has provided compelling evidence for the occurrence of two distinct quenching mechanisms. In one case the electron-poor ethylene *t*-DCE interacts with the nucleophilic faces of the excited carbonyl group and in the other case the electron-rich ethylene *c*-DEE interacts with the electrophilic (half-filled) n orbital of the excited carbonyl group.

(8) Alfred P. Sloan Fellow, 1966–1970; to whom correspondence should be addressed.

(9) National Institutes of Health Predoctoral Fellow, 1966–1970.

(10) National Science Foundation Predoctoral Fellow, 1968–1970.

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Tris[3-(*tert*-butylhydroxymethylene)-*d*-camphorato]europium(III). A Reagent for Determining Enantiomeric Purity¹

Sir:

Examination of the ¹H nmr spectra of polar chiral substances in solutions of optically active alcohols or amines has proved a valuable method for the direct determination of enantiomeric purity.^{2,3} However, the magnitude of the chemical-shift difference between corresponding protons of enantiomers obtained using this technique is normally small,² and restricts its utility in applications involving complex spectra. We wish to report the observation of relatively large frequency differences between corresponding resonances of enantiomeric amines dissolved in achiral solvents containing tris[3-(*tert*-butylhydroxymethylene)-*d*-camphorato]europium(III) (**2**). These observations indicate that **2** and related compounds should provide the basis for a useful method for determining the enantiomeric purity of certain compounds for which procedures based on diastereomeric interaction between solute and solvent fail.

Compound **2** was prepared by conversion of *d*-camphor to *tert*-butylhydroxymethylene-*d*-camphor (**1**),⁴ followed by reaction of the latter compound with europium(III) trichloride in the presence of base.⁵ The properties of **2** resemble those of tris(dipivaloylmethido)europium(III), except that **2** is appreciably the more soluble in nonpolar solvents. The nmr spectrum of **2** is localized between +2 and –1 ppm from TMS.

Figure 1 illustrates the influence of **2** on the spectrum of a representative chiral amine, α -phenylethylamine (**3**). The large downfield shift of the resonances of **3** from their positions in the absence of **2** is the expected result of pseudocontact interaction between the eu-

(1) Supported by the National Institutes of Health, Grant No. GM 16020.

(2) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **91**, 5150 (1969), and references therein.

(3) M. Raban and K. Mislaw, *Top. Stereochem.*, **2**, 199 (1967).

(4) The procedure followed was modeled on that of B. O. Linn and C. R. Hauser, *J. Amer. Chem. Soc.*, **78**, 6066 (1956). Compound **1** had bp 87–95° (0.05 mm). *Anal.* Calcd for C₁₂H₂₀O₂: C, 76.22; H, 10.24. Found: C, 76.11; H, 10.28.

(5) K. J. Eisentraut and R. E. Sievers, *ibid.*, **87**, 5254 (1965). The work-up described by these authors was modified by omission of the sublimation step, and purification of the crude product by extraction into absolute ethanol, filtration, precipitation by addition of water, and dehydration under vacuum: mp 131–134°. *Anal.* Calcd for C₃₅H₅₉O₅Eu: C, 62.99; H, 8.11. Found: C, 62.71; H, 8.19.