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Quenching of the Fluorescence of 2-Norbornanone and Derivatives by Electron-Rich and Electron-Poor Ethylenes

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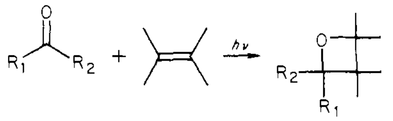
Abstract: The rate constants for fluorescence quenching of a series of substituted 2-norbornanones by *trans*-dicyanoethylene (*t*-DCE) and *cis*-diethoxyethylene (*c*-DEE) have been determined. The effects of ketone structure on the n,π^* singlet reactivity for the two olefins are discussed. The rate of quenching by *t*-DCE was reduced by substituents which block access to the exo face of the carbonyl, whereas quenching by *c*-DEE was most strongly influenced by substituents which increased the steric hindrance in the carbonyl plane near the oxygen atom. The differing structure–reactivity correlations provide evidence for two distinct quenching mechanisms consistent with a simple model for the spatial distribution of electron density in the n,π^* state. The electron-poor olefin *t*-DCE interacts preferentially with the nucleophilic π^* system of the n,π^* excited carbonyl, while the electron-rich olefin *c*-DEE interacts with the half-filled electrophilic n orbital on the carbonyl oxygen. The variation of *t*-DCE fluorescence quenching rates with ketone substitution follows a pattern similar to that observed for the ground-state reduction of 2-norbornanones by sodium borohydride. The results are discussed briefly in terms of elementary orbital interactions between an n,π^* state and an electron-poor or an electron-rich ethylene.

Introduction

Oxetane formation via the [2 + 2] photocycloaddition of carbonyl compounds to olefins and other unsaturated substrates (the Paterno–Buchi reaction, eq 1) has been the subject of extensive synthetic[1,2] mechanistic studies[3-5] and theoretical analyses.[6-8] Photocycloadditions of alkyl and aryl aldehydes and ketones with olefins and 1,3-dienes have been the most widely investigated.[1-8] The scope of the reaction and its synthetic utility have been discussed in several reviews.[2]



(1)

More recent studies have broadened the range of reactants to include photocycloadditions between alkyl ketones and electron-rich and electron-poor olefins, and have sought to characterize the excited states involved and the detailed sequence of events following the ketone n,π^* state–olefin encounter.[4] Product-distribution and quantum-yield studies together with insights into the steric and electronic requirements for the initial interaction obtained from quenching studies have helped to define the factors governing bond formation.

Steric interactions between quenchers and ketone n,π^* excited states have also been found to have an important influence on the rate of quenching.[1] Therefore, steric effects provide another probe for the stereochemical requirements for exciplex formation. For example, Barltrop and Carless[9] have found that α-methylacrylonitrile quenches acetone fluorescence at approximately the same rate as acrylonitrile, but crotonitrile, which has a β-methyl group, quenches an order of magnitude more slowly.

In studies of acetone and norcaphor fluorescence quenching by electron-rich olefins, plots of $\ln [k_q^f/(k_{\mathrm{diff}} - k_q^f)]$ vs. olefin ionization potentials were found to exhibit virtually the same slope but with different intercepts.[10] It was suggested that the nature of the charge-transfer interaction in the exciplex is similar for acetone and norcamphor, but that there is a difference in the environment of interaction which might be attributed to the amount of steric hindrance presented by the ketone to the approach of the olefins.

Steric Approach Control vs. Product Development Control

Steric approach control in the sodium borohydride reduction of a series of methyl-substituted 2-norbornanones has been demonstrated.[11] For example, it has been shown that $NaBH_4$ attacks the carbonyl π system of norcamphor (**1**) preferentially from the less sterically hindered exo face, and the thermodynamically less stable endo alcohol is the major product.[11b] Blocking of the exo face by the introduction of a syn 7-methyl group in 7,7-dimethylnorcamphor (**3**) slows down the overall rate of reduction and results in favored attack from the endo face of the carbonyl. We selected a series of appropriately substituted 2-norbornanones as model systems for the investigation of the preferred approach of electron-rich and of electron-poor ethylenes in the quenching of the n,π^* singlet states of alkanones.

Spectroscopic and Dynamic Properties of 2-Norbornanones

The absorption and fluorescence spectra of norcamphor are representative of the series of 2-norbornanones studied in this investigation.[12] The absorption spectrum of norcamphor consists of a broad envelope maximizing at 289 nm in acetonitrile solution (ϵ 24.7) and exhibiting some vibrational structure. The emission spectrum is broad and unstructured, maximizing at 410 nm. The absorption and emission maxima for the other 2-norbornanones in the series fall within a relatively narrow wavelength range: $\lambda_{\max}$ 288–301 nm for absorption and 395–412 nm for emission. The

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(4) (a) Turro, N. J.; Wriede, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 6863. (b) *Ibid.* **1970**, *92*, 320. (c) Turro, N. J.; Wriede, P. A.; Dalton, J. C. *Ibid.* **1968**, *90*, 3274.

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(12) Waddell, W. H.; Turro, N. J.; Farrington, G. *Mol. Photochem.* **1976**, *7*, 475.

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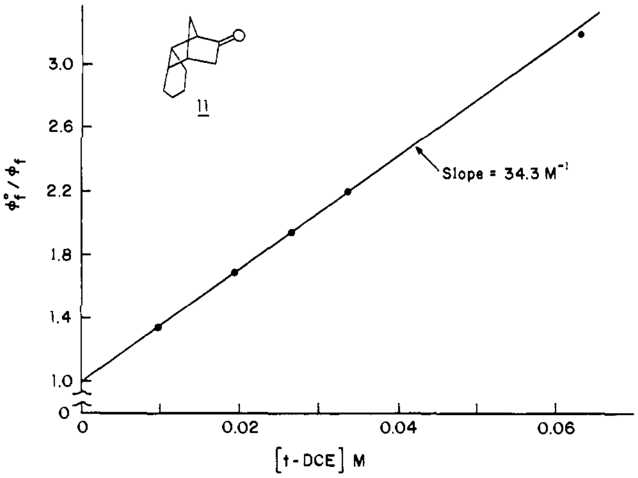


Figure 1. Fluorescence quenching of **11** by *t*-DCE.

singlet lifetimes for the norbornanone vary from 2.6 to 6.2 ns.

Fluorescence Quenching of 2-Norbornanones by *t*-DCE and *c*-DEE[13]

The fluorescence quenching of 2-norbornanones was studied with *trans*-dicyanoethylene (*t*-DCE) and *cis*-diethoxyethylene (*c*-DEE) as representative electron-poor and electron-rich olefins, respectively. A plot of ϕ_f^0/ϕ_f vs. quencher concentration can be generated in the usual manner[14] and is expected to be linear from the Stern–Volmer relationship:

$$\phi_f^0/\phi_f = 1 + k_q^f\tau_s[Q] \qquad (2)$$

The plots of ϕ_f^0/ϕ_f vs. quencher concentration for **11** with *t*-DCE and *c*-DEE (Figure 1 and 2) are representative of the results obtained in these quenching experiments.[15]

The results of the fluorescence quenching of variously substituted norbornanones are summarized in Table I and discussed below.

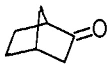
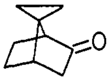
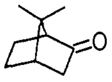
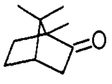
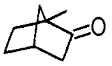
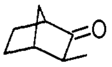
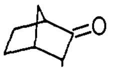
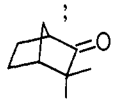
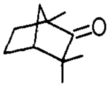
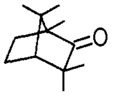
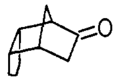
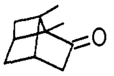
Quenching by *t*-DCE

The rate of quenching by *t*-DCE is most strongly affected by groups above the carbonyl plane which block access to the exo portion of the π system (Table I). Ketones **1**, **7**, and **11**, which are unhindered toward exo approach, have the largest values for k_q^f. The quenching rate drops to intermediate values for **5**, **6**, **8**, and **9**, where methyl groups at the 1 and 3-exo positions partially interfere with exo approach, and k_q^f is the lowest for ketones **3**, **4**, and **10**, which have syn 7-methyl groups rendering the exo π system least accessible. The preference for exo attack by *t*-DCE on the bicyclic ketone singlets is supported by the quenching rates for **7** and **11**; the endo 3-methyl in **7** and fused ring in **11** should increase the steric hindrance to endo approach, but k_q^f for these ketones is essentially the same as for **1**.

These substituent effects are closely paralleled by those found[11b] for the rate of reduction by $NaBH_4$ as shown by the comparative data for the series of ketones in Table II. Increasing steric hindrance to exo approach decreases k_q^f with *t*-DCE and likewise decreases k_r and reduces the endo:exo ratio of the product alcohols from $NaBH_4$ reduction. A plot of log k_q^f vs. log $k_r^{NaBH_4}$ for the series (Figure 3) shows a correlation which suggests that the free energies of the two processes are affected in a related manner by steric hindrance. No such correlation is found for *c*-DEE.

The similarity between the steric requirements for the quenching and reduction processes is emphasized by the results for ketones **2** and **12**. Fluorescence quenching of **2** and **12** by *t*-DCE gave values of k_q^f which appeared anomalously high in view of the presence of a methylene (**2**) or methyl (**12**) group above the carbonyl exo face. The k_q^f for **2** approximates that of norcamphor, implying that the syn 7-methylene in **2** provides little more steric hindrance than a syn 7-hydrogen. The syn 7-methyl of **12** does

Table I. Fluorescence Quenching of 2-Norbornanones by *t*-DCE and *c*-DEE

No.	Ketone	$k_q^f\tau_s$ (M^{-1})(a) t-DCE	$k_q^f\tau_s$ (M^{-1})(a) c-DEE	τ_s(nsec)(b)	$k_q^f \times 10^{-9}$ $M^{-1}sec^{-1}$ t-DCE	$k_q^f \times 10^{-9}$ $M^{-1}sec^{-1}$ c-DEE
1		29	7.1	5.7	5.1	1.2
2		28	6.9	5.9	4.7	1.2
3		5.0	7.3	5.0	1.0	1.5
4		5.6	2.6	4.7	1.2	0.55
5		14	2.7	4.8	2.9	0.56
6		14	5.1	6.0	2.3	0.85
7		21	2.6	4.4	4.8	0.59
8		4.7	0.6	(c)	(c)	(c)
9		5.2	0.4	2.9	1.8	0.14
10		1.5	<0.1	3.1	0.48	<0.03
11		34	8.1	6.2	5.5	1.3
12		17	3.9	4.9	3.4	0.8

[a] Slopes of the Stern–Volmer plots of ϕ_f^0/ϕ_f vs. quencher concentration for 0.1 M solutions of ketone in acetonitrile at room temperature; values are ±5%. [b] Measured by the single-photon counting technique at room temperature; acetonitrile solutions of ketones (3-5 × 10^{-2} M); values undeconvoluted, ±0.1 ns. [c] τ_s too short for accurate determination of k_q^f.

Table II. Fluorescence Quenching and Sodium Borohydride Reduction of 2-Norboranones

no.	$k_q^f \times 10^{-9}$, M^{-1} s^{-1} *t*-DCE	$k_q^f \times 10^{-9}$, M^{-1} s^{-1} *c*-DEE	$NaBH_4$ $k_r \times 10^4$, M^{-1} s^{-1}	$NaBH_4$ product alcohols endo:exo
1	5.1	1.2	24^b	$87{:}13^b$
2	4.7	1.2	12^b	$75{:}25^b$
3	1.0	1.5	0.2^b	$20{:}80^b$
4	1.2	0.55	0.026^b	$14{:}86^b$
5	2.9	0.56	3.6^c	$85{:}15^c$
12	3.4	0.8	1.7^c	$\sim 50{:}50^{c,d}$

[a] 0.1 M solutions of ketones in acetonitrile. [b] Reductions in 2-propanol at 25 ± 1 °C (ref 11b). [c] Reduction of 0.1 M ketone with 0.02 M $NaBH_4$ in 2-propanol at 25 ± 1 °C; isomer ratio estimated by GLC (12 × 1/4 in. 20% FFAP on Chromosorb P). [d] Isomer ratio estimated by NMR.

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(13) Turro, N. J.; Dalton, J. C.; Farrington, G.; Niemczyk, M.; Pond, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 6978.

(14) See ref 1, Chapter 8.

(15) The shape of the fluorescence envelope remains roughly constant as the intensity is decreased with increasing quencher concentrations. The measurement of Φ_f by peak height should therefore be equivalent to integration of the area under the fluorescence curve.

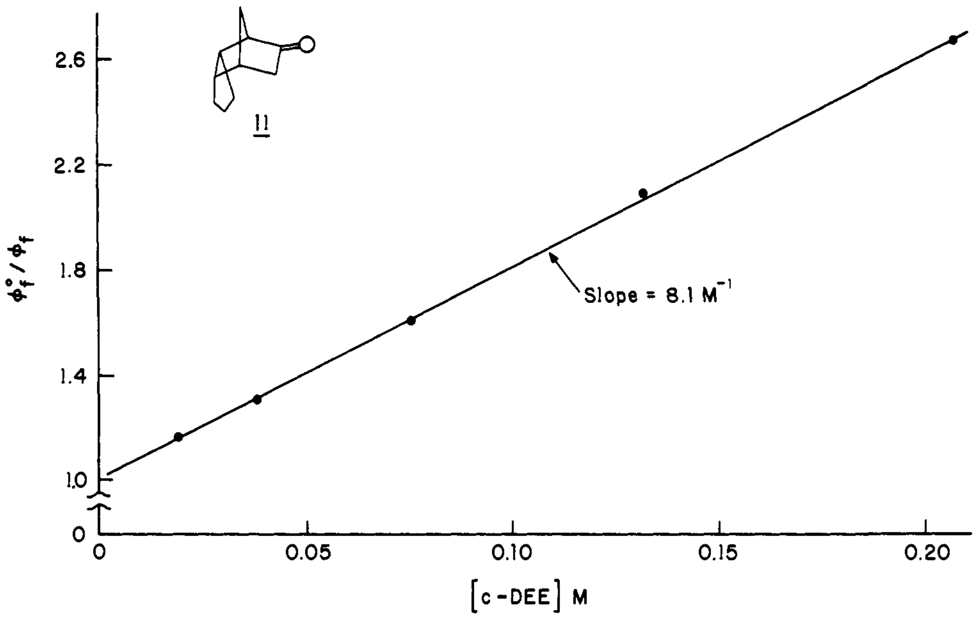

Figure 2. Fluorescence quenching of **11** by *c*-DEE.

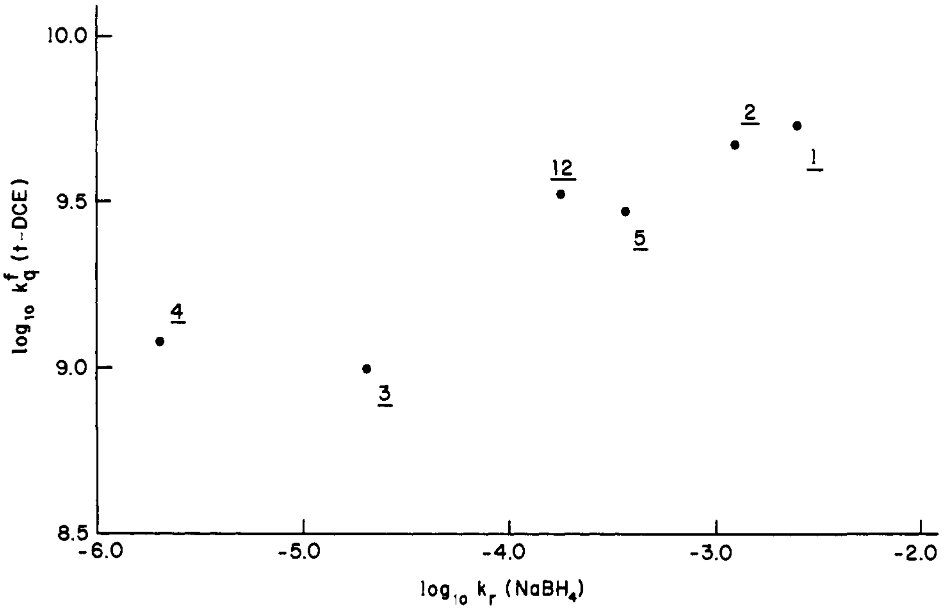

Figure 3. Correlation of the rate constants for quenching by *t*-DCE with the rate constants for reduction by $NaBH_4$.

reduce k_q^f, but the quenching rate for **12** is still a factor of 3 higher than that for **3** or **4**, which also have syn 7-methyl groups. These results are similar to those found for $NaBH_4$ reduction,[11b] as shown by the data in Table II. Both the rate of reduction and the endo:exo product ratio from **2** are similar to those for norcamphor; k_r for **12** is a factor of 65 higher than that for camphor (**4**) and the endo:exo product ratio for **12** is 50:50 vs. 14:86 for camphor, indicating a reduced hindrance to exo attack in **12**.

A comparison of the k_q^f and k_r values for the ketones in Table II also shows that, although the pattern of substituent effects is similar, there is a large difference in range. The k_q^f values for *t*–DCE vary by only about a factor of 5, whereas the k_r for $NaBH_4$ changes by nearly a factor of 10^3. Thus, while both fluorescence quenching by *t*-DCE and reduction by $NaBH_4$ appear to proceed via interaction with the carbonyl π^* system, the quenching may involve a looser association between the n,π^* state and olefin in the transition state for quenching than is present between $NaBH_4$ and the carbonyl ground state in the transition state for reduction.

Quenching by *c*-DEE

While the rates of fluorescence quenching for *t*-DCE in the series **1**–**12** appear to depend on accessibility of the exo face of the carbonyl system, the rates of fluorescence quenching by *c*-DEE display a totally different pattern of response to ketone structure (Table I). For example, the k_q^f for quenching of **1** and **3** by *c*-DEE are approximately equal, whereas k_q^f with *t*-DCE is a factor of 5 lower for **3**. The data in Table I indicates that k_q^f for *c*-DEE is most affected by groups in the plane of the carbonyl which hinder access to the half-filled n orbital of the n,π^* singlet. The in-plane approach to ketones **1**–**3** and **11** is relatively unhindered and these display the highest k_q^f with *c*-DEE. Approach to one side of the carbonyl is hindered for **4**–**8** and **12**, and k_q^f is reduced. **9** and **10** are hindered on both sides in the carbonyl plane and are quenched at the slowest rate.

The k_q^f values for **6** and **7** with *c*-DEE indicate that the endo 3-methyl group in **7** hinders the approach of *c*-DEE more than the exo 3-methyl group in **6**. In fact, the steric hindrance in **7** is similar to that for the 1-methyl group of **5**, which is positioned directly in the carbonyl plane. In norcamphor the carbonyl plane bisects the angle between the 3-endo and 3-exo hydrogens, and substituents in these positions would therefore be expected to provide equivalent steric hindrance if the norbornane ring system is undistorted. A distortion of **7** may arise, as a result of steric interference between the endo 3-methyl group and the endo 5-

Table III. Fluorescence Quenching of 2-Norbornanones by *cis*-1,3-Pentadiene and Biacetyl

no.	*cis*-1,3-pentadiene[a] $k_q^f \times 10^7$, M^{-1} s^{-1}	biacetyl[b] $k_q^f \times 10^7$, M^{-1} s^{-1}
1	3.2	840
3	2.8	760
4	1.4	
6	1.8	
9	<0.5	610
11	3.3	800

[a] In benzene solution, ref 9b. [b] Reference 17b.

hydrogen atom,[16] twisting the methyl group into the plane of the carbonyl and increasing the hindrance to quenching by *c*-DEE. The exo 3-methyl in **6** would not be expected to interact strongly with the syn 7-hydrogen to twist the exo 3-methyl downward, and should therefore present less in-plane steric bulk to *c*-DEE approach.

The response of the rate constants for fluorescence quenching to changes in ketone structure has also been studied for 1,3-dienes and biacetyl in a similar series of substituted 2-norbornanones. The data in Table III show that *cis*-1,3-pentadiene (*c*-PD) is affected in much the same way as *c*-DEE, exhibiting a preference for edge approach to the carbonyl; k_q^f with norcamphor (**1**) and 7,7-dimethylnorcamphor (**3**) are similar, but k_q^f for fenchone (**9**) is greatly reduced. The rate constants for *c*-PD are also about a factor of 40 lower than that of *c*-DEE, in line with the higher ionization potential for *c*-PD (8.65 eV) than *c*-DEE (8.15 eV). The reactivity patterns of *c*-PD and *c*-DEE are both consistent with the diene acting as an electron-rich olefin toward the ketone n,π* state.

In contrast to the results with *c*-DEE, *t*-DCE, and *c*-PD, quenching by biacetyl is relatively insensitive to ketone structure—e.g., k_q^f for ketones **1** and **9** differ by less than 40%. Since biacetyl is known to quench alkanone singlets by collisional energy transfer, the data suggest that the quenching by olefins and dienes proceeds via other mechanisms. The results with *c*-DEE and *t*-DCE point to a specificity of interaction for electron-rich and electron-poor olefins which confirms the amphoteric nature of the n,π* state.

Theoretical Description of Ketone-Olefin Cycloadditions Using State Correlation Diagrams

State correlation diagrams (Salem diagrams) have recently found great utility in analyzing photochemical reaction mechanisms by providing a qualitative description of the potential-energy surfaces linking reactant and product states.[8] Of particular importance are surface crossings or avoided crossings revealed by the diagrams, since these have implications as to plausible pathways which can be explored by an excited state, to the energy barriers which may exist, and to sources of reaction inefficiency.[18] Conclusions based on qualitative consideration of state correlation diagrams have been supported by ab initio calculations of potential-energy surfaces[19] and the diagrams have thus proved to be a simple and reliable means of gaining insight into the electronic course of reactions.

Theoretical Features of the Addition of Ketone n,π* States to Electron-Rich and Electron-Poor Olefins

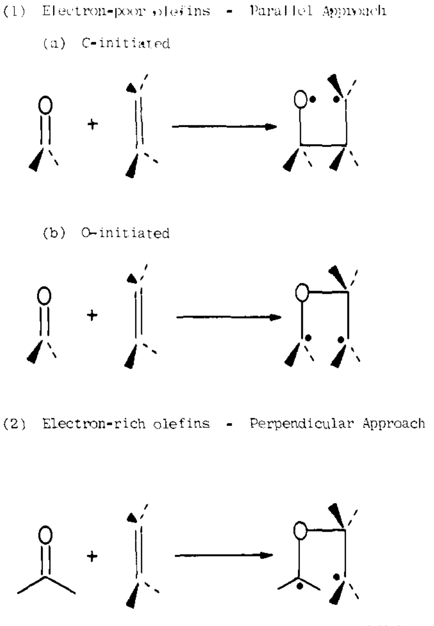

Figure 4. Possible routes for ketone n,π* state additions to olefins.

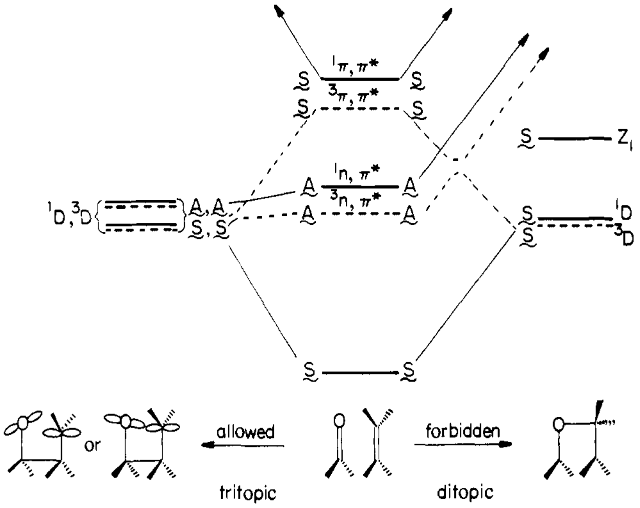

Figure 5. Salem diagram for the ditopic and the tritopic addition of ketones to ethylenes via a parallel geometry.

State correlation diagrams for the addition of ketone n,π* states to electron-rich and electron-poor olefins have been constructed.[8,18] In the case of addition to electron-rich olefins, the reaction may be considered as an attack of the carbonyl n orbital on the olefin, with the ketone and olefin π systems in a perpendicular conformation, to generate a 1,4-biradical intermediate. The addition to electron-poor olefins occurs via an interaction of the π* systems of the ketone and of the olefin in a parallel configuration. The parallel approach between the π systems allows for initial bond formation to the olefin to occur for either the carbonyl carbon or oxygen, which can be viewed as the two extremes of the quasi-concerted cycloaddition process, to generate different 1,4 biradicals. These addition processes are summarized in Figure 4.

Although available evidence suggests that exciplex formation occurs between n,π* states and both electron-rich and electron-poor olefins,[9] the exciplexes are presumed to be bound by relatively loose interactions between excited ketones and olefins which have the same geometry as that for eventual bond formation, but are not otherwise characterizable with regard to their symmetry properties, etc. Correlation diagrams may therefore be constructed for the simple additions involving biradicals as the primary products. Of the three reactions listed in Figure 4, the perpendicular approach for electron-rich olefins has been disussed.[8,18] It has been noted that an adiabatic connection exists between the reactants with the ketone in its n,π* state and the diradical primary product.[18]

In the case of the parallel approach, a bond between the carbonyl oxygen atom and the olefin (O→C) or between the carbonyl carbon and the olefin (C→C) occurs as the diradical is formed. Figure 5 displays the Salem diagram for these interactions. From

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the figure, it can be seen that the O→C pathway is ditopic and forbidden in the sense that no adiabatic n,π^*→D correlation exists. On the other hand, the C→C pathway is tritopic; the reaction possesses an adiabatic n,π^*→D correlation. From Figure 5 it is logical to conclude, therefore, that a diradical of the type $\dot{\mathrm{C}}$–C–C–$\dot{\mathrm{O}}$ is favored over a diradical of the type $\dot{\mathrm{C}}$–O–C–$\dot{\mathrm{C}}$. This conclusion provides a natural explanation of the regiospecificity of the photoaddition of acetone to cyanoethylenes,[10] which can be now readily rationalized in terms of the best biradical rule,[3a] as long as the proper and pertinent diradical ($\dot{\mathrm{C}}$–C–C–$\dot{\mathrm{O}}$) is considered in the analysis.

Conclusion

The rate constants for fluorescence quenching of 2-norbornanones by *t*-DCE and *c*-DEE are consistent with the expectation that substituents which block access to the exo face of the excited carbonyl function will mainly suppress quenching by *t*-DCE, whereas substituents that block access to the edges of the excited carbonyl function will mainly suppress quenching by *c*-DEE. The role of electronic effects (correlations of quenching with IP, EA, and excitation energies) is probably small with most of the ketones studied; we feel that it is possible that such factors may play a minor role in the cases of heavily α-methylated ketones.

Experimental Section

Fluorescence lifetime measurements were made at room temperature using the single-photon counting technique.[20] Excitation was provided by an air spark lamp which had a pulse half-width of approximately 2 ns. The fluorescence was monitored at right angles to the excitation using a Jarrel-Ash 1/4M monochromator and an Amperex 56 AVP phototube in conjunction with a Hewlett-Packard 5214L preset counter and a Northern Econ II multichannel pulse height analyzer. The reported lifetimes were obtained from plots of log (number of counts) vs. channels (each channel width about 0.236 ns), which were found to be linear over at least one order of magnitude in the number of counts. The data were not deconvoluted to subtract out the lamp function or scatter.

Purification of Materials for Fluorescence Quenching, Singlet Lifetime, and Relative Quantum Yield Determinations. Acetonitrile. Matheson Coleman and Bell (MCB) 99+ Chromatoquality or Fisher reagent grade acetonitrile was purified by the method of O'Donnell et al.[21] To approximately 2.5 L of acetonitrile in a 5-L round-bottom flask were added 30 g of Na_2CO_3 and 45 g of $KMnO_4$; the mixture was heated and stirred for 2 h, then rapidly distilled. The first 300 mL was discarded and the remaining 2.2 L collected in a dried flask; sufficient concentrated H_2SO_4 was added to reduce the pH below 3.0, and a white precipitate formed. The acidified acetonitrile was allowed to stand for 1 h, and the precipitate was then filtered off and the acetonitrile distilled through a 3-ft column packed with glass helices at a rate of 10–15 mL/h. A forerun of about 300 mL was discarded, and the remaining 1.5–2.0 L collected in dried containers. The MCB material purified as above was UV transparent down to 230 nm. Even better results could be obtained starting with the Fisher acetonitrile; the only observable absorptions were small peaks at about 210 and 190 nm.

***trans*-1,2-Dicyanoethylene (*t*-DCE).** Commerical material (Aldrich) contained an impurity with λ_{max} (CH_3CN) 270 nm and a significant tail absorption extending above 313 nm which could not be removed by sublimation. The *t*-DCE was therefore dissolved in a minimum amount of acetone and chromatographed on a column of Woelm neutral alumina by eluting with 3:1 pentane/ether. The middle fractions (about 75–80% of the initial amount) were combined and sublimed to give *t*-DCE with no observable absorption above 250 nm.

***cis*-1,2-Diethoxyethylene (*c*-DEE).**[22] The material prepared by pyrolysis of 1,1,2-triethoxyethane was purified by GLC (10 ft × $^1/_4$ in. 20% XF-1150 on base-washed Chromosorb P, CT = 105 °C); the chromatograph injection port and detector were carefully base washed with a KOH/MeOH solution to prevent decomposition of the vinyl ether.

Bicyclic ketones 1–12 were purified by preparative GLC (12 ft × $^1/_4$ in. 20% XF-1150 on Chromosorb, CT = 100–120 °C), and microdistilled or sublimed prior to use.

Norcamphor (1), camphor (4), fenchone (9), camphenilone (8), and tricyclo[5.2.1.0^{2,6}]decan-9-one (11) were purchased from commercial sources.

***exo*- and *endo*-3-methylnorcamphor (6 and 7)** were prepared from norcamphor by the method of Corey et al.[23] Alkylation using methyl iodide with triphenylmethylsodium as the base resulted in a product with >95% exo stereochemistry by GLC analysis. Subsequent epimerization by refluxing with 3% NaOMe/MeOH resulted in a mixture of isomers in a 55:45 endo:exo ratio, and separation was achieved by preparative GLC (20 ft × 1/4 in 10% FFAP on Chromosorb P, CT = 170 °C).

1-Methylnorcamphor (5) was prepared from norcamphor by the method of Bartlett and Singer.[24]

3,3-Dimethylcamphor (10) was prepared by treating a benzene solution of camphor with $NaNH_2$ and methyl iodide according to the method of Haller and Bauer.[25]

Carvonecamphor (12) was prepared via the photolysis of a solution of carvone in 4:1 dioxane/H_2O by a modification of the method of Meinwald and Schneider.[26]

Spiro[cyclopropane-1,7′-norbornan]-2′-one (2) and 7,7-dimethylnorcamphor (3) were synthesized as described by Turro and Farrington.[27]

General Procedure for Stern–Volmer Quenching Measurements. A 0.1 M solution of ketone in acetonitrile was prepared and 2 mL pipetted into each of two 1-cm^2 quartz fluorescence cells fitted with Teflon caps. Aliquots of solid *t*-DCE or liquid *c*-DEE were added to one cell and the peak height of the fluorescence λ_{max} was recorded on a Perkin-Elmer MPF-2A spectrophotometer with excitation at 313 nm. The other cell, to which no quencher was added, served as a reference standard, and the peak height for the sample solution at each quencher concentration was compared with that of the standard to compensate for any fluctuations in the excitation source intensity. At least five determinations of sample peak height vs. standard were taken at each quencher concentration, and the variation was found to be ±2%. The initial sample/standard peak height ratio was defined as ϕ_f^0, and subsequent sample/standard ratios provided the values of ϕ_f from which plots of ϕ_f^0/ϕ_f vs. quencher concentration could be derived. The absorbance of all solutions was checked periodically with a Gilford UV spectrophotometer to determine if any competitive absorption due to the quencher was occurring, but in no case did the quencher cause the absorbance of the solution to increase.

Procedure for Relative Quantum Yield Determinations. A merry-go-round apparatus was used to ensure the simultaneous irradiation of several samples with the same light intensity over a period of time. The apparatus consisted of an electronically driven turntable which revolved around a light source; holes in the turntable rim were designed to accommodate test tubes containing the samples to be irradiated. The entire turntable was placed in a large water bath which maintained a constant temperature (25 ± 2 °C) during the irradiation. The light source, a Hanovia Type L-679A-36 450-W medium-pressure mercury arc lamp, was contained in a water-cooled quartz reactor fitted with a Pyrex filter sleeve; the reactor was surrounded by a Pyrex immersion well jacket containing a 313-nm filter solution (0.002 M K_2CrO_4 in a 1% aqueous solution of K_2CO_3).

The samples to be irradiated were placed in 10 × 75 mm Pyrex test tubes (Corning) which had been cleaned with Chromerge solution, washed with aqueous NH_4OH, thoroughly rinsed with distilled water, and oven dried. The test tubes were stoppered with serum caps.

Solutions of norcamphor, 7,7-dimethylnorcamphor, and spiro[cyclopropane-1,7′-norbornan]-2′-one in purified acetonitrile were prepared and the optical densities were measured.

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