of alkylbenzenes, indicates that decay of the arene-like excited state is considerably accelerated by the presence of the diene unit. We believe that the two chromophoric units are coupled in the lowest excited states and that molecular rearrangement is one of the paths by which electronic excitation is dissipated through the diene structure. We also suspect that the chemical reactions are related to the bimolecular quenching of fluorescence of aromatic compounds by dienes.[8]

Two other possibilities for the formation of **3** are immediately evident. Firstly, the divinylmethanes **2**, formed in a primary photochemical process, could rearrange through a secondary process to give vinylcyclopropanes.[6] This possibility was eliminated by our inability to effect any rearrangement of **3c**, either under direct irradiation in hexane or benzene solution, or with high-energy triplet sensitizers. Secondly, vinylcyclopropanes could conceivably arise from a 1,2-hydrogen atom migration. However, this process is impossible in **1b**, and the nmr spectrum of **1c**, which contains neither a methylene doublet nor a ring methyl doublet, clearly eliminates this pathway for **1c**.

The geometrical isomers of **1** are not easily separated by vapor chromatography.[9] Partial separation of the *cis–trans* isomers of **1c** has been achieved. In this case, isomerization of the diene unit proceeds more rapidly than rearrangement to **2c** and **3c**. As yet, we have neither determined quantum yields for the various processes, nor determined if **2** and **3** are formed with equal facility from both *cis* and *trans* isomers of **1**. *cis*-**3c** and *trans*-**3c** readily interconvert under reaction conditions or upon triplet sensitization. By starting with isomerically pure **1c** and carrying the reaction to low conversions, we hope to determine the stereospecificity of vinylcyclopropane formation.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-1479, and the National Research Council of Canada.

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(8) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

(9) *cis–trans* isomers of **1a,b** are evident from the nmr spectra of the dienes.

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Received January 22, 1970

Mechanisms of Excited State Deactivation. Quenching of Excited Singlets by Nucleophiles

Sir:

Excited states frequently have much shorter lifetimes in solution than in the gas phase or in rigid media. In addition to energy transfer and relaxation processes, several types of excited state solute and excited state solvent interactions including complex formation,[1] hydrogen abstraction,[2] reversible addition,[3] and electron transfer[4] have recently been reported. In the present communication we report the quenching of fluorescence of several electron-deficient compounds by a variety of nucleophiles. This quenching apparently is caused by addition of nucleophiles to excited singlet states; attack by nucleophiles may lead to addition products but in many cases addition followed by elimination simply provides a mechanism for radiationless deactivation.

Table I. Quenching of Fluorescence by Nucleophiles[a]

	4,4′-BPE-DMFB[b]		MAFB[c]		Riboflavin[d]
Nucleophile	$k_q\tau$, M^{-1} [e]	k_q/k_w	$k_q\tau$, M^{-1}	k_q/k_w	$k_q\tau$, M^{-1}
H_2O	0.19	1.0	0.04	1.0	
SO_4^{2-}	0.39	2.0	0.08	2.0	0.01
C_2H_5OH	0.4	2.1	0.14	3.6	0.02
NO_3^-			0.15	3.7	0.03
$C_2H_5OC_2H_5$	0.21	1.1	0.30	7.5	
$CH_3CO_2^-$	1.8	9.5	0.39	9.7	0.08
$ClCH_2CO_2^-$			2.2	56	0.46
C_5H_5N	3.0	16			
Cl^-	3.4	18	67	1700	0.68
n-C_4H_9Cl	0.00	0.0	0.00	0.0	
SCN^-					104[f]

[a] Measured on a Hitachi Perkin-Elmer MPF-2A. Solutions degassed by bubbling with argon or by the freeze–pump–thaw method. Fluorescence of 4,4′-BPE-DMFB and MAFB was measured in acetonitrile or 90% water–10% acetonitrile by volume, and $k_q\tau$ values were corrected for competitive water quenching. [b] λ_{ex} = 313 nm. [c] λ_{ex} = 403 nm. [d] Measured in water; λ_{ex} = 468 nm. [e] The product, $k_q\tau$ (k_q is the rate constant for quenching and τ is the fluorescence lifetime), was obtained from the slope of a Stern–Volmer plot. [f] Slight ground-state reaction was observed. No new fluorescence was observed in the presence of any quencher studied.

Typical of compounds whose excited singlets react with nucleophiles are quaternary salts of nitrogen heterocycles such as acridine, the 1,2-bispyridylethylenes, and stilbazoles as well as polar, neutral molecules such as riboflavin. Representative data for quenching of fluorescence of methylacridinium fluoroborate (MAFB) (**1**), the dimethylfluoroborate of 1,2-bis(4-pyridyl)ethylene (4,4′-BPE-DMFB) (**2**), and riboflavin by nucleophiles are listed in Table I. Quenching rate constants are correlated fairly well (correlation coefficients 0.991 for **1** and 0.990 for **2**) with the two-parameter Edwards equation[5] for nucleophilicity

$$\log k_N/k_W = \alpha E_n + \beta H$$

Substrate parameters for **1** are $\alpha = 2.17 \pm 0.15$ and $\beta = -0.125 \pm 0.053$; those for **2** are $\alpha = 0.960 \pm 0.078$ and $\beta = -0.0150 \pm 0.017$. These are not very different from those for organic substrates in nucleophilic displacements.[6] Quenching constants for **2** and the dimethiodide of 1,2-bis(3-pyridyl)ethylene (**3**) increase in the series *t*-butyl alcohol, water, and ethanol; this is the predicted order of nucleophilicity. This result, together with the Edwards equation correlation, suggests that the present phenomena cannot be accounted for by electron transfer. Evidence that fluorescence quenching by chloride ion is a consequence of nucleophilicity and not a heavy atom effect comes from our finding that 1-chlorobutane does not quench

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(1) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(2) See, for example, P. J. Wagner and A. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968).

(3) J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969); J. Saltiel, *et al.*, *ibid.*, **92**, 411 (1970).

(4) N. J. Turro and R. Engel, *ibid.*, **91**, 7113 (1969); *Mol. Photochem.*, **1**, 143 (1969).

(5) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954); *ibid.*, **78**, 1819 (1956).

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 254.

excited **1** or **2**. Except where noted, the nucleophiles listed in the table do not react with ground states of **1**, **2**, or riboflavin; more reactive nucleophiles such as CN^- and aliphatic amines react with ground states of **1** and **2**. Reaction of excited singlets of **2** and **3** with water or ethanol leads to the formation of isolable adducts;[7] however there is no correlation of k_q values with quantum efficiencies for adduct formation. Several nucleophiles that give higher k_q values than water, such as ether, pyridine, and inorganic ions, do not produce adducts with either **2** or **3**. For **1**, roughly the same pattern is observed: concentrations of nucleophile high enough to quench most of the fluorescence lead to adduct formation with very low efficiency for chloride ($\phi \sim 0.001$) and acetate ($\phi \sim 0.004$).

Attack of excited states by nucleophiles is not without precedent; photochemical nucleophilic substitution and addition reactions have been previously reported for aromatic nitro compounds[8,9] and aromatic acetylenes.[10] These reactions have been monitored by product formation as opposed to the current observation of excited state deactivation frequently with no product formation. It is perhaps surprising that excited states with supposed diradical character are attacked so readily by nucleophiles; the attack by nucleophiles on radical cations of aromatic hydrocarbons (generated by anodic oxidation)[11] offers an interesting analogy to the present observations.

We have extended our investigation to uncharged substrates such as riboflavin and pyrimidine bases to determine whether the short singlet lifetimes,[12] reported medium and substituent effects on fluorescence,[13] photoaddition,[14] and photohydration[15,16] for these compounds can be attributed, in part, to interactions with nucleophiles. 1,3-Dimethyluracil (**4**) proved to be a useful model compound for quenching studies. Although hydroxide and bromide react with **4** in the ground state, weaker nucleophiles such as acetate, sulfate, and chloride ions do not quench its fluorescence. Fluorescence of **4** is quenched weakly by water ($k_q\tau$ = 0.1 M^{-1} in acetonitrile); however, dilute HCl (up to 0.1 M in 90% water–10% acetonitrile) strongly quenches fluorescence of **4** while promoting no ground-state reaction. Photohydration evidently originates by photoprotonation of excited singlets of **4**;[17] the quenching correlates with an increase in photohydrate yield with decreasing pH.[16] Whether the reported quenching of purine base fluorescence by ions[19] is due to nucleophilic attack remains to be determined.

Riboflavin presents an interesting case; its strong fluorescence in aqueous solution is quenched both by nucleophiles (Table I) and by acids ($k_q\tau$ for acetic acid = 2.1 M^{-1}) which do not react in the ground state.[20] An explanation for this is offered by calculations which suggest increased polarity in excited states of riboflavin.[21] The sensitivity of excited riboflavin toward nucleophiles is probably related to its ease of photoreduction.[13]

Acknowledgment. We are grateful for support of this work by the U. S. Army Research Office, Durham (Grant DA-ARO-D-31-124-G1097), and the National Science Foundation (through a Science Development Award).

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[7] M. T. McCall and D. G. Whitten, *J. Amer. Chem. Soc.*, **91**, 5681 (1969); in addition we find that quenching of the fluorescence of *trans*-**2** is concurrent with quenching of *trans* → *cis* photoisomerization. Photoisomerization of *trans*-**2** proceeds from the singlet but not from the triplet.

[8] E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968), and references therein.

[9] R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969).

[10] T. D. Roberts, L. Ardemagni, and H. Schechter, *ibid.*, **91**, 6185 (1969).

[11] R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

[12] J. Eisinger, *Photochem. Photobiol.*, **7**, 597 (1968).

[13] For a review on flavins see G. R. Penzer and G. K. Radda, *Quart. Rev. Chem. Soc.*, **21**, 43 (1967).

[14] K. C. Smith, *Photochem. Photobiol.*, **7**, 651 (1968).

[15] H. E. Johns, *ibid.*, **7**, 633 (1968).

[16] J. G. Burr, B. R. Gordon, and E. H. Park, *ibid.*, **8**, 73 (1968); J. G. Burr, *Advan. Photochem.*, **6**, 193 (1968).

[17] This contrasts to photoprotonation of cyclic olefins[18] which has been proposed to proceed *via* reaction of a transoid (ground state) photoproduct.

[18] P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969).

[19] D. C. Ward and E. Reich, *J. Biol. Chem.*, **244**, 1228 (1969).

[20] Although rates of quenching by nucleophiles do not correlate well using the Edwards equation, the rates increase qualitatively with increasing nucleophilicity.

[21] P. S. Song, *J. Phys. Chem.*, **72**, 536 (1968).

[22] National Aeronautics and Space Administration Predoctoral Fellow, 1966–1969.

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Three-Dimensional Macrocyclic Encapsulation Reactions. I. Synthesis of Six-Coordinate Complexes with Nonoctahedral Stereochemistry

Sir:

The original proposal by Busch[1] that complexes containing completely encapsulated metal ions should be obtainable has been followed by the recent synthesis of two such "clathro-chelates" of cobalt,[2] $[Co(dmg)_3(BF)_2]^{0,+}$. We report here a synthetic procedure and supporting characterization data which demonstrate entry to a new class of clathro chelates. The members of this class possess a rigid bicyclic ligand structure which is expected to stabilize trigonal prismatic (TP) or near-TP stereochemistry, and thereby facilitate a systematic study of this stereochemistry. In discrete species TP structures have been proven (by X-ray methods) only for $[Co(dmg)_3(BF)_2]$,[2] certain metal tris(dithiolenes),[3] one diastereoisomer of $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$,[4] and 1,3,5-tris(2-pyridinaldimino)cyclohexanezinc(II) cation,[5] $[Zn(py_3tach)]^{2+}$. The structure of the latter complex and the ring-closure reaction of Boston and Rose[2] have been relevant factors

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[1] D. H. Busch, *Rec. Chem. Progr.*, **25**, 107 (1964).

[2] (a) D. R. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6859 (1968); (b) D. R. Boston and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR-96. The nearly trigonal prismatic nature of the Co(II) complex has been established by X-ray diffraction (E. C. Lingafelter, *et al.*, submitted for publication; N. J. Rose, private communication).

[3] H. B. Gray, R. Eisenberg, and E. I. Stiefel, *Advan. Chem. Ser.*, **No. 62**, 641 (1967); J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

[4] J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, **91**, 2394 (1969).

[5] (a) W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969); (b) R. A. D. Wentworth, W. O. Gillum, and R. F. Childers, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR-194.