through a square-root function, and the small positive deviation at higher temperatures is thought to be real.

The fact that the magnetic moments reported for the europium complex are slightly below that expected for a $J = {}^{5}/_{2}$ system may be a consequence of a slight shift in the g value. Such a shift has been noted for the $4f^7$ Gd^{3+} ion in metallic gadolinium and attributed to an interaction of the core electrons with the conduction band electrons.[11]

Further studies of the magnetic susceptibility and electron spin resonance of these and similar complexes are in progress.

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Enhancement of Biacetyl Luminescence by Deuteration[1,2]

Sir:

The mechanism of radiationless transitions between electronic states has been the subject of considerable theoretical[3] and experimental[4] study. Since nonradiative, rather than radiative, transitions are lifetime determining for many molecules of photochemical interest,[5] knowledge regarding the detailed nature of how one electronic state passes radiationlessly to another electronic state is crucial for the proper understanding of photochemical efficiencies.

Available theories emphasize either the intramolecular[3a-c] or the intermolecular[3d] effects which determine the rates of radiationless conversions. It is theoretically[3a,6a] expected, and experimentally found,[4,6] that the substitution of deuterium for hydrogen lowers the rate constant for radiationless transitions substantially, but has only a minor effect on radiative rates.[7] However, this effect has not been observed in the condensed phases for any molecules if the states undergoing radiative interconversion are similar in energy.[7] Essentially all of the data published to date pertains to the effect of deuterium substitution on organic molecules in rigid media.[7] Since biacetyl emits both fluorescence[8] and phosphorescence[9] even in fluid solution,[10,11] we have selected this relatively unique case to study how radiationless processes are affected by deuteration, both internally and externally.

Tables I and II present our findings on the luminescence of $CH_3COCOCH_3$ (**1**-H) and $CD_3COCOCD_3$ (**1**-D) under various conditions.[12] The measured lifetimes agree with those in the literature, being higher than those previously[13] reported for **1**-H at 77°K and approaching the highest values reported in fluid solution.[14] We thus feel that adventitious quenchers are not playing a significant role in our measurements.

Table I. Deuterium Enhancement at 77°K[a]

Biacetyl concn, *M*	τ_p, msec	τ_p(deuterated), msec
0.10	2.40	3.32
0.05	2.48	3.35
0.01	2.42	3.41
0.005	2.57	3.30
0.058[b]	1.91	2.78
0.058[c]	2.05	2.82

[a] In 5:5:2 ether:isopentane:ethyl alcohol glass unless otherwise stated. [b] In 3:1 ether:isopropyl alcohol. [c] In 3:1 ether-d_{10}:isopropyl alcohol-d_8.

Table II. Deuterium Enhancement at 25°

Biacetyl concn, *M*	τ_p, msec	τ_p(deuterated), msec
0.05[a]	0.46	0.49
0.05[b]	0.46	0.61
0.01[a]	0.45	0.62
0.01[b]	0.53	0.77
0.005[a]	0.50	0.70
0.005[b]	0.56	0.82

[a] In benzene. [b] In benzene-d_6.

Salient features of our data are the *enhanced fluorescence and phosphorescence of* **1**-*D over* **1**-*H in* C_6H_6 *and the enhanced phosphorescence of both* **1**-*H and* **1**-*D in* C_6D_6. An increase in fluorescence is not expected for the $S_1(n,\pi^*) \rightsquigarrow T_1(n,\pi^*)$ crossing of biacetyl, because these states are separated in energy[15] by only 10 kcal/mole. Nonetheless, the fluorescence intensity of biacetyl increases by 50% upon deuteration in EPA at −198° and by 20% at 25° in benzene. An intermolecular deuterium enhancement of luminescence has not been previously observed for an organic molecule in solution and is surprising.[4b,16]

We have corroborated the enhancement of fluorescence of **1**-D or **1**-H by direct lifetime measurements[17]

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of 0.05 *M* benzene solutions of **1**-H (τ_f = 10.0 nsec) and **1**-D (τ_f = 11.7 nsec).

An independent check of some of our spectroscopic data at 25° was possible since Stern–Volmer quenching of **1**-H and **1**-D by $(CH_3)_2CHOH$ was observed.

$$\Phi_p^0/\Phi_p = 1 + k_q\tau_p[Q]$$

These results are reported in Table III and are consistent with a deuterium enhancement of lifetime and also with literature data[14a,18] for quenching of triplet **1**-H.

Table III. Stern–Volmer Quenching by Isopropyl Alcohol

Biacetyl concn, *M*	$k_q\tau_p$, M^{-1}	k_q, 10^3 l. mole^{-1} sec$^{-1\,a}$
0.05^b	1.50	3.3
0.05^c	1.55	3.2
0.05^d	1.63	3.5
0.05^e	2.22	3.6
0.01^b	1.50	3.3
0.01^c	1.66	2.7
0.01^d	1.57	3.0
0.01^e	2.28	3.0
0.005^b	1.57	3.1
0.005^c	1.92	2.7

[a] k_q calculated from τ_p values in Table II. [b] **1**-H in benzene. [c] **1**-D in benzene. [d] **1**-H in benzene-d_6. [e] **1**-D in benzene-d_6.

In conclusion, the response of the radiationless rate processes of biacetyl toward intra- and intermolecular deuterium substitutions appears to be unique among studies reported to date. This uniqueness derives in part from the dearth of published data concerning deuterium effects on molecules other than aromatic hydrocarbons, but implies that a theoretical study of a possible special role of the n,π^* state in determining radiation less rates should be considered.[19]

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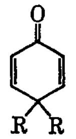
A Criterion for Zwitterionic Intermediates in the Photochemistry of 2,5-Cyclohexadienones

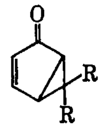
Sir:

The wealth of information on the photochemistry of 2,5-cyclohexadienones which has appeared in the literature in the past 12 years has been interpreted, almost without exception, in terms of zwitterionic species as intermediates.[1,2] This belief in ionic pathways seems to be based on the parallelism between the chemistry of the phototransformations and polar rearrangements of nonphotochemical origin in related compounds.

A possible test for the nature of the intermediates in these systems is a study of the behavior of isolated molecules of the reactant, *i.e.*, in the vapor phase at low pressure. At the photon energies used in the excitation of the dienones (<4 eV), in isolated molecules, it is unlikely that polar structures in which unit charges are separated by the distance of one C–C bond are attainable.[3] On the other hand, in polar solvents the large dielectric constant of the medium, as well as solvation, can lower the energy (with respect to the ground state) of these structures to a point where they may be accessible to the electronically excited dienone molecules. Hence a comparison of the photochemistry of a given compound in the gas phase at low pressure and in solution in a polar solvent can be used as a significant test for the intermediacy of ionic species along a given pathway. By the use of this reasoning, we shall demonstrate that in a typical 4,4-disubstituted 2,5-cyclohexadienone (I) the photoisomerization to a 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-one (II) and in turn to the 6,6-disubstituted cyclohexa-2,4-dienone (III) need not involve zwitterionic species while the photorearrangements of II to the phenols IV and V are, in all probability, polar reactions.



Ia, R = CH_3
b, R = C_6H_5



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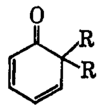

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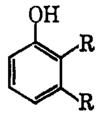
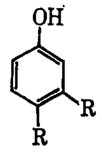
b, R = C_6H_5



IVa, R = CH_3
b, R = C_6H_5



Va, R = CH_3
b, R = C_6H_5

Irradiation of 4,4-dimethylcyclohexa-2,5-dienone (Ia) at 3000–3700 Å in solution in cyclohexane to conversions of 40% gave two isomeric ketones. One of these was identified as 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (IIa) on the basis of its infrared (conjugated C=O at 5.85 μ; medium absorptions at 7.49, 8.48, 11.72, and 11.90 μ), nmr (quartet at τ 2.73 (1 H), doublet at 4.18 (1 H), quartet at 7.73 (1 H), doublet 8.20 (1 H), and singlets at 8.77 (3 H) and 8.85 (3 H)), mass (parent peak at 122), and ultraviolet spectra (structureless absorption similar to IIb).[4] The second compound was identified as 6,6-dimethylcyclohexa-2,4-dienone (IIIa)[5] by comparing its spectra with those of an authentic sample.[6] Irradiation of Ia at the same wavelength in aqueous dioxane gave, in addition to IIa, two compounds which were separated by extraction with sodium hydroxide. By comparison with authentic samples on a thin layer chromatogram these compounds were identified as the phenols IVa and Va, the latter being in ex-

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