ure 1.[6] All bond distances and angles agree well, within experimental error (0.02 Å and 2°), with generally accepted values.[7] There were no abnormally short intermolecular contracts.

The unusual Lythrumine skeleton has recently been identified in *Lythrum anceps*, a member of the Lythraceae family which is native to Japan.[8] Another structural type with a piperidine ring (**4**) in place of the quinolizidine ring has also been isolated from *L. anceps*.

We isolated a third structural varient from *L. lanceolatum*, the lactone alkaloid decinine (**5**), which was found previously in the Lythraceae plants *Decodon verticillatus*,[9] *Heimia* species[10] (as the dehydro derivatives, lythrine), and *Lagerstroemia indica*.[11] This is the first observation of the lactone structural type in a *Lythrum* species. This observation supports the taxonomical grouping of *Lythrum* together with *Decodon*, *Heimia*, and *Lagerstroemia* in the Lythraceae plant family. Furthermore, this finding suggests that all three structural types of Lythraceae alkaloid (**1**, **4**, and **5**) have a common biosynthesis.[12,13]

Acknowledgment. We thank Professor Robert Godfrey of Florida State University for assistance in locating and collecting plant material. We thank the National Institutes of Health for a Career Development Award (GM 6380) to J. P. F.

Supplementary Material Available. A listing of fractional coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6467.

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(11) J. P. Ferris, R. C. Briner, and C. B. Boyce, *J. Amer. Chem. Soc.*, **93**, 2958 (1971).

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(13) The biosynthesis proposed for **5**[12] can be readily accommodated to account for the formation of the *Lythrum* alkaloids. Oxidation of the proposed isopelletierine intermediate and condensation of the resulting enamine with acetoacetate gives 2,6-diacetonylpiperideine. The subsequent condensation of this piperidine derivative with *p*-oxygenated benzaldehydes and oxidative phenyl coupling follows familiar routes to **1** and **4**.

(14) Camille and Henry Drefus Foundation Awardee, 1972–1977. Fellow of the Alfred P. Sloan Foundation, 1973–1975.

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Tetramethyl-1,2-dioxetane. Simple Procedures for Chemiexcitation or Photoexcitation of Acetone Phosphorescence in Fluid Solution[1]

Sir:

In spite of the tremendous amount of published work[2] concerned with the photochemistry of alkanones in fluid solution, attempts to observe phosphorescence from simple alkanones[3] by conventional spectrophotoluminescence techniques have apparently been unsuccessful.[4,5] For example, it has been reported that no phosphorescence could be detected from either acetone or acetone-d_6 in degassed solvents at room temperature or even in solutions at Dry Ice temperature.[4] Furthermore, it has been reported that the photoluminescence of acetone is unaffected by the presence of dissolved oxygen.[4,6] In view of these reported observations, we,[7] and apparently other workers,[6,8,9] have assumed that the photoluminescence observed when acetone is excited in fluid solution is pure fluorescence and that the phosphorescence of acetone is difficult or impossible to observe by conventional photoluminescence techniques.[10] In spite of the above experimental reports, acetone phosphorescence has been detected by time-resolved flash photolysis[5] and by time-correlated single-photon counting.[11,12] Each

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(1) Molecular Photochemistry. 70. Paper 69: P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973). Paper 68: P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *ibid.*, **95**, 3025 (1973).

(2) For a review see N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 5, 92 (1972).

(3) Studies of the phosphorescence of organic molecules in fluid solution have been very intense recently because of the theoretical implications and practical importance of such research: C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **65**, 2823 (1969); *Chem. Commun.*, 749 (1968); J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970); W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969); *Chem. Commun.*, 1087 (1969); A. F. Vando and D. M. Hercules, *J. Amer. Chem. Soc.*, **92**, 3573 (1970); C. A. Parker and A. Hatchard, *J. Phys. Chem.*, 66, 2506 (1962); M. A. Slifkin and R. H. Walmsley, *Photochem. Photobiol.*, **13**, 57 (1971); (i) J. Langelaar, R. P. H. Rettschnick, and G. J. Hoijtink, *J. Chem. Phys.*, **54**, 1 (1971); S. C. Tsai and G. W. Robinson, *ibid.*, **49**, 3184 (1968); C. A. Parker, *Ber. Bunsenges. Phys. Chem.*, **74**, 764 (1970); M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, **68**, 539 (1972); R. W. Yip, R. O. Loutfy, Y. L. Chow, and L. K. Magdzinski, *Can. J. Chem.*, **50**, 3426 (1972); D. I. Schuster, T. M. Weil, and A. M. Halpern, *J. Amer. Chem. Soc.*, **94**, 8248 (1972).

(4) (a) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966); (b) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(5) The only report of phosphorescence of triplet acetone in fluid solution required a flash experiment in which the emission intensity after a 30 μsec delay of a 5 J photoflash was measured point-by-point: G. Porter, R. W. Yip, J. M. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, 67, 3149 (1971). This method of obtaining a phosphorescence spectrum is quite elaborate and unconventional and might be taken to imply that the authors were unsuccessful in obtaining acetone phosphorescence by conventional spectrophotoluminescence techniques. See also R. W. Yip, R. O. Loutfy, Y. L. Chow, and L. K. Magdzinski, *Can. J. Chem.*, 50, 3426 (1972).

(6) M. O'Sullivan and A. Testa, *J. Amer. Chem. Soc.*, 92, 5842 (1970).

(7) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, 21, 499 (1970).

(8) A. Halpern and W. R. Ware, *J. Chem. Phys.*, **54**, 1271 (1971).

(9) G. D. Renkes and F. S. Wettack, *J. Amer. Chem. Soc.*, **91**, 7514 (1969).

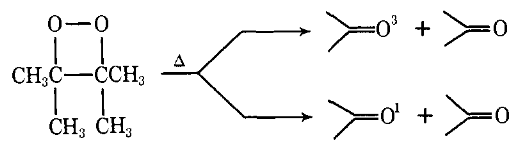
(10) Basically the observation of phosphorescence in fluid solution is a problem in sensitivity with instrumental noise, fluorescence, and chemical quenching of triplets contributing to make detection of phosphorescence difficult. For a review of the problems involved see C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968, p 397 ff.

(11) J. C. Dalton, R. R. Hautala, D. R. Charney, J. J. Snyder, and N. J. Turro, *J. Amer. Chem. Soc.*, in press; A. Yekta, Columbia University, unpublished results.

(12) We thank Professer A. Halpern of New York University for verifying these phosphorescence results on his single-photon counting apparatus.

of these techniques is complicated and not as generally available as standard spectrophotofluorimeters. We have employed conventional spectrophotoluminescence techniques and found that, contrary to expectations based on reports in the literature, acetone phosphorescence can be obtained quite readily in fluid solution of ordinary organic solvents, either by chemiexcitation or photoexcitation techniques.

The thermolysis of tetramethyl-1,2-dioxetane (**1**) produces triplet acetone (^{3}K) as the major product in good yield (eq 1).[13] Minor amounts of singlet acetone



(1)

(2)

1

(^{1}K) are also produced (eq 2).[13] At any given temperature, the intensity of *direct* chemiluminescence (acetone fluorescence and phosphorescence) from **1** is given by eq 3, where ϕ_*^S and ϕ_*^T are the excitation efficiencies for formation of ^{1}K and ^{3}K, respectively, ϕ_F and ϕ_P are the fluorescence and phosphorescence yields of acetone, k_1 is the unimolecular rate constant (sec^{-1}) for *total* disappearance of **1**, and [**1**] is the concentration of **1** in moles/liter. Under these conditions the absolute intensity of direct chemiluminescence (I_{Cl}) is in einsteins/(liter sec). In the presence of oxygen (aerated solution) in ordinary organic solvents (*e.g.*, benzene, Freon, acetonitrile)[11] $\phi_*^S\phi_F \gg \phi_*^T\phi_P$ because of the tremendous quenching effect of oxygen[14] on ^{3}K. Thus, eq 4 is an accurate relationship between the intensities of direct chemiluminescence from **1** in the presence ($I_{\mathrm{Cl}}^{O_2}$) and absence (I_{Cl}) of air.

$$I_{\mathrm{Cl}} = (\phi_*^S\phi_F + \phi_*^T\phi_P)k_1[\mathbf{1}] \qquad (3)$$

$$\frac{I_{\mathrm{Cl}}}{I_{\mathrm{Cl}}^{O_2}} = 1 + \frac{\phi_*^T\phi_P}{\phi_*^S\phi_F} \qquad (4)$$

Equation 4 serves as a basis for estimating whether or not it is feasible to detect acetone phosphorescence from **1** in ordinary fluid organic solvents. The excitation ratio ϕ_*^T/ϕ_*^S for **1** is proposed[13,15] to be about the order 10^2 and ϕ_F for acetone is close to 10^{-3} near room temperature.[6,8,16] Furthermore, since intersystem crossing occurs with essentially unit effiecicny for acetone singlets,[4] $\phi_P = k_P^\circ\tau_P$, where k_P° is the inherent phosphorescence rate constant of acetone and τ_P is the experimental phosphorescence lifetime under a specific set of conditions. We[11] have measured τ_P to be $\sim 10^{-5}$–10^{-6} sec^{-1} for degassed acetonitrile solutions of acetone and k_P° is reported[17] to be of the order of 10^2 sec^{-1}. Thus, from eq 4, we conclude that we should see chemiluminescence (mainly acetone phosphorescence) enhancements of the order of 10^2 upon degassing acetonitrile solutions of **1**, unless the presence of **1** results in technical or chemical complications.[18]

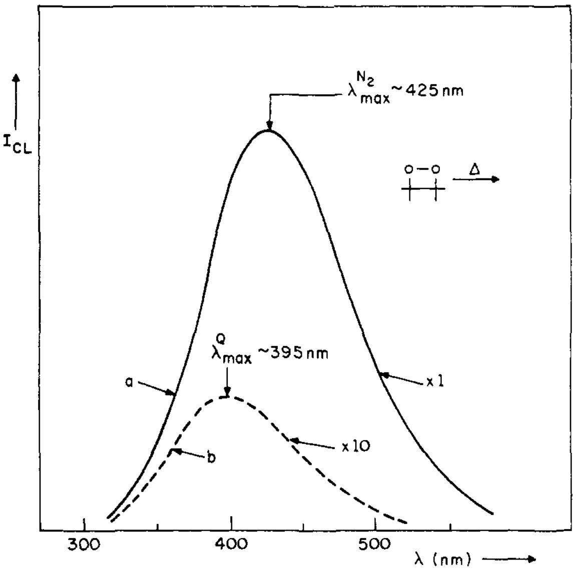


Figure 1. Chemiexcited phosphorescence (curve a) and fluorescence (curve b) of acetone obtained on thermoysis of 10^{-2} *M* tetramethyl-1,2-dioxetane in Freon-113 or acetonitrile at 40°. Intensities are uncorrected and given in arbitrary units. Curve a was obtained by purging the solutions with nitrogen; curve b was obtained for aerated solutions containing 10^{-1} *M* acrylonitrile. The uncorrected maximum of acetone phosphorescence obtained at low temperature (77°K) in ethyl alcohol–ether corresponds closely to the maximum of curve a.

Indeed, simple nitrogen purging of acetonitrile solutions of **1** at 30° results in a tremendous enhancement ($\sim 10^2$) of chemiluminescence from **1** (Figure 1). Importantly, the maximum of the chemiluminescence emission shifts from 395 nm (position of photoexcited acetone *fluorescence*)[19] to about 425 nm as the result of simple "degassing" with nitrogen. We assign this new chemiluminescence to acetone phosphorescence because of the following observations: (a) the separation of the chemiluminescence of **1** in aerated solution (CAS) and the new chemiluminescence of **1** in nitrogen degassed solution (CNS) equals that ($\sim$30 nm) reported for acetone fluorescence and phosphorescence;[20-22] (b) the CNS (425-nm emission) is strongly quenched by addition of oxygen, acrylonitrile, and 1,3-pentadiene, each quencher being known[2] as essentially a diffusion

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(13) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(14) Oxygen is an efficient but apparently not necessarily a diffusion controlled quencher of carbonyl triplets: P. B. Merkel and D. R. Kearns, *J. Chem. Phys.*, **58**, 398 (1973).

(15) N. J. Turro, H. C. Steinmetzer, and P. Lechtken, *Justus Liebigs Ann. Chem.*, in press.

(16) An earlier report[4] of $\phi_F = 0.01$ is apparently too high. See ref 8 for a discussion of this point.

(17) E. H. Bilmore, G. E. Gibson, and D. S. McClure, *Justus Liebigs Ann. Chem.*, 20, 829 (1952); **23**, 399 (1955).

(18) At high concentrations ($\sim$0.1 *M*) or in the absence of triplet quenchers, a quantum chain reaction, in which an acetone triplet destroys a molecule of 1 to produce another acetone triplet in a chain process, determines the rate of decomposition of 1: P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973).

(19) The results reported in Figures 1 and 2 are uncorrected raw data from a Hitachi-Perkin Elmer MPF-2A spectrophotometer. The combination of broad maximum and relatively weak signals makes for rather large corrections for lamp, monochromator, phototube, and other instrumental factors.[10] When these corrections are made, however, our values ($\sim$405 nm) are within the experimental error of those reported in the literature.[4,6,8,9]

(20) The same problem of instrumental corrections[19] applies to phosphorescence. We feel confident, however, that the emission at 420–425 nm (Figures 1 and 2) is indeed acetone phosphorescence because on our instrument, we find that acetone phosphorescence at 77°K (ethyl alcohol–ether, 1:1) maximizes at 425 nm and has a lifetime (0.5 msec) quite close to that reported in the literature.[21] When instrumental corrections are made, the emission maxima of curves a in Figures 1 and 2 fall in the region of 440–450 nm, within the experimental error of literature values for acetone phosphorescence.[5,22]

(21) J. C. Miller and R. F. Borkman, *J. Chem. Phys.*, **56**, 3727 (1972).

(22) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **92**, 258 (1970).

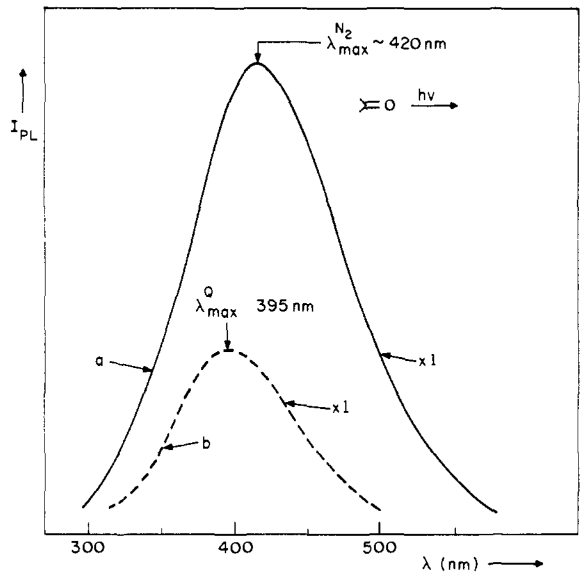

Figure 2. Photoexcited acetone luminescence (curve a) and fluorescence (curve b). Acetone was 0.1 *M* in acetonitrile or Freon-113 at 3°. Intensities are uncorrected and in arbitrary units. Curve a was obtained by purging the solutions with nitrogen; curve b was obtained for aerated solutions containing 10^{-1} *M* acrylonitrile. The intensity of the maximum of curve a is approximately three times that of curve b under comparable conditions; however, even higher intensities, corresponding to an increase in the contribution of acetone phosphorescence, can be achieved by vacuum degassing and rigorous solvent and solute purification.

controlled quencher of ^{3}K with negligible effect on the emission at 395 nm; (c) the quenching effect by O_2 is totally reversible, bubbling with nitrogen resulting in CAS, but purging with nitrogen after addition of 1,3-pentadiene does not bring back the CNS; (d) the intensity of 9,10-dibromoanthracene chemiluminescence which is activated mainly by triplet–singlet energy transfer is tremendously enhanced by nitrogen deoxygenation.

These results, in fact, suggested that acetone phosphorescence should be detected under the conventional spectrophotoluminescence conditions by simple deoxygenation of the sample by nitrogen bubbling. Indeed, we were gratified to find deoxygenation of acetonitrile solutions of acetone either with nitrogen purging or freeze–thaw cycles on a vacuum line allows ready detection of a new acetone photoluminescence (Figure 2). The lifetime of this emission was found to be of the order 2–20 μsec, depending on the thoroughness of degassing and purification of solvent and acetone. The effect of degassing on the photoluminescence of cyclohexanone (τ_P ~3 μsec and limited by α cleavage[7]) is much less than for acetone and *no effect* of degassing was observed for cyclopentanone (τ_P ~0.3 μsec).[7]

It is important to note that within the experimental error $\phi_*{}^T$ is ~0.5, calculated (eq 4) from the work reported here and the literature values of $\phi_F{}^5$ and $\phi_*{}^S$, and the inherent phosphorescent lifetime. This is the same value deduced from chemical titration of acetone triplets generated from thermolysis of **1**.[13]

In conclusion, relatively intense acetone phosphorescence can be easily observed in fluid solution near room temperature by simple nitrogen degassing of solutions of **1** in acetonitrile and other photochemically "inert" solvents. This result opens many new and exciting possibilities for study and use of alkanone phosphorescence in solution. In particular, contradictory conconclusions[23,24] concerning the kinetics of acetone decay processes and photoreactions may now be resolved. For example, we have studied the Stern–Volmer quenching of the CNS of **1** by cyclohexane (10^{-2}–0.5 *M*) in acetonitrile at 50° and obtained a linear quenching plot, with a slope of 2.7 M^{-1}. The lifetime of acetone triplets at this temperature in acetonitrile was determined to be ~8×10^{-6} sec by independent measurements by single photon counting. Thus, the rate constant for quenching of acetone triplets by cyclohexane is calculated to be 3.4×10^5 M^{-1} sec^{-1}. We feel that this value is in excellent agreement with a value (3.2×10^{-5} M^{-1} sec^{-1}) measured by the time delayed phosphorescence technique at 25°.

Acknowledgments. The authors gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant AFOSR-70-1848) and by the National Science Foundation (Grant NSF-GP-26602X). We also wish to thank Mr. David Charney for assistance and advice in measurement of the lifetime and time resolved emission of acetone triplets. We would also like to thank Mr. Neil Schore for helpful discussions and comments concerning the ideas and results reported here.

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(23) The status of the dynamics of acetone triplets is quite confusing since conflicting conclusions and evaluations of lifetimes appear in the literature. For example, "energy hopping" between acetone molecules has been invoked[4] to explain increasing Stern–Volmer quenching constants as one proceeds from hexane to acetone as solvent. This interpretation has been challenged[24] on the basis of new Stern–Volmer quenching data. The assumptions used to interpret the data have, in turn, been challenged as incorrect.[5]

(24) P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966).

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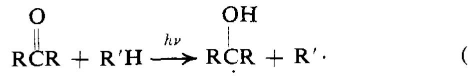
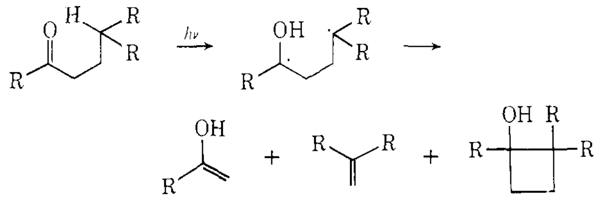
Entropic Control of the Photochemical Reactivity of Alkyl Phenyl Ketones[1]

Sir:

The inter- and intramolecular hydrogen abstraction reactions of carbonyl compounds (eq 1, 2) are among



$$\overset{\displaystyle O}{\overset{\|}{RCR}} + R'H \xrightarrow{h\nu} \overset{\displaystyle OH}{\overset{|}{R\dot{C}R}} + R'\cdot \qquad (1)$$



(2)

the most extensively studied photochemical reactions.[2] The formation of the intermediate radical pair or 1,4-biradical is normally described in terms of transition-

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(1) The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and PPG Industries for support of this research.

(2) For recent reviews, see (a) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, 21, 499 (1970); (b) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).