Photochemistry of Phosphate Esters: α-Keto Phosphates as a Photoprotecting Group for Caged Phosphate

Richard S. Givens,* Phillip S. Athey,† Bogdan Matuszewski,‡ L. William Kueper, III, Jie-you Xue,§ and Thomas Fister

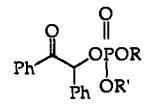
Contribution from the Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045

Received January 8, 1993

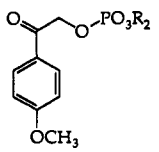
Abstract: Irradiation of two families of α-keto phosphates yielded rearrangement products and deprotected phosphates as the major products. For both sets of reactants, the triplet excited state of the ketone reacted with quantum efficiencies that ranged from 0.10 to 0.38. Desyl phosphates yielded 2-phenylbenzo[*b*]furan independent of the nature of the solvent whereas phosphate esters of α-hydroxy-*p*-methoxyacetophenone rearranged to esters of *p*-methoxyphenylacetic acid. In all cases, the phosphate group with the remaining ligands intact was released in nearly quantitative yield. The desyl group was further developed as a *cage* ligand for cAMP. Upon photolysis, the desyl caged ester of cAMP (**13**) quantitatively released the nucleotide with a quantum efficiency of 0.33 ± 0.01 and a unimolecular rate constant of $7.1 \times 10^8\ s^{-1}$. Additional synthetic, product, and mechanistic studies are reported for the two series of α-keto phosphates.

In earlier publications,[1] we reported that benzyl and 1- and 2-naphthylmethyl phosphates undergo efficient, photochemically induced nucleophilic substitution reactions in which phosphate functions as a nucleofuge. We provided evidence through oxygen-18 labeling, stereochemical, and substituent studies that photolysis of the carbon–oxygen bond of benzylic phosphates produced a reactive benzyl cation–phosphate anion pair.[1a-c] A comparison of phosphate with other photoactive nucleofugal groups by Pincock *et al.*[2a] established its efficacy as a good photolabile leaving group. Furthermore, we have shown that efficient reactions of the resultant carbocation with nucleophiles or nucleophilic solvents generally produce good yields of substitution products.

We now report details on the photochemistry of two families of α-keto phosphates, 2-oxo-1,2-diphenylethyl phosphate[1d] (*e.g.*, desyl phosphates **1a–c**) and 2-(4-methoxyphenyl)-2-oxoethyl phosphate (*e.g.*, α-phenacyl phosphate **2a**), and application of these reactions for the photorelease of a nucleotide, cAMP.



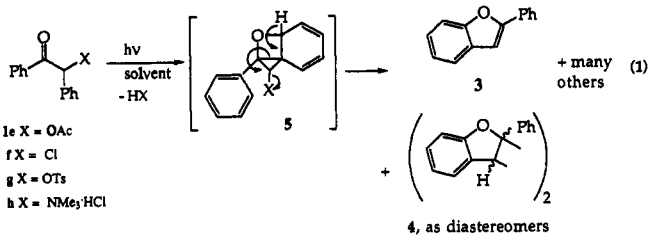
1a: R = R' = CH_2CH_3
b: R = $CH(CH_3)_2$; R' = H or Na^+
c: R = R' = H or Na^+
d: α-D, R= R' = CH_2CH_3



2a

Through these investigations, we have shown that α-keto phosphates are kinetically superior alternatives to *o*-nitrobenzyl esters[3,4] for the photorelease of biologically important phosphates.

The desyl chromophore was first investigated as a possible photoprotecting group for carboxylic acids (*e.g.*, **1e**) by Sheehan and Wilson in 1964.[5] Among the minor photoproducts were the photocyclization product 2-phenylbenzo[*b*]furan (**3**) and its photodimers **4** (eq 1). The efficiency for conversion of the desyl



1e X = OAc
f X = Cl
g X = OTs
h X = NMe_3·HCl

4, as diastereomers

(1)

ester to **3** was shown to be highly dependent on the nature of the substituents on the benzyl aromatic ring, with the *m*-methoxy substitution giving the highest yields of the benzofuran. The suggested mechanism for the formation of benzofuran began with n,π* excitation of the ketone followed by intramolecular cyclization to form oxabicyclo[2.1.0]pentane intermediate **5**. Benzyl desyl sulfide was also shown to cyclize exclusively to 2-phenylbenzo[*b*]thiophene upon irradiation,[6] in agreement with the mechanism suggested earlier by Sheehan *et al.*[5]

The photochemistry of other, closely related α-keto derivatives is exemplified by the series of substituted phenacyl chlorides **2b**. In 1961, Anderson and Reese[7] reported that phenacyl chlorides containing electron-donating groups at the *para* and *ortho* positions (*e.g.*, 4-OH, 4-OCH_3, and 2-OCH_3), upon photolysis, rearranged primarily to esters (*e.g.*, **6**, eq 2), whereas electron-withdrawing substituents led exclusively to reduction product 4-methoxyacetophenone (**2e**). Few other reports relevant to the photochemistry of 4-methoxyphenacyl derivatives appeared until

† Current address: Dow Chemical Company, Freeport, TX 77541.
‡ Current address: Merck Research Laboratories, West Point, PA 19486.
§ Current address: Department of Chemistry, Nankai University, Tianjin, Peoples Republic of China.

(1) (a) Givens, R. S.; Matuszewski, B. *J. Am. Chem. Soc.* **1984**, *106*, 6860. (b) Givens, R. S.; Matuszewski, B.; Athey, P. S.; Stoner, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 6016. (c) Givens, R. S.; Singh, R. *Tetrahedron Lett.* **1991**, *48*, 7013. (d) A preliminary account has appeared; see: Givens, R. S.; Athey, P. S.; Matuszewski, B.; Kueper, L. W., III; Xue, J.-y. *J. Am. Chem. Soc.* **1992**, *114*, 8708.

(2) (a) Pincock, J. A.; Arnold, B.; Jurgens, A. *Can. J. Chem.* **1985**, *63*, 3140. (b) Arris, J.; Braddily, J.; Buchanan, J. G.; Thain, E. M. *J. Chem. Soc., Chem. Commun.* **1956**, 4968. (c) Baldwin, J. E.; McConnaughie, A. W.; Moloney, M. G.; Pratt, A. J.; Shim, S. B. *Tetrahedron* **1990**, *46*, 6879–6884.

(3) Givens, R. S.; Kueper, L. W., III. *Chem. Rev.* **1993**, *93*, 55–66.

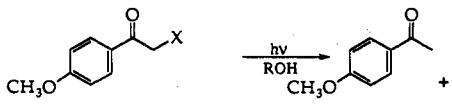
(4) (a) Engels, J.; Schlaeger, E. J. *Med. Chem.* **1977**, *20*, 907. (b) Nerbonne, J. M.; Richard, S.; Nargeot, J.; Lester, H. A. *Nature* **1984**, *310*, 74. (c) Nargeot, J.; Nerbonne, J. M.; Engels, J.; Lester, H. A. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 2395. (d) Kaplan, J. H.; Forbush, B.; Hoffman, J. F. *Biochemistry*, **1978**, *17*, 1929. (e) McCray, J. A.; Trentham, D. R.; Reid, G. P.; Walker, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 7170. (f) McCray, J. A.; Trentham, D. R. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 239. (g) Corrie, J. E. T.; Trentham, D. R. Caged Nucleotides and Neurotransmitters. In *Bioorganic Photochemistry*; Morrison, H., Ed.; Wiley: New York, 1993; Vol. 2.

(5) (a) Sheehan, J. C.; Wilson, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 5277. (b) Sheehan, J. C.; Wilson, R. M.; Oxford, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 7222.

(6) Sheehan, J. C.; Umezawa, K. *J. Org. Chem.* **1973**, *38*, 3771.

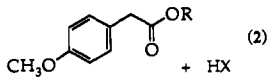
(7) Anderson, J. D.; Reese, C. B. *Tetrahedron Lett.* **1962**, 1.

0002-7863/93/1515-6001$04.00/0



2a: X = $O_2P(OEt)_2$
b: X = Cl
c: X = O_2CR
d: X = OPO_3H_2

2e: X = H

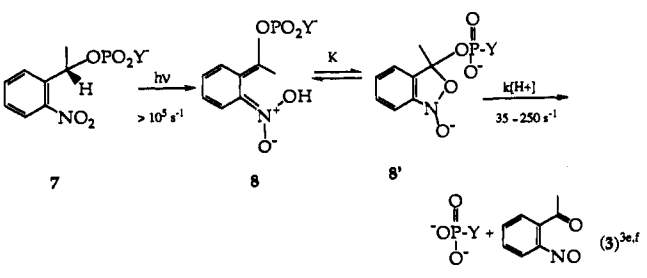


(2)

6a R = CH_3
b R = $C(CH_3)_3$

Sheehan *et al.*[5] demonstrated their usefulness as photoprotecting groups for simple carboxylic acid derivatives. In a comprehensive study, a series of phenacyl-protected esters was shown to liberate the free acid and 4-methoxyacetophenone (**2e**) as exclusive photoproducts in either ethanol or dioxane. Concurrent with our earlier studies on **1a–c**, Epstein *et al.*[8] reported the photochemistry of diethyl 4-methoxyphenacyl phosphate (**2a**) in dioxane. In accord with Sheehan's studies,[5] Epstein reported that 4-methoxyacetophenone was the exclusive product which resulted from the homolysis of the α-carbon–phosphate bond followed by hydrogen abstraction from the solvent by the α-keto radical, paralleling the photochemistry of the corresponding carboxylate esters. Epstein further suggested that the 4-methoxyphenacyl group might serve as a photoprotecting group for nucleotides. Baldwin *et al.*[2c] reported that 4-methoxyphenacyl dihydrogen phosphate (**2d**) also gave 4-methoxyacetophenone as the only ketone product. However, when compared with the benzoin and 2-nitrobenzyl dihydrogen phosphates, he found that **2d** was the least efficient in the release of inorganic phosphate (P_i).

These studies are the result of an intense interest by mechanistic biochemists in the general design and application of photoprotecting groups for phosphates, a subject of a series of recent reviews by Corrie and Trentham,[4f,g] Lester *et al.*,[9] and Givens and Kueper.[3] These reviews provide a detailed analysis of the parameters which influence the photochemistry of protecting or *cage* groups including the irradiation conditions, solvents, and structure. According to Lester,[9] ideal cage groups should possess the following five properties: (1) good solubility in water at high ionic strength, (2) rapid and efficient photoreactivity, (3) good thermal and solvolytic stability, (4) high absorptivity at wavelengths greater than 310 nm, and (5) biological stability (inertness) of the released protection group. One of the few functional groups that meets most of the criteria is the *o*-nitro-α-phenylethyl group (*e.g.*, **7**, eq 3).[4] Upon irradiation, caged *o*-nitro-α-phenylethyl



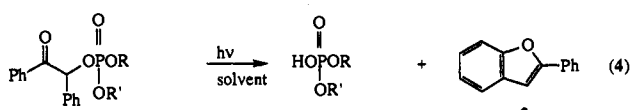
7 8 8'

(3)[3e,f]

derivatives of phosphates, amides, carboxylic esters, and ethers usually release the corresponding nucleofuge in good yields.[4] However, a well-known limitation of the *o*-nitro-α-phenylethyl group is the slow release of the ligand from a relatively long-lived *aci*-nitro intermediate. For *o*-nitro-α-phenylethyl phosphates (eq 3), the rate of release of the phosphate is limited by the rate of hydrolysis of the enol ether formed upon photolysis (*e.g.*, release of ATP from *o*-nitro-α-phenylethyl ATP occurs through *aci*-nitro intermediate **8**; the intermediate decays with a rate of only 86 s^{-1} at pH 7.1).[4e-g] A second major disadvantage derives from the highly absorbing products that often interfere with spectroscopic analysis of the reactions of the released nucleotide and the extent of conversion of the caged nucleotide. Finally, α-nitrosoacetophenone is not biochemically benign (a violation of Lester's fifth rule) and may interfere with the normal biochemical functions under investigation.

Results

Synthesis and Exploratory Photochemistry. Desyl Phosphates. Desyl diethyl phosphate (diethyl 2-oxo-1,2-diphenylethyl phosphate, **1a**) was synthesized by modification of the known procedures for esterification of diethyl phosphorochloridate with the appropriate alcohol.[10] Irradiation of **1a** at 300 nm in acetonitrile, methanol, or benzene resulted in the formation of 2-phenylbenzo[*b*]furan (**3**) as a primary product as established by HPLC analysis, isolation, and spectroscopic identification (eq 4). The time-dependent disappearance of **1a** was not significantly



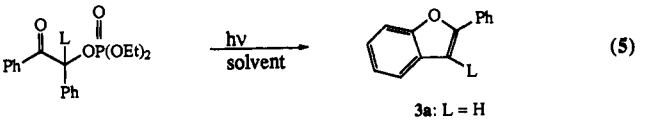
(4)

1a: R = R' = CH_2CH_3
b: R = $CH(CH_3)_2$; R' = H or Na^+
c: R = R' = H or Na^+

9a: R = R' = Et
9b: R = $CH(Me)_2$; R' = H or Na^+
9c: R = R' = H or Na^+

influenced by the nature of the solvent. At low conversions (<15%), furan **3** was the only detected product resulting from the desyl group. At higher conversions, photodimerization of **3** to **4** (a mixture of isomers) was also observed. The formation of photodimers **4** was considerably suppressed when irradiations were conducted at 350 nm where **3** absorbs only weakly. Phosphates **9a–c** were not isolated but shown to be present by ^{31}P NMR.

1-Deuteriodesyl diethyl phosphate (**1d**, eq 5) was synthesized by a procedure analogous to that for **1a** from benzoin-α-*d* which was synthesized by sodium amalgam reduction of benzil followed by the addition of D_2O. The labeled ester was irradiated at 350 nm in methanol, benzene, or benzene moistened with H_2O. In all cases, the major photoproduct was 3-deuterio-2-phenylbenzo[*b*]furan (**3b**, eq 5). The deuterium content of the photoproduct



(5)

1a: L = H
1d: L = D

3a: L = H
3b: L = D

was the same as that of the starting α-keto phosphate. Similarly, when unlabeled phosphate ester **1a** was irradiated in methanol-*O*-*d* or benzene moistened with D_2O, the solvent deuterium was not incorporated. The mass spectral data and isotope content of the photoproducts from irradiation in several deuterated solvents are given in Tables I and II, respectively.

In order to have access to a variety of mixed desyl esters, an alternative to the available procedures for the synthesis of mixed phosphates was developed. The common strategy of the addition of 1 equiv of an alcohol to either a di- or triactivated phosphate equivalent (*i.e.*, mono- and diester phosphorochloridates) followed by the addition of a second alcohol often leads to complicated,

(8) (a) Epstein, W. M.; Garrossian, M. *J. Chem. Soc., Chem. Commun.* **1987**, 532. (b) Baldwin, J. E.; McConnaughie, A. W.; Moloney, M. G.; Pratt, A. J.; Shim, S. B. *Tetrahedron* **1990**, *19*, 6879.

(9) (a) Gurney, A. M.; Lester, H. A. *Physiol. Rev.* **1987**, *67*, 583. (b) Lester, H. A.; Nerbonne, J. M. *Annu. Rev. Biophys. Bioeng.* **1982**, *11*, 151.

(10) Kenner, G. W.; Mather, J. *J. Chem. Soc.* **1956**, 3524.

Table I. Mass Spectral Data of 2-Phenylbenzo[*b*]furan Obtained upon Irradiation of Desyl Diethyl Phosphates **1a** and **1d**

irradiated phosphate[a]	reaction solvent	fragmentation pattern for **3**, relative intensity at *m/e*							
		196	195	194	167	166	165	140	139
1a	CH_3OH	1.6	16.0	100	*[c]	6.7	44.7	*	5.1
1a	CH_3OD	1.4	16.1	100	*	11.3	76.0	2.3	19.4
1a	C_6H_6	1.6	16.0	100	*	5.9	39.1	*	4.8
1a	CH_3CN	1.9	16.4	100	*	*	38.1	*	*
1d	CH_3OH	16.3	100	26.4	6.3	42.6	20.9	4.6	2.8
1d	C_6H_6	16.9	100	26.8	7.0	46.6	23.7	6.9	4.2
1d	C_6H_6/D_2O	16.8	100	26.9	3.7	51.2	26.3	8.0	5.0
1a[b]			*	100	*	6.2	43.2	*	6.2

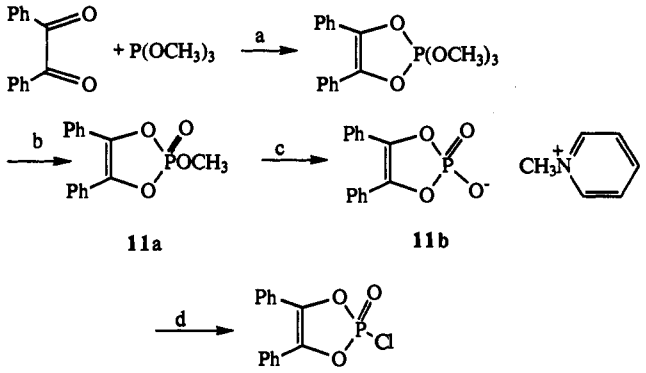
[a] See Experimental Section for details. [b] Vebrel, J.; Roche, M.; Goreg, J. Org. Mass Spectrom. **1977**, *12*, 751. [c] The asterisk indicates negligible intensity.

Table II. Isotopic Distribution of Deuterium for **1d** and **3** from the Photolysis of 2-Deuterio Desyl Phosphate **1d**

compd	irradiation solvent	isotopic purities (%)[a]		
		d_0	d_1	d_2
3	CH_3OH	21.51	78.04	0.45
3	C_6H_6	21.75	77.39	0.68
3	C_6H_6/D_2O	21.67	77.39	0.94
1d	(starting ester)	20.64	79.36	

[a] Determined from analysis of the mass spectral data (see Table I).

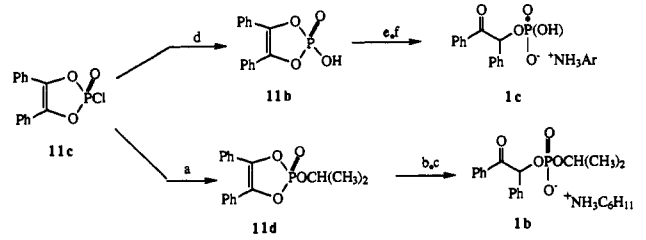
Scheme I. Synthesis of Dioxaphosphole Reagent for Desyl Phosphate Ester Syntheses[a]



11c (overall yield from benzil > 90%)

[a] (a) Acetonitrile; (b) CH_3COBr, acetonitrile; (c) pyridine, benzene; (d) Cl_2CO, benzene.[14]

Scheme II. Synthesis of Desyl Phosphates from Dioxaphosphole **11c**[a]



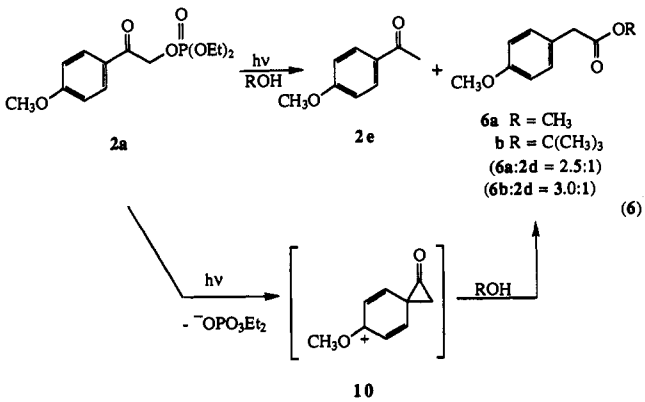
[a] (a) $HOCH(CH_3)_2$, Et_3N, THF; (b) H_2O, THF; (c) cyclohexylamine, ether; (d) 1 equiv of H_2O, THF; (e) 1 equiv of H_2O, THF; (f) aniline, ethanol.

intractable mixtures[11] of mono-, di-, and trisubstituted phosphates. Therefore, we developed a synthetic scheme for mixed desyl phosphates using a variation of the strategy of Ramirez[12] in which he exploited acetoin as a base-labile phosphate ligand. As illustrated in Schemes I and II, replacing biacetyl with benzil and omitting the final base treatment deprotection step made a direct entry to specifically substituted desyl phosphates available. With this approach, mixed desyl tri-, di-, and monophosphates (*e.g.*, **1a–c**) were readily obtained.

Irradiation of desyl isopropyl monohydrogen phosphate (**1b**) or desyl dihydrogen phosphate (**1c**) at 350 nm in acidic media (pH <2) produced isopropyl dihydrogen phosphate (**9b**) or phosphoric acid (**9c**), respectively, along with 2-phenylbenzo-[*b*]furan (**3**) in nearly quantitative yield (eq 4). Trace amounts of benzil and other unidentified products were also detected.

Similarly, photolysis of **1b** or **1c** in H_2O/CH_3CN (3:2) at pH 7 gave the same two major products but at only 7% of the efficiency observed at pH 2. The disappearance efficiency of **1b** or **1c** determined by ^{31}P NMR indicated a much higher efficiency for the disappearance of these esters (Table III). No other major products were detected, however. A slight increase in efficiency for the formation of benzil was noted, accompanied by the appearance of its golden yellow color.

4-Methoxyphenacyl Diethyl Phosphate. 4-Methoxyphenacyl diethyl phosphate (diethyl 2-(4-methoxyphenyl)-2-oxoethyl phosphate, **2a**) was synthesized following the same methodology utilized for the synthesis of **1a**.[10] Photolysis of **2a** in methanol or *tert*-butyl alcohol produced the corresponding rearranged esters 4-methoxyphenylacetates **6a** and **6b** and 4-methoxyacetophenone (**2e**, eq 6). The structures of **2e** and **6** were established by



coinjection of authentic samples on a capillary gas chromatography column (*i.e.*, DB-1) and by the identical mass spectral fragmentation patterns of **2e** and **6** compared with those of authentic samples from independent syntheses.

Desyl Adenosine Cyclic 3',5'-Monophosphate. Desyl adenosine cyclic 3',5'-monophosphate (adenosine cyclic 3',5'-(2-oxo-1,2-diphenylethyl) phosphate, **13**) was synthesized from cAMP (**12**) as shown in eq 7, using a procedure requiring a significantly shorter reaction time in comparison with that of the diazo ketone reaction methodology.[4e,11] Using a simple S_N2 strategy, addition of 5 equiv of desyl bromide to the tri-*n*-butylammonium salt of cAMP in a mixture of *N,N*-dimethylacetamide and tri-*n*-

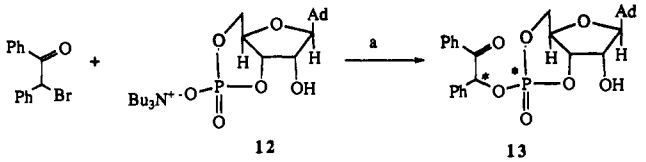
(11) Scheit, K. H. *Nucleotide Analogues Synthesis and Biological Functions*; Wiley-Interscience: New York, 1980; pp 195–218.

(12) The method of Ramirez (Ramirez, F.; Marecek, J. F. *Synthesis* **1985**, 449.) was adapted for the synthesis of the diphenyl 1,3,2λ⁵-dioxaphosphole and phosphate derivatives.

Table III. Quantum Efficiencies Φ^a for Photolysis of Desyl Phosphate Esters **1a–c** at 350 nm

ester 1	solvent	pH	$\Phi_{Dis}{}^b$	$\Phi_{App}{}^b$	$\Phi'_{App}{}^c$
1a	C_6H_6	*d*	0.28	0.26	*d*
1b	H_2O/CH_3CN^e	1.9	0.37	0.20	0.12
1b	H_2O/CH_3CN^f	7.0	*g*	0.07	0.013
1c	H_2O/CH_3CN^e	1.9	0.38	0.14	0.15
1c	H_2O/CH_3CN^f	7.0	*g*	0.08	0.01

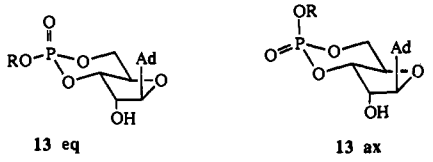
[a] Disappearance of **1a–c** and appearance of **3** and **9**. [b] Φ_{Dis} = disappearance of **1** and Φ_{App} = appearance of **3**. [c] Φ'_{App} = appearance of **9**. [d] Not determined. [e] Perchloric acid/CH_3CN = 3:2. [f] Aqueous buffer/CH_3CN = 3:2. [g] ^{31}P NMR indicated rapid disappearance, but no other products were detected.



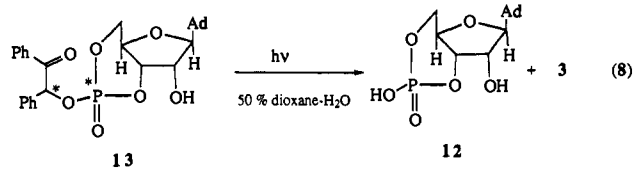
a) N,N-Dimethylacetamide, tri-*n*-butylamine, 100°C.

(7)

butylamine gave, after 1 h, 15–20% isolated yields of a diastereomeric mixture of **13 ax** and **13 eq**.[11,13,15]



Photolysis of the mixture of diastereomers of desyl adenosine cyclic 3′,5′-monophosphate (**13 ax**/**13 eq** = 9:11) at 350 nm in a 1:1 mixture of aqueous buffer (pH 7.2)/dioxane produced two products, liberated adenosine cyclic 3′,5′-monophosphate (**12**) and 2-phenylbenzo[*b*]furan (**3**, eq 8). The two diastereomers



(8)

disappeared at nearly the same rate with the axial isomer reacting slightly faster. Monitoring the photolysis by ^{31}P NMR revealed that the release of **12** from **13** was free of side reactions (see Figure 1).

Determination of Quantum Efficiencies and Multiplicity. The quantum efficiencies for the appearance of 2-phenylbenzo[*b*]furan (**3**) and disappearance of desyl phosphates **1a–c**, (Table III) were determined by GLC or HPLC analysis of aliquots taken at regular intervals from samples irradiated in a Rayonet merry-go-round apparatus fitted with either RPR 3000-Å or RPR 3500-Å lamps. The light output was determined by ferrioxalate actinometry.[16] Phosphorescence spectra of **1a–c** and benzoin exhibited similar (0,0) bands, indicating triplet energies of 73 ± 1 kcal/mol for each ketone.

Stern–Volmer (SV) quenching studies of the appearance of **3** or disappearance of **1a** obtained with either *trans*-piperylene (E_T = 55 kcal/mol)[17] or naphthalene (E_T = 62 kcal/mol)[17] in benzene gave good, linear correlations with identical slopes, demonstrating a reactive triplet excited state. Assuming diffusion-controlled quenching by naphthalene ($k_{diff} = 10^{10}$ M^{-1} s^{-1}),[22] the lifetime of the triplet state of **1a** was estimated to be 3 ns. Similarly, a lifetime of 6 ns was obtained from the quenching of the formation of **3a** by *trans*-piperylene.

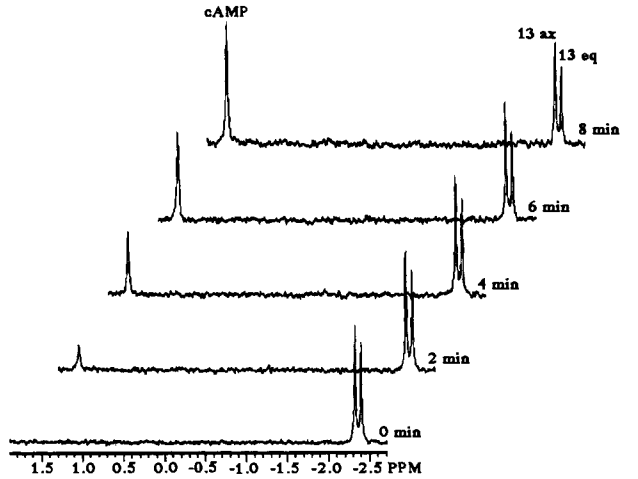


Figure 1. ^{31}P NMR (121.4 MHz; Varian XL-300, heteronuclear decoupled, 1024 transients) of the irradiation at 350 nm of desyl cAMP (δ 2.36 (**13 ax**) and 2.28 (**13 eq**)) releasing cAMP (**12**) (δ 1.73, s) as a function of irradiation time.

By analogy, it was anticipated that the reactive excited state for mono- and dihydrogen desyl derivatives **1b** and **1c** in aqueous acetonitrile would also be triplet. Quenching of the disappearance of **1b** and **1c** as well as the appearance of 2-phenylbenzo[*b*]furan (**3**) by sodium 2-naphthalenesulfonate (E_T = 62 kcal/mol)[17] gave lifetimes of 4.4 and 3.3 ns, respectively, for the triplet states. The diffusion rate constant for the binary solvent mixture of aqueous buffer and acetonitrile (3:2) was estimated[21] to be *ca.* 1.1×10^{10} M^{-1} s^{-1}. The rate constants for release of phosphate, calculated from the efficiencies for reaction and the triplet lifetimes, were 8×10^7 and 9×10^7 s^{-1}, respectively.

The quantum efficiencies for the appearance of the esters of 4-methoxyphenylacetates **6a,b** and 4-methoxyacetophenone (**2e**) from irradiation of **2a** in methanol or benzene/*tert*-butyl alcohol are given in Table IV. The multiplicity of the excited state was determined to be triplet by a SV quenching study employing naphthalene (E_T = 62 kcal/mol).[17] The formations of **2e** and **6** were both quenched at approximately the same rate (K_{SV} = (4.9 ± 0.5 × 10^3 and (4.2 ± 0.4) × 10^3 M^{-1}, respectively). Lifetimes were 0.33 ± 0.03 and 0.39 ± 0.04 μs, respectively, assuming a rate constant for diffusion in methanol of 1.26×10^{10} M^{-1} s^{-1}.[22] These data gave a calculated rate constant of (5.1 ± 0.5) × 10^5 s^{-1} for release of phosphate from **2a**. The rate constant for formation of the reduction product in neat methanol was (2.1 ± 0.2) × 10^5 s^{-1}.

A solvent isotope effect study was performed using methanol, methanol-*O*-*d*, and methanol-d_4 to probe the origin of photore-

(13) Two chiral centers are generated by esterification of cAMP. ^{31}P NMR (Figure 1) shows only two broad signals (heteronuclear decoupled) which we have tentatively assigned as axial and equatorial isomers **13 ax** and **13 eq**, respectively.[4a] The two isomers are formed in a ratio of 9:11 (**13 ax**:**13 eq**).

(14) Phosgene is a colorless, highly toxic gas which should be handled only in the hood. The gas condenses at about 0 °C.

(15) Ramirez, F.; Tsuboi, H.; Okazaki, H.; Marecek, J. F. *Tetrahedron Lett.* **1982**, *23*, 5375.

(16) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, A* **1956**, *A220*, 518.

(17) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 55.

(18) Davies, W; Middleton, S. *J. Chem. Soc.* **1958**, 822.

(19) Kranch, C. H.; Metzner, W.; Schenck, G. O. *Chem. Ber.* **1966**, *99*, 1723.

(20) Parkanyi, C.; Lablache-Combier, A.; Marko, I.; Offenberg, H. *J. Org. Chem.* **1976**, *41*, 151.

(21) Diffusion rates were estimated from the viscosities reported for binary solvents. See: Melander, W.; Horvath, C. *J. Chromatogr. Sci.* **1977**, *15*, 393. Timmermans, J. *Physico-Chemical Constants of Binary Systems in Concentrated Solutions*; Interscience: London (GB), 1960; Vol. 4, p 165.

(22) The diffusion rates were estimated from the modified Debye equation: $k_{diff} = 8RT/3000\eta$ at 40 °C and the viscosity given in poise. Scaiano, J. C. *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989; Vol. II, Chapter 14.

Table IV. Quantum Efficiencies Φ^a for Photolysis of 4-Methoxyphenacyl Diethyl Phosphate Ester (**2a**) at 300 nm in Methanol and *tert*-Butyl Alcohol and the Isotope Effects for the Formation of **2e** and **6a** Observed for Irradiation in Deuterated Methanol

solvent	Φ_{Dis}(**2a**)	Φ_{App}(**6a,b**)	$k_{H/D}$(**6a**)	Φ_{App}(**2e**)	$k_{H/D}$(**2e**)
benzene/*tert*-butyl alcohol	0.036	0.026		0.0074	
CH_3OH	0.42	0.20		0.07	
CD_3OD		0.14	1.4 ± 0.1	0.013	5.4 ± 0.5
CH_3OD		0.11	1.82 ± 0.2	0.053	1.3 ± 0.1

[a] Error limits for the quantum efficiencies are estimated to be ±10%.

Table V. Quantum Efficiencies Φ for Photolysis of Desyl Adenosine Cyclic 3′,5′-Monophosphate (**13**) at 350 nm in 1:1 Aqueous Buffer–Dioxane

aqueous buffer	pH	Φ_{-13}	Φ_{12}	Φ_3
Tris (D_2O)	7.3	0.39	0.34	0.19
Tris (D_2O)	7.3	0.37	0.33	0.16
Tris (H_2O)	7.3	0.37	0.34	0.17
phosphate (D_2O)	8.4	*a*	*a*	0.17
phosphate (H_2O)	8.4	*a*	*a*	0.17
perchloric (D_2O) acid	1.6	0.40	0.36	0.16

[a] The Φ_{-13} or Φ_{12} could not be measured due to the interference of the ^{31}P signal from the buffer.

Table VI. Half-life ($t_{1/2}$) for Desyl Adenosine Cyclic 3′,5′-Monophosphate (**13**) in 50:50 Aqueous Buffer:Dioxane

aqueous buffer	pH	$t_{1/2}$ (h)
Tris (D_2O)	7.2	>72
Tris (H_2O)	7.2	>60
phosphate (H_2O)	8.5	13
phosphate (D_2O)	8.4	13
Tris (H_2O)	8.4	13
perchloric acid (D_2O)	1.8	50

duction product **2e**. Comparison of the relative efficiencies for irradiation of **2a** in methanol-*O*-*d* with those in methanol revealed a small isotope effect of 1.3 and 1.8 for formation of **2e** and **6a**, respectively (Table IV). However, when the irradiation was carried out in methanol-d_4, a large solvent isotope effect of 5.4 was found for the appearance of **2e**, whereas the isotope effect for **6a** remained essentially unchanged at 1.4.

Finally, the quantum efficiencies for the appearance of **3** and cAMP (**12**) were determined by HPLC analysis in the same manner as described for the analysis of **1b** and **1c** and by ^{31}P NMR analysis. The quantum efficiencies for the disappearance of **13** and the appearance of **12** were nearly identical, whereas the measured appearance efficiency of **3** was usually much lower, primarily due to the low solubility of **3** (Table V). A standard SV quenching experiment of **13** with sodium 2-naphthalenesulfonate gave a triplet lifetime of 0.52 ± 0.1 ns using a rate constant for diffusion[21] of 4.4×10^{10} M^{-1} s^{-1} for the binary solvent of 1:1 aqueous buffer and dioxane.

The stability of desyl cAMP (**13**) in aqueous solutions at pH 1.8, 7.2, and 8.4 was established through half-life determinations (Table VI). In basic media, **13** is unstable and undergoes hydrolysis of the cyclic phosphate forming desyl adenosine 3′- or 5′-monophosphate.[23] At neutral and low pHs, the ester is stable to hydrolysis within the time frame of the photochemical experiments.

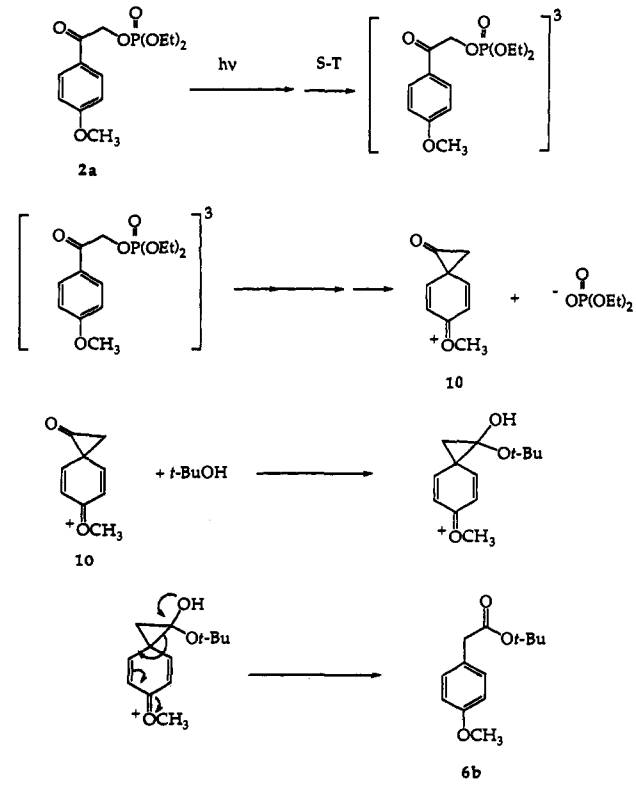
The phosphorescence spectrum of **13** indicated that the lowest triplet-state energy was 73 ± 1 kcal/mol, in agreement with the other desyl mono-, di-, and triphosphates reported in this study.

Discussion

Our recent studies[1a-c] of the photochemistry of arylmethyl phosphates and our earlier report of the photochemistry of an

(23) Corrie[4g] has suggested that neighboring group participation by the desyl carbonyl may enhance the rate of hydrolysis of α-keto phosphates under mildly basic conditions.

Scheme III. Photorearrangements of **2a** in *tert*-Butyl Alcohol[a]



[a] S–T = singlet–triplet crossing.

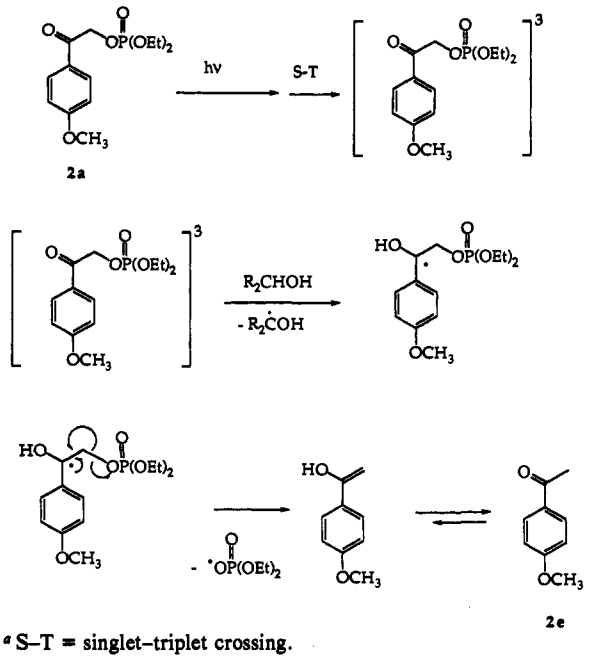
α-keto phosphate[1a] have shown that these reactions occur by a photochemically induced dissociation through ionic intermediates. This was first established for benzylic and arylmethyl phosphates[1a-c] and is now extended to the desyl[1d] and 4-methoxyphenacyl[7] phosphates reported here.

As reported earlier, our studies of desyl phosphate derivatives have demonstrated a recurring pattern of reactivity in which the desyl moiety is converted to 2-phenylbenzo[*b*]furan (**3**) irrespective of the solvent or the structure of the desyl phosphate ester.[1a,d] The release of the phosphate with its attendant ligands is also independent of the solvent. The overall process is highly efficient and emanates from the triplet state of the desyl group. While the mechanistic details for the cyclization of the desyl moiety are not known, a reasonable pathway would be that shown in Scheme V in which photolysis initially generates a desyl cation–phosphate anion pair. This is in accord with the mechanistic picture we had previously developed from our extensive investigations of benzilic phosphates.[1a-c]

We were quite puzzled, then, when reports appeared[8] on the photolysis of closely related α-keto phosphates **2a** and **2d**. Epstein[8a] and Baldwin[8b] both reported that the fate of the 4-methoxyphenacyl moiety upon photolysis of 4-methoxyphenacyl phosphate esters **2a** and **2d** was to form a reduction product, 4-methoxyacetophenone (**2e**). No rearrangement products of the type reported for other phenacyl derivatives[7] were indicated.

4-Methoxyphenacyl Phosphate Photochemistry. 4-Methoxyphenacyl phosphate **2a** was reexamined in a search for other reaction products indicative of a carbocation intermediate. In fact, a relatively efficient carbocation rearrangement of **2a** to *tert*-butyl 4-methoxyphenylacetate was discovered to occur for irradiations in *tert*-butyl alcohol/benzene, a poor hydrogen-atom-donating medium (eq 2). Photoreduction product **2e** was also found, albeit as the minor product. Finally, a small amount of α-*tert*-butoxy-*p*-methoxyacetophenone was observed and is most probably derived from a competing ground-state solvolysis process. The reaction was quenched with naphthalene, consistent with the

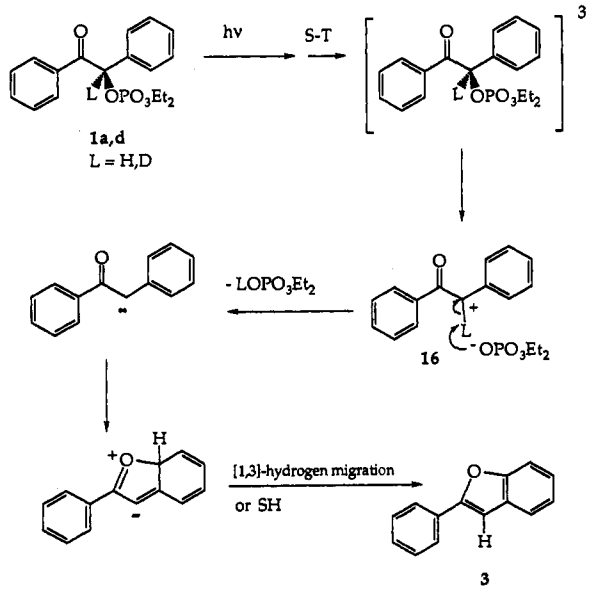
Scheme IV. Mechanism for the Reduction Product from **2a** in MeOH or Dioxane[a]



2a 2e

[a] S–T = singlet–triplet crossing.

Scheme V. Carbene Route to the Formation of 2-Phenylbenzo[*b*]furan (**3**)[a]



1a,d
L = H,D

16 3

[a] S–T = singlet–triplet crossing.

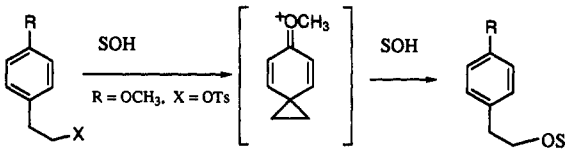
triplet-state assignment determined for the analogous desyl derivative. Thus, our results contrast with those reported for photolysis of **2a** in *p*-dioxane, a good hydrogen-atom-donating solvent, where photoreduction is apparently the major or possibly the exclusive process.[8]

We also reexamined the photoreaction of **2a** in methanol, an alternative to *p*-dioxane as a good hydrogen-atom source. Here, again, we found that photoreduction competed with the rearrangement but the process remained a minor one (Table IV). The quantum efficiencies for **2e** and **6** in methanol were an order of magnitude higher than in *tert*-butyl alcohol/benzene, due in part to the combination of lower polarity and poorer hydrogen-atom-donating power of the *tert*-butyl alcohol/benzene solvent.

From the quenching data, a pseudo-first-order rate constant of 2.1×10^5 s^{-1} was calculated for the formation of **2e** by an intermolecular hydrogen-atom abstraction from methanol, which is comparable to the corresponding rate constant for *intramolecular* hydrogen abstraction by other 4-methoxy-substituted phenone triplets (*i.e.*, *p*-methoxyvalerophenone, $k_r = 7.7 \times 10^5$ s^{-1}) in methanol.[24] Wagner,[24] Yang,[25] and Pitts[26] have noted that the contribution of the lower lying $(\pi,\pi^*)^3$ state to the excited-state reactivity of *p*-methoxyaryl ketones renders it much less reactive, more than an order of magnitude lower than a pure n,π^* triplet, in hydrogen abstraction reactions. In our case, however, the lower hydrogen abstraction reactivity is offset by the competing rearrangement photochemistry, even in methanol.

The formation of 4-methoxyacetophenone (**2e**) in *tert*-butyl alcohol/benzene is more difficult to accord with this mechanism. One possibility is a competing, minor direct homolysis of the C–O phosphate bond to form a triplet radical pair which could abstract a hydrogen atom from the solvent or any other adventitious hydrogen donor to provide **2e**. In the absence of any hydrogen donor, recombination or coupling reactions might compete but were not investigated.

Clearly, the dominant process in both polar solvents examined here is the rearrangement to 4-methoxyphenylacetate which occurs in methanol with a rate constant of 5.1×10^5 s^{-1}, as determined from the quenching data. The acetophenone–phenylacetate rearrangement has excellent literature precedence in a number of solvolytic studies of β-phenethyl derivatives[27] (*e.g.*, **14**, eq 9) and in a report of related photochemical reactions of



(9)

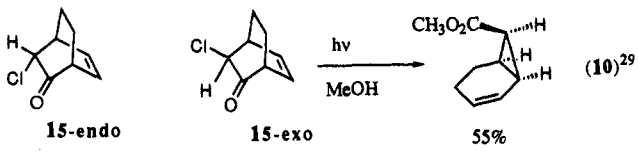
14, R = OCH_3, OH, Cl
X = OTs, OBs, Br

α-phenacyl chlorides[7] (*e.g.*, **2b**). Anderson and Reese[7] observed that 2- and 4-methoxyphenacyl chlorides gave appreciable yields of ethyl 2- and 4-methoxyphenylacetates when irradiated in ethanol. These examples of neighboring group participation in a photochemical reaction also exhibited the same sensitivity to substituent effects on migratory aptitude of the aryl group, paralleling that in the ground-state reactions.[29] While no mechanistic studies are available for phenacyl chlorides, both radical and ionic intermediates have been suggested.

Evidence for radical intermediates has been reported for homolysis of α-carbonyl photolysis reactions in some related bicyclic α-chloro β,γ-enones where participation of the carbon–carbon double bond is observed. For the endo isomer, where back-side π-participation is stereoelectronically not feasible, evidence for radical intermediates was forthcoming from photolysis in the presence of iodide as a chlorine-atom-trapping agent. The observation of I_2^- indicated a successful trap.[29] Exo isomer **15**, which produced no I_2^-, gave a single, major rearrangement product resulting from π-bond participation (eq 10). A general mechanistic picture for the rearrangement of α-keto phosphates is shown in Scheme III.

The origin of the reduction product in methanol and dioxane must be derived from a second pathway, either (1) hydrogen-

(24) (a) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604. (b) Wagner, P. J.; Kamppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5898.
(25) Yang, N. C.; Dusenbery, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 5899.
(26) Pitts, J. N.; Johnson, H. W.; Kuwana, T. *J. Phys. Chem.* **1962**, *66*, 2456.
(27) Streitwieser, A. *Solvolytic Displacement Reactions*; Mcgraw Hill: New York, 1962.
(28) (a) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863; **1952**, *74*, 2129; **1964**, *86*, 3767. (b) Olah, G. A.; Singh, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 3265. (c) Fornorini, S.; Muraglia, V. *J. Am. Chem. Soc.* **1989**, *111*, 873.
(29) (a) Givens, R. S.; Strekowski, L.; Devonshire, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1637. (b) Givens, R. S.; Strekowski, L. *J. Am. Chem. Soc.* **1975**, *97*, 5867.



atom abstraction from the solvent by a carbonyl π,π^* (mixed with n,π^*) triplet followed by homolysis of the carbon–oxygen bond of the phosphate or (2) the reverse order of these two steps in which homolysis precedes hydrogen-atom abstraction. The primary isotope effect of 5.4 for the photoreduction process which is observed *only in methanol-d_4* and *the absence of an isotope effect on the rearrangement process* coupled with *the lower overall efficiency for ketone disappearance in tert-butyl alcohol/benzene* suggests that the timing for the hydrogen abstraction is *prior to C–O bond rupture* whereas the photosolvolysis occurs *directly* from the triplet excited state. These results require two separate mechanisms for rearrangement and reduction which are outlined in Schemes III and IV, respectively.

Desyl Phosphates Photochemistry. While the acetophenone phosphate provided an interesting model for "caged" chromophores, we chose to pursue on our earlier investigation of the desyl derivatives. Our intent was to take advantage of the higher efficiency of the desyl phosphates, their simplified photoproduct mixture, and the minimal solvent effects on both the efficiency and the product mixture.[1a]

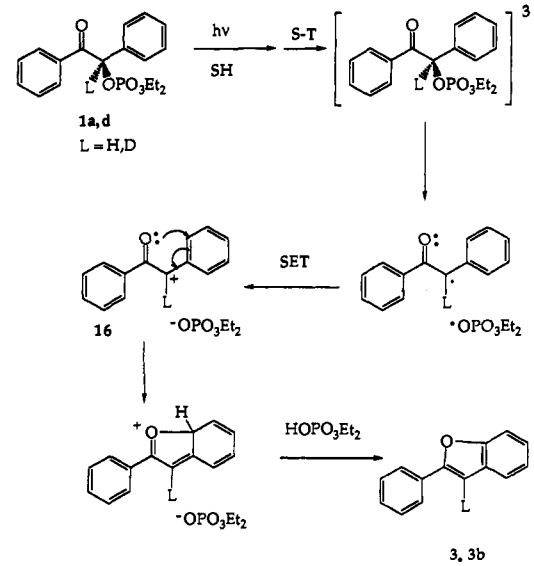
An important consideration in the development of the desyl group as a useful cage was also the ease of synthesis of mixed esters containing the benzoin ligand. A possible entry to desyl esters was envisaged through adapting Ramirez and Marecek's[15] synthesis of acetoin phosphates to our target esters. As illustrated in Scheme I, benzil was readily converted into diphenyl phosphorochloridate **11c** in greater than 90% overall yield. The entire sequence was run without isolation or purification of intermediate dioxaphosphole.

As shown earlier by Ramirez and Marecek,[15] phosphorohloridates react sequentially with a variety of alcohols to yield mixed di- or triesters of acetoin phosphate, each addition requiring a progressively stronger base to effect the transformation. In the Ramirez strategy, the acetoin ligand is the removable protecting group, excised last by hydrolysis. Our strategy differs only in the activation requirement of the final step, namely, removal of the desyl group by photoactivated heterolysis. The advantages of this strategy derive both from the specificity of incorporating individual ligands sequentially and in the direct generation of the photolabile desyl (*i.e.*, α-keto) ester. Furthermore, the sequence is economical because only *1 molar equiv* of alcohol per ligand is required. Scheme II provides two examples, a simple, mixed isopropyl desyl phosphate diester (**1b**) and an unsubstituted desyl phosphate monoester (**1c**) which were synthesized using the dioxaphosphole strategy.

Other synthetic strategies were also employed for mixed desyl esters, such as the reaction of diethyl phosphorochloridates with benzoin.[10] We were also able to effect esterification with an S_N2 strategy by reacting the tri-*n*-butylammonium phosphate salt of cAMP in *N,N*-dimethylacetamide (DMA) with desyl bromide (eq 7). The yields from this reaction are significantly lower (15–20%) than the other routes noted above but are similar to those obtained with other caged derivatization reactions.[4e,f] Fortunately, the nucleotide can be recycled to increase the product yield by this route.

The photolysis of triester **2a** in methanol, benzene, and acetonitrile gave excellent yields of 2-phenylbenzo[*b*]furan (**3**) and diethyl phosphate (**9a**) with an efficiency of nearly 30%.[1a,b] Likewise, the salts of water-soluble esters **1b** and **1c** gave just two products in aqueous acetonitrile but at reduced efficiencies (eq 4 and Table III). In fact, the reaction was shown to be pH sensitive, occurring most efficiently at pH <2.0. At pH 7–8, the release of phosphate was an order of magnitude less efficient, reflecting its reduced nucleofugacity. It should be noted that the ^{31}P NMR signals of **1b** and **1c** disappeared with a higher efficiency, forming, as yet, unknown products.

Scheme VI. Ion Pair Route to 2-Phenylbenzo[*b*]furan[a]



[a] S–T = singlet–triplet crossing, SET = single-electron transfer.

These reactions, like their counterpart triester **1a** in benzene, could be effectively quenched by triplet quenchers. A SV study of the reaction in benzene gave a lifetime of 2–7 ns for the triplet of **1a**. Similar studies of **1b** and **1c** gave lifetimes of 4 and 3 ns at pH 1.5. Thus, all three desyl phosphates appear to proceed, at least qualitatively, by a common pathway from the triplet excited state. Solvent and pH moderate the degree of reactivity but do not alter the course of the reaction.

As noted earlier, the pathway leading to the furan and phosphate from the triplet state of the ketone is unknown. According to the earlier studies on related desyl derivatives (*e.g.*, **1e–h**, eq 1) by Sheehan and Wilson,[5] the major chemical pathway out of the desyl triplet is homolysis yielding a complicated mixture of coupling and addition products. The much simpler product mixture from our phosphate esters is not representative of those reported for such leaving groups as $OCOCH_3$, Cl, OTs, or $HNMe_3^+$, suggesting a different operational pathway.[5]

A possible alternative would be through a carbene intermediate as depicted in Scheme V. To test for this route, α-deuterated desyl ester **1d** was synthesized (Table I) and irradiated. Irradiation of phosphate ester **1d** under a variety of conditions, including solvent mixtures which would allow rapid exchange with solvent, produced 3-deuterio-2-phenylbenzo[*b*]furan that contained the same degree of deuteration as the starting ester (Table II). These results clearly rule out a carbene mechanism or any process requiring removal of the methine hydrogen. Control experiments with unlabeled ester showed that these observations were not the result of a primary isotope effect and that hydrogen–deuterium exchange in the starting phosphate does not occur (Table II).

A second, alternative mechanism parallels that of our earlier suggested mechanisms for photosolvolysis of arylmethyl esters, differing only in the multiplicity of the reactive excited state. As illustrated in Scheme VI, initial homolysis produces a radical pair which undergoes rapid electron transfer to yield the ion pair. At what stage the carbonyl oxygen–carbon bond formation actually occurs is not known. However, we suggest that ring closure *follows* electron transfer rather than precedes it simply because the desyl photochemistry reported earlier by Sheehan[4,5] does not include the cyclized furan among the *major* photoproducts. Furthermore, the results noted earlier for 4-methox-

yphenacyl phosphate suggest that the homolysis pathway should produce the 1,2-diphenylethanone which was not observed here. After closure, the phosphate ion is then well-situated to act as a general base toward the removal of the bridgehead proton, thus completing the reaction.

The alternative to the sequence outlined in Scheme VI is the formation of a charge-transfer (electron-transfer) excited state which decays by homolysis of the C–O bond leading directly to ion pair **16** (Scheme V). We have not obtained evidence for the intermediacy of such a charge-transfer excited state, however. Additional studies are in progress to further explore the mechanism of these desyl ester photorearrangements.

A Cage Reaction, Desyl cAMP. cAMP was chosen to illustrate the application of the phosphate release reaction for a caged nucleotide. Desyl cAMP (**13**) was conveniently prepared by the reaction of the tri-*n*-butylammonium salt of cAMP with desyl bromide in *N*,*N*-dimethylacetamide, which gave a mixture of two diastereomeric esters, with the axial isomer in slight excess (11:9).

The triester had been specifically chosen to avoid the pH dependence on the photolysis reaction efficiency that had been observed for the desyl and isopropyl desyl phosphates. As shown in Table V, this indeed proved to be the case for irradiation of the mixture in 50% aqueous buffer/dioxane which gave cAMP (**12**) in high efficiency (0.33) and good yield. The equatorial isomer reacted slightly more efficiently than the axial isomer. ^{31}P NMR spectra (Figure 1) gave evidence for a single phosphorus-containing product which was shown to be cAMP by spectroscopic and HPLC comparison with the authentic sample. Likewise, the only other product detected by HPLC was benzo[*b*]furan **3**.

The reaction was readily quenched by naphthalenesulfonate, yielding a measured lifetime for the triplet of approximately 0.52 ± 0.1 ns from the SV study, assuming a diffusion rate for naphthalenesulfonate in 1:1 aqueous buffer:dioxane of 4.4×10^{-10} M^{-1} s^{-1}.[21,22] The rate constant for release of cAMP was calculated ($k_r = \Phi_r/\tau_s$) to be 7.1×10^8 s^{-1}. This rate constant is at least 3 orders of magnitude greater than those reported for a variety of other cage release reactions.[3,4e-g]

Conclusions

These initial studies on desyl and 2-hydroxy-4′-methoxyacetophenone phosphates illustrate the potential of these groups as cages for nucleotide phosphates. The rates of C–O cleavage for the desyl phosphates are at least 3–6 orders of magnitude faster than those reported for irradiations of *o*-nitrobenzyl derivatives.[3e-g] The reaction efficiencies for the desyl phosphates are uniformly good and appear to be independent of the nature of the solvent or the structure of the phosphate but are pH dependent. A second major advantage of the desyl ligand is that the furan product is relatively unreactive, a feature that is not true for the photoproducts of *o*-nitrobenzyl derivatives. Work currently in progress will further explore other analogues in the 4-methoxyphenacyl and desyl phosphate series.

Experimental Section

General Methods. Benzoin (Eastman), diethyl phosphorochloridate (Aldrich), 2-hydroxy-4′-methoxyacetophenone (Aldrich), phosphoric acid (Aldrich), desyl bromide (Aldrich), (–)-adenosine cyclic 3′,5′-monophosphate (Aldrich), and 2-naphthalenesulfonic acid (Aldrich) were used without further purification. Diethyl ether (technical grade), methylene chloride (technical grade), pyridine (Fisher), acetonitrile (Fisher), and triethylamine (Eastman) were distilled from calcium hydride. *tert*-Butyl alcohol (Fisher), 2-propanol (Fisher), methanol (Fisher), and acetone (Fisher) were distilled from 4-Å molecular sieves. Cyclohexylamine (Eastman) was distilled from potassium hydroxide. Acetyl bromide (Aldrich) was freshly distilled before use. Trimethyl phosphite (Aldrich) was distilled from sodium. *N*,*N*-Dimethylacetamide was stored over BaO and then decanted and distilled under vacuum. Phosgene (Linde) was collected in a dry ice trap prior to use (Caution!).[14] Benzene and tetrahydrofuran were refluxed over sodium benzophenone ketyl prior to distillation. The ion-exchange resin was Amberlite IR-120 (Mallinckrodt). Deuterium oxide (D_2O) and deuteriochloroform ($CDCl_3$) were purchased from Cambridge Isotopes.

High-performance liquid chromatography (HPLC) was performed with an LKB 2150 HPLC pump equipped with a Perkin-Elmer LC-55B spectrophotometer (monitored at 254 nm for the benzyl derivatives and 280 nm for the desyl derivatives) using an ODS hypersil reverse-phase column (14.3 × 0.3 cm). A gradient two-pump program was utilized for the analysis of mono- and dihydrogen phosphates **1b** and **1c** and for the analysis of the desyl ester of cAMP (**13**). Pump A was 90% aqueous buffer (0.019 mM tetrabutyl ammonium hydrogen sulfate) and 10% acetonitrile. Pump B was 90% acetonitrile and 10% water. An initial flow rate of 0.75 mL/min was established for 5 min, composed of 75% A and 25% B. The flow rate was then linearly increased from 0.75 to 0.80 mL/min for 5 min with B increasing to 45% and then linearly increased further from 0.80 to 1.0 mL/min for the next 15 min with B increasing from 45 to 95%. These final parameters were maintained for an additional 5 min or until complete elution of analytes had occurred. Analysis of **13** was performed under the same conditions except that B was initially 20%.

Ultraviolet (UV) spectra were determined with a Hewlett-Packard Model 8450A spectrophotometer. Infrared spectroscopy (IR) was performed using a Beckman Acculab 3 spectrophotometer or a Bomem MB-101 single-beam FTIR. Melting points were measured with a Fischer-Johns or Thomas-Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) was performed using a Varian XL-300 spectrometer with tetramethylsilane or chloroform as an internal standard for proton and carbon spectra, respectively, and with 85% H_3PO_4 as an external reference ($\delta = 0.0$) for phosphorous spectra. In cases in which analysis of carbon spectra of compounds in D_2O were performed, deuterated chloroform was used as an external reference. A Jenco pH meter was employed for all pH measurements. Phosphorescence spectra were performed on an Aminco-Bowman Model 4-8202 spectrophotofluorometer. Photolysis studies were performed with a Rayonet merry-go-round apparatus equipped with 4 × RPR 2540-Å, 2, 4, or 16 × RPR 3000-Å, or 4 × RPR 3500-Å lamps. The light output for quantum efficiency determinations was measured using the potassium ferrioxalate method.[16]

Desyl Diethyl Phosphate (1a). The diethyl desyl esters were synthesized by the method of Kenner and Mather[10] as adapted for the synthesis of benzyl diethyl phosphate reported in our earlier paper.[1b] In A 50-mL three-necked flask fitted with an addition funnel, a mechanical stirrer, and a thermometer was placed 6.367 g (30 mmol) of benzoin in 8.0 mL of pyridine. The mixture was cooled to 0 °C, and 6.567 g (38.1 mmol) of diethyl phosphorochloridate was slowly added. The mixture was allowed to stir at 0 °C for 2 h and then overnight at room temperature. Water (50 mL) was added and the mixture extracted with ether (3 × 50 mL). The combined organic layers were washed with 1 N H_2SO_4 (2 × 50 mL), 5% sodium bicarbonate (1 × 50 mL), water (3 × 50 mL), and brine (1 x 50 mL), dried over $MgSO_4$, and filtered. Removal of the ether and distillation under reduced pressure gave 9.1 g (87%) of crude desyl diethyl phosphate (**1a**). Part of this material (5.0 g) was purified on silica gel (SilicAR CC-7, 2.5- × 60-cm column, 200-mL fractions), giving, in fractions 21–26, (70–90% ether–hexane) 3.93 g (68%) of **1a** as a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.4 (t, $J = 7.5$ Hz, 6H), 4.1 (m, $J = 7.5$ Hz, 4H), 6.60 (d, $J = 8.5$ Hz, 1H), 7.17–7.50 (m, 8H), 7.78–8.00 (m, 2H); IR (CCl_4) 3062, 3030, 2982, 2931, 2910, 2870, 1698, 1679, 1593, 1490, 1470, 1442, 1390, 1365, 1270, 1260, 1220, 1178, 1164, 1096, 1035, 998, 980, 895, 862, 838, 690, 664 cm^{-1}; mass spectrum, *m/e* (rel intensity) 77 (41), 81 (18), 90 (3), 91 (21), 99 (19), 105 (100), 109 (23), 127 (11), 167 (3), 195 (2), 243 (58), 348 (5, M^+), 349 (1, $M^+ + 1$); UV (MeOH), λ_{max} (ϵ) 316 (327), 250 (13 000). Anal. Calcd for $C_{18}H_{21}O_5P$: C, 62.07; H, 6.08. Found: C, 61.68; H, 6.14.

2-Deuteriobenzoin (2-Deuterio-2-hydroxy-1,2-diphenylethanone). Benzil (9.0 g, 43 mmol) was stirred for 6 h with 100 g of sodium amalgam (containing 2.1 g of sodium, 0.09 mol) in a mixture of anhydrous ether and dry toluene at room temperature under nitrogen. The orange-colored mixture was cooled in an ice bath, and 25 mL of deuterium oxide (99.8% D) was carefully added dropwise over a period of 20 min with constant stirring. After stirring for 3 h, the white precipitate was filtered and washed with a 1:1 mixture of dry ether and toluene. Recrystallization from ethanol gave 4.8 g (52.7% yield) of 2-deuteriobenzoin: mp 134–136 °C; ^1H NMR ($CDCl_3$) δ 4.54 (s, 1H), 5.92 (d, very weak), 7.26–7.52 and 7.90–7.93 (m, total 10H); IR (KBr) 3424, 3070, 3036, 2364, 2332, 1674, 1596, 1576, 1556, 1538, 1490, 1450, 1336, 1264, 1200, 1114, 1080,

1018, 970, 936, 918, 840, 756, 704, 696, 682 cm^{-1}; GC–MS, *m/e* (rel intensity) 214 (19, M + 1), 213 (103, M$^+$).

1-Deuteriodesyl Diethyl Phosphate (1d). A mixture of 1.8 g (8.4 mmol) of 2-deuteriobenzoin and 2.46 g (0.03 mol, 2.5 mL) of dry pyridine was cooled in an ice bath. To this mixture was added 2.08 g (0.012 mol, 1.8 mL) of distilled diethyl phosphorochloridate over a period of 2 h with constant stirring. After an additional 2 days of stirring at room temperature, water (10 mL) was added. The mixture was extracted with ether (3 × 25 mL) the combined ether layers were washed with 1 N H_2SO_4 (2 × 25 mL), 5% sodium bicarbonate (1 × 25 mL), water (3 × 25 mL), and brine (1 × 25 mL). The ether layer was then dried with $MgSO_4$. Removal of the ether afforded 1.83 g of crude **1d**. The residue was chromatographed on silica gel (SilicAR CC-7, 1- × 25-cm, fraction volume 50 mL). Gradient elution with 20–50% ether–hexane gave, in fractions 5–11, 1.59 g (54.3%) of desired phosphate ester **1d**. This material was a slightly yellow oil. After a few days of standing at room temperature, the oil solidified: ^{1}H NMR ($CDCl_3$) δ 1.33 (m, 6H), 4.10 (m, 4H), 6.60 (d, very weak), 7.51–7.33 (m, 8H), 7.90–7.93 (m, 2H); IR (CCl_4) 3080, 2990, 2920, 2390, 1700 s, 1600, 1448, 1394, 1370, 1274 s, 1256 s, 1220, 1164, 1116, 1098, 1036 s, 1016 s, 986 s, 884, 696 s, 668 cm^{-1}; mass spectrum *m/e* (rel intensity) 349 (2.4, M$^+$), 348 (0.5), 244 (40.0), 243 (10.3), 166 (10.3), 165 (6.3), 109 (30.5), 108 (15.5), 107 (6.2), 106 (9.2), 105 (100), 81 (23.1), 80 (14.2), 78 (11.4), 77 (63.9), 51 (29.4), 50 (7.4).

4-Methoxyphenacyl Diethyl Phosphate (2a). A solution containing 3.32 g (0.02 mol) of 2-hydroxy-4′-methoxyacetophenone and 3.24 mL of pyridine was cooled to 0 °C before 3.42 g (0.02 mol) of diethyl phosphorochloridate was added slowly to avoid overheating. The mixture was allowed to stir at 0 °C for 2 h and then allowed to stir overnight at room temperature. The same workup procedure employed for **1a** was implemented for **2a**. The compound was purified by flash chromatography (hexane:ethyl acetate = 3:1) on silica gel (4.0 × 30 cm) to yield 3.71 g of **2a** (61% yield): ^{1}H NMR ($CDCl_3$) δ 1.4 (t, *J* = 7.5 Hz, 6H), 3.7 (s, 3H), 4.1 (m, *J* = 7.5 Hz, 4H), 5.1 (d, *J* = 8.5 Hz, 2H), 6.7–7.7 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 15.62 (d, *J* = 6.7 Hz), 55.06, 63.78 (d, *J* = 5.9 Hz), 68.02 (d, *J* = 5.5 Hz), 113.62, 126.46, 129.59, 163.64, 190.21 (d, *J* = 5.1 Hz); IR (neat) 3010, 2960, 1705, 1600, 1520, 1450, 1375, 1250, 1180 cm^{-1}; exact mass calcd for $C_{13}H_{19}O_5P$ 302.0918, found 302.09245. Anal. Calcd for $C_{13}H_{19}O_5P$: C, 51.66; H, 6.34. Found: C, 51.80; H, 7.01.

2,2,2-Trimethoxy-4,5-diphenyl-1,3,2λ^5-dioxaphosphole. Benzil (35 g, 0.17 mol) was added to a stirred solution of freshly distilled trimethyl phosphite (24 g, 0.19 mol) in 20 mL of methylene chloride at 0 °C over a 2-h period. After an additional hour of stirring at 0 °C, the solvent was removed by a Rotovap, leaving a viscous, yellow oil. The oil was used without further purification. The crude yield was nearly quantitative as determined by ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 3.73 (d, *J* = 13.2 Hz, 9H), 7.26 (m, 6H), 7.53 (d, *J* = 1.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.6 (d, *J* = 10.5 Hz, CH_3), 126.5, 127.8, 128.3, 130.8 (d, *J* = 12.5 Hz, $COP(OCH_3)_3$), 133.9; ^{31}P NMR ($CDCl_3$, 85% H_3PO_4 as standard) heteronuclear decoupled δ 7.97 (m, *J* = 13.2); IR (neat) 3200–2800, 1600, 1450, 1175 ($POCH_3$), 1070, 750 cm^{-1}.

2-Methoxy-4,5-diphenyl-2-oxo-1,3,2λ^5-dioxaphosphole (11a).[12] Trimethoxydioxaphosphole was dissolved in 80 mL of dry acetonitrile. In one portion, 3.0 mL (3.9 g, 0.032 mol) of freshly distilled acetyl bromide was added to the stirred solution. Because the reaction was exothermic, the remaining 11.0 mL (16.7 g, 0.137 mol) of acetyl bromide was added slowly over a 1-h period at a rate which kept the solution at 50 °C. The reaction was followed by the chemical shift and growth of the methoxy doublet in ^{1}H NMR. After the reaction was completed, the solvent was evaporated to yield a thick, yellow oil which was not further purified. The crude yield was >95% based on ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 3.94 (d, *J* = 12.3 Hz, 3H), 7.3 (m, 6H), 7.4 (m, 4H); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4 as standard) heteronuclear decoupled δ 7.92 (m, *J* = 11.3 Hz); IR (neat) 3100, 1600, 1450, 1300, 1250 cm^{-1}.

1′-Methylpyridinium 4,5-Diphenyl-2-oxido-2-oxo-1,3,2λ^5-dioxaphosphole (11b).[12] A solution of dioxaphosphole **11a** (48 g, 0.16 mol) and pyridine (36 g, 0.53 mol) in 90 mL of dry benzene was heated at gentle reflux with stirring for 7 h. The mixture was then allowed to cool to 20 °C and the precipitate filtered and washed thoroughly with benzene (2 × 50 mL) under argon. The fine crystalline salt was dried at 25 °C at 0.3 Torr for 12 h and stored under dry argon. The isolated yield was 95% (57 g, 0.15 mol): mp 149–151 °C; ^{1}H NMR (DMSO) δ 4.4 (s, 3H), 7.25 (m, 6H), 7.4 (m, 2H), 8.0 (t, *J* = 6.8 Hz, 2H), 8.5 (t, 1H), 9.0 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (DMSO) δ 47.8, 126.22, 127.6, 127.73, 128.32, 131.32 (d, *J* = 9.25 Hz), 134.54, 144.92, 145.52; ^{31}P NMR (D_2O) heteronuclear decoupled δ 11.62 (s); IR (KBr) 3500, 3100, 1650, 1505, 1455, 1270, 1140, 1080, 960, 840, 790, 770, 710 cm^{-1}.

2-Chloro-4,5-diphenyl-2-oxo-1,3,2λ^5-dioxaphosphole (11c).[12] Phosgene (3 mL, 0.43 mol) was collected in a cold trap and then evaporated slowly (30 min) into a stirred suspension of the salt of **11b** (5 g, 0.136 mol) in 15 mL of benzene at 0 °C (Caution!).[14] Rapid evolution of carbon dioxide was observed during the first 15 min. After an additional 30 min at 0 °C and 30 h at room temperature, *N*-methylpyridinium chloride was filtered off under argon inside the hood (Caution!)[14] and washed with benzene (2 × 10 mL). The combined filtrate and washings were evaporated in the hood (Caution!).[14] The resulting light yellow oil, which was not purified further, was used immediately in the next step (phosphorochloridate **11c** is sensitive to moisture). The overall yield from benzil to phosphorochloridate **11c** was greater than 90%: ^{1}H NMR ($CDCl_3$) 7.3–7.5 (m, 10H); ^{31}P NMR ($CDCl_3$) heteronuclear decoupled δ 16.4 (s); IR (neat) 3100, 1500, 1450, 1330, 1230 cm^{-1}.

Desyl Isopropyl Monohydrogen Phosphate (Isopropyl 2-Oxo-1,2-diphenylethyl Phosphate, 1b). A methylene chloride solution containing 1 equiv of isopropyl alcohol and 1 equiv of triethylamine was added dropwise to a stirred solution containing 1 equiv of phosphorochloridate **11c** (0.3–0.4 M) in methylene chloride at 0 °C. The mixture was allowed to warm to room temperature over a 2-h period. The ^{1}H NMR spectrum of the reaction mixture showed an isopropyl methine proton at δ 4.9 for the intermediate cyclic triester which shifted upfield to δ 4.6 after hydrolysis. The cyclic triester was hydrolyzed by the dropwise addition of a THF solution containing 1.5 equiv of H_2O at 0 °C. After the solution was stirred for 30 min, the solvent was evaporated, leaving a dark orange oil. A crude ^{31}P NMR ($CDCl_3$) revealed two products, the diester (δ −4.36; d, *J* = 7.6 Hz) and monoester (δ −3.18; d, *J* = 8.0 Hz), present in a ratio of 3:1, respectively. The diester was isolated after initially trapping the monoester by dissolving the residue in ethanol and adding 2 equiv of aniline. The resulting anilinium salt of **1b** was filtered, and the filtrate was evaporated on a Rotovap, yielding an orange oil. NMR confirmed that the benzoin monoester had been removed. The oily desyl isopropyl diester was dissolved in diethyl ether and then reacted with an excess of 2 equiv of cyclohexylamine. The resulting ammonium salt was filtered, rinsed with cold ether (3 × 10 mL), and isolated in a 61% yield: mp 153 °C dec. Anal. Calcd for $C_{23}H_{32}NO_5P$: C, 63.74; H, 7.39; N, 3.23. Found: C, 63.40; H, 7.40; N, 3.38.

Desyl Isopropyl Monohydrogen Phosphate, Sodium Salt (Na$^+$,1b). The corresponding ammonium salt was dissolved in a minimum amount of deionized water with heating and then passed through a sodium ion-exchange column (1.5 × 20 cm). The resulting eluant was lyophilized yielding a white powder: mp 219 °C dec; ^{1}H NMR (D_2O) δ 0.87 (d, *J* = 6.2 Hz, 3H), 0.94 (d, *J* = 6.2 Hz, 3H), 4.16 (m, *J* = 6.3 Hz, 1H), 6.41 (d, *J* = 8.8 Hz, 2H), 7.30 (m, 8H), 7.75 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (D_2O) δ 25.68 (d, *J* = 4.7 Hz), 25.82 (d, *J* = 4.7 Hz), 73.38 (d, *J* = 6.0 Hz), 81.2 (d, 4.7 Hz), 130.39, 131.42, 131.54, 131.70, 136.49, 136.83, 138.13 (d, *J* = 4.8 Hz), 201.28 (d, *J* = 4.24 Hz); ^{31}P NMR ($CDCl_3$) δ −4.36 (m, *J* = 7.6 Hz); IR (KBr) 3100, 1700, 1600, 1450, 1400, 1375, 1250, 1150, 1000 cm^{-1}; UV (H_2O) λ_{max} (ε) 251 (12 000); mass spectrum *m/e* (rel intensity) 335 (M$^+$, 0.42), 292 (9.9), 274 (22), 229 (11), 187 (56), 165 (16), 105 (100), 77 (89).

Desyl Dihydrogen Phosphate, Aniline Salt ($C_6H_5NH_3^+$,1b). By the same procedure employed in the synthesis of **1b**, 5.0 g (13.6 mmol) of the *N*-methylpyridinium salt of **11b** was treated with phosgene[14] as previously described. After workup, the oil was taken up in 30 mL of tetrahydrofuran and cooled to 0 °C, to which was added dropwise with stirring 0.50 g (28 mmol) of water in 10 mL of THF. During the addition, the color changed from orange to yellow. After 30 min, the solvent was removed to yield a yellow oil which was dissolved in 30–40 mL of ethanol, to which was added 1.9 g (20 mmol) of aniline. The resulting anilinium salt precipitated within a few minutes. The isolated yield of the salt of **1c** was 4.80 g (13.0 mmol, 92% yield). The crude salt was recrystallized from ethanol: mp 131–140 °C dec; IR (KBr) 3400–2200, 1700, 1600, 1580, 1500, 1450, 1220, 1190, 1080, 980 cm^{-1}. Anal. Calcd for $C_{20}H_{20}NO_5P$: C, 62.34; H, 5.23; N, 3.63. Found: C, 61.58; H, 5.59; N, 3.01. This salt is very hygroscopic. Thus, an accurate CHN analysis proved elusive.

Desyl Dihydrogen Phosphate, Sodium Salt (Na$^+$,1c). Desyl phosphoric aniline salt **1b** (0.52 g, 1.38 mmol) was dissolved with heating in 30 mL of deionized water. The solution was allowed to cool and then passed through a sodium ion-exchange column (1.5 cm × 22 cm). Approximately 125 mL of the eluant was collected in a tared flask and the water removed by lyophilization. The sodium salt of **1c**, a white powder, was isolated in 87% yield (0.42 g, 1.2 mmol): mp 180–83 °C dec; ^{1}H NMR (D_2O) δ 6.46 (d, *J* = 8.5 Hz, 1H), 7.2–7.5 (m, 8H), 7.84 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (D_2O) δ 81.32 (d, *J* = 4.22 Hz), 130.61, 131.67, 131.72,

131.96, 136.82, 137.10, 138.43 (d, $J \approx 4.6$ Hz), 202.01; IR (KBr) 3480, 3020, 1680, 1580, 1480, 1430, 1240, 1200, 1180, 1060 cm^{-1}; UV (H_2O) λ_{max} (ϵ) 251 (11 000), 323 (400). Anal. Calcd for $C_{14}H_{12}O_5PNa \cdot 1H_2O$: C, 50.61; H, 4.25. Found: C, 51.08; H, 4.00. This is a hygroscopic salt. The CH analysis reported was the best one obtained.

Desyl Dihydrogen Phosphate (1c). Monodesyl aniline salt (0.31 g, 0.8 mmol) was dissolved in 25 mL of deionized water with heating. The solution was allowed to cool and then eluted through an acid ion-exchange column (1.5 cm × 22 cm). The eluant was collected until it was no longer acidic. The water was removed by lyophilization to yield the white crystalline free acid, 0.21 g (0.7 mmol), in 90% yield of **1c**. The free acid was very hygroscopic, and thus, the corresponding sodium salt was employed for photochemical studies.

Tri-*n*-butylammonium Salt of (−)-Adenosine Cyclic 3′,5′-Phosphate (12). To 1.0 g (2.9 mmol) of (−)-adenosine 3′,5′-cyclic phosphate (cAMP, **12**) in 250 mL of deionized water was added 1.1 equiv of tri-*n*-butylamine. The water was removed by lyophilization, yielding a white salt (1.5 g, 2.9 mmol, 100% conversion); mp ≈ 120 °C dec; ^{1}H NMR (D_2O) δ 0.79 (t, J = 7.3 Hz, 9H), 1.24 (m, J = 7.3 Hz, 6H), 1.52 (m, J = 3.4 Hz, 6H), 2.98 (m, 6H), 4.18 (m, 2H), 4.35 (m, 1H), 4.43 (m, 1H), 4.61 (m, 1H), 6.03 (s, 1H), 8.08 (s, 1H), 8.09 (s, 1H); ^{31}P NMR (D_2O) δ −0.91 (ddd).

Desyl Adenosine Cyclic 3′,5′-Phosphate (13). The procedure of Ramirez[15] was adapted to the synthesis of **13**. The tri-*n*-butylammonium salt of cAMP (**12**) (0.5 g, 0.97 mmol) was dissolved in 11 mL of freshly distilled *N*,*N*-dimethylacetamide and 1.7 mL of tri-*n*-butylamine in a 100-mL round-bottom flask. To this mixture at 100 °C was added dropwise, over a 10–15 min period, a solution of desyl bromide (1.3 g, 4.75 mmol) in 3 mL of *N*,*N*-dimethylacetamide. After 45–60 min at 100 °C, the reaction mixture was cooled to room temperature. Monitoring of the reaction by TLC in a 90% $CHCl_3$ and 10% methanol solvent system revealed the appearance of the phosphate triester with an R_f of 0.4. After the reaction was cooled to room temperature, the solvent was removed by distillation with a Kugelrohr distillation apparatus. A ^{31}P NMR ($CDCl_3$) of the resulting dark orange oil indicated the reaction was 20–25% complete. The oil was washed three times with hexane and then dissolved in a minimal amount of chloroform and separated by flash chromatography on a silica column (20 × 3 cm). Elution using 100% chloroform removed the unreacted desyl bromide and nonpolar derivatives of desyl bromide from the column (this was easily noted by the yellow band which readily eluted from the column). The solvent system was then adjusted to 5% methanol and 95% chloroform and the cyclic triester eluted in fractions 20–25 (fraction size ≈ 25 mL). Appropriate fractions were combined, and the solvent was removed by evaporation under reduced pressure (Rotovap). The major impurity found in the triester was tri-*n*-butylamine which was detected by ^{1}H NMR. Final purification was achieved by dissolving the residue in chloroform and eluting it off a flash silica column as previously described, using 100% chloroform to first elute the amine followed by elution of the triester with 5% methanol in chloroform. Detection of eluted amine was not possible; thus, complete removal of tri-*n*-butylamine was achieved by repeating the above chromatography until complete purity was achieved. Typically, a 100-mg sample was isolated (20% yield): ^{1}H NMR (DMSO) δ 4.0 (m, 1H), 4.25 (m, 2H), 4.4–4.8 (m, 5H), 5.35 (m, 1H), 5.55 (m, 1H), 6.05 (s, 1H), 6.07(s, 1H), 6.35 (br doublets, 2 OH), 7.05 (overlapping doublets, 2H), 7.25–7.7 (m, 16 H), 7.8–7.96 (m, 6H), 8.2 (s, 1H), 8.27 (s, 1H), (Figure 1); ^{31}P NMR (DMSO) heteronuclear decoupled δ −5.5 and −6.3; IR (KBr) 1700, 1650, 1600, 1300, 1000, 925, 840, 700 cm^{-1}; UV (H_2O) λ_{max} (ϵ) 253 (20 000), 320 (500); mass spectrum (FAB$^+$) 524 (M^+), 330, 195, 115.

Photochemistry. General Procedure for Photolysis of 1a and 2a. Into a 2- × 18-mm quartz or Pyrex tube was placed 10 mL of an alcohol solution containing phosphate ester **1a** or **2a** and an appropriate GLC internal standard. The concentration of the phosphate was adjusted to assure complete absorption of the incident radiation (>3 OD) at the excitation wavelength. The tubes were sealed with a septum, deaerated with argon for at least 20 min, and photolyzed in the apparatus previously described in the general Experimental Section (4 × RPR 2540-Å lamps for **1a** and 16 × RPR 3000-Å lamps for **2**). Aliquots of 100 μL were removed periodically, stored in the cold, and analyzed by GLC. A 1–3 μL-aliquot of the mixture was injected onto the GLC. The initial concentrations and conditions are given in the procedures below. The isolated yields reported are corrected for recovered ester.

Photolysis of 1a in Acetonitrile, Methanol, or Benzene. Placed in separate Pyrex tubes were 102.5 mg (0.294 mmol), 128.4 mg (0.369 mmol), and 101.0 mg (0.290 mmol) of desyl diethyl phosphate (**1a**) and 15 mL of acetonitrile, methanol, and benzene, respectively. Each solution was deaerated with nitrogen for 30 min and irradiated using 16 × RPR 3000-Å lamps. An efficient disappearance of starting material and formation of a single, major product, **3**, was observed. Upon prolonged irradiation, **3** was slowly converted to two new products, regardless of the solvent. For example, after irradiation of **1a** in methanol for 7.5 h, some solid material crystallized yielding, after washing with ethanol, slightly yellow crystals, mp 278–283 °C, probably a mixture of dimers **4** (lit.[18,19] mp 279–280 °C). A control experiment in which **1a** was stirred in a photolysis tube in methanol covered with foil and placed in the "merry-go-round" for the same period of time as that of the irradiated solution (T = 40 °C) was monitored for possible thermal (ground-state) reactivity. No disappearance of **1a** or formation of **3** was noted.

Isolation of **3** from the photolysis of 515.2 mg (1.48 mmol) of **1a** in acetonitrile yielded, after removal of solvent, 525.3 mg of a brown, solid residue which was chromatographed on silica gel (SilicAR CC-7, 1.5- × 30-cm column, fraction volume 25 mL). Eluting with hexane gave, in fractions 3–4, 77.3 mg (37% isolated yield) of 2-phenylbenzo[*b*]furan (**3**) as white crystals, mp 120–121 °C (lit.[18] mp 120–121 °C). Eluting with 4% ether–hexane gave, in fractions 10–14, 24.2 mg of a white solid, mp 253–266 °C, comprised mostly (90%) of a 1:1 mixture of the two dimers of **3**. Spectral data of **3**: ^{1}H NMR (CCl_4) δ 6.93 (s, 1H), [(7.90–7.73) m + (7.57–7.07) m, 9H]; IR (KBr) 3038, 3020, 1605, 1590 m, 1573 w, 1548, 1480, 1458, 1441, 1430 s, 1360 m, 1321, 1310 w, 1292, 1282, 1260 m, 1247, 1198, 1160 s, 1133 w, 1098, 1065, 1029, 1010 s, 1000, 960 w, 920 m, 910 vs, 871, 794, 753, 735, 728 vs, 680 s, 646, 600 w cm^{-1}; mass spectrum m/e (rel intensity) 196 (1.9, M^+ + 2), 195 (16.4, M^+ + 1), 194 (100.0, M^+), 165 (38.1); UV (MeOH) λ_{max} (ϵ) 315 (22 930), 302 (32 220). Anal. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.95; H, 5.00.

Photolysis of 1a in Methanol at 350 nm. In a Pyrex tube were placed 199.8 mg (0.574 mmol) of **1a** and 10 mL of methanol. The solution was deaerated with nitrogen and irradiated for 5 h with 12 × RPR 3500-Å lamps (66% ester conversion). After solvent removal, the yellow residue was chromatographed on silica gel, as described before, yielding 47.1 mg of **3** (64% isolated yield) and 5.7 mg of a complicated mixture of minor products, none of which corresponded to the dimer of **3**.

Photolysis of 2-Phenyl[*b*]benzofuran (3) in Acetonitrile at 300 nm. A solution of 5.6 mg (28.9 μmol) of **3** in 2 mL of acetonitrile was deaerated and then irradiated for 2 h in a quartz tube (0.5 cm in diameter) with 16 × RPR 3000-Å lamps. Some crystals deposited on the wall of the tube. Two products were detected by GLC. These products were the same dimeric mixture (by GLC coinjections) as that obtained during prolonged irradiation of **1a** at 300 nm in different solvents (vide supra). After solvent removal, the crystals were recrystallized from benzene, giving material with mp 278–281 °C (lit.[16] mp 279–290 or 283–284 °C).

Photolysis of 2-Deuteriodesyl Diethyl Phosphate (1d) in Methanol. A solution of 131 mg (0.357 mmol) of **1d** in 15 mL of methanol was placed in a Pyrex tube and deaerated with nitrogen for 30 min. The sample was irradiated with 4 × RPR 3500-Å lamps for 109 min. Removal of the solvent gave 131 mg of a yellow, solid residue which was chromatographed on silica gel (SilicAR CC-7, 1- × 25-cm, fraction volume 25 mL). Eluting with hexane gave, in fractions 2–3, 27.0 mg (79% isolated yield) of 3-deuterio-2-phenylbenzo[*b*]furan (**3b**) as white crystals, mp 120–121 °C; eluting with 10% ether–hexane gave, in fraction 5, 3 mg of a white solid identified as the dimer of **3**. Spectral data of **3**: ^{1}H NMR ($CDCl_3$) δ 7.03 (s, very weak), 7.18–7.60 (m), 7.86–7.88 (m, total 9H); IR (KBr) 3450 s, 3060, 2380, 1772, 1718, 1684, 1654, 1638, 1618, 1560, 1492 s, 1470, 1454 s, 1444, 1350, 1296, 1270, 1260 s, 1210, 1110, 1070 s, 1028, 934, 918, 904 s, 856, 810, 778, 746 s, 694 s cm^{-1}; mass spectrum m/e (rel intensity) 196 (M^+ + 1, 16.3), 195 (M^+, 100.0), 194 (26.4), 166 (42.6), 165 (20.9), 164 (6.2) 140 (4.6), 139 (2.8), 83 (14.8), 82 (10.2), 77 (3.6), 64 (3.0), 63 (5.6), 51 (5.3).

Photolysis of 2-Deuteriodesyl Diethyl Phosphate (1d) in Benzene. A solution of 113 mg (0.324 mmol) of **1d** in 15 mL of dry benzene was deaerated with nitrogen for 30 min and irradiated with 12 × RPR 3500-Å lamps for 100 min, as before. Removal of the solvent left 118 mg of a solid yellow residue which was chromatographed on silica gel (SilicAR CC-7, 1- × 25-cm, fraction volume 25 mL). Eluting with hexane gave, in fractions 2–3 , 27.2 mg (72% isolated yield) of **3b**. The spectral data of the material was the same as that of **3b** in methanol.

Photolysis of 2-Deuteriodesyl Diethyl Phosphate (1d) in Benzene Moistened with D_2O. A solution of 115 mg (0.329 mmol) of phosphate **1d** in 15 mL of benzene moistened with D_2O was deaerated with nitrogen for 30 min and irradiated for 100 min with 4 × 3500-Å lamps, as before. Removal of the solvent gave 118 mg of solid residue which was chromatographed on silica gel (SilicAR CC-7, 1- × 25-cm, fraction volume 25 mL). Eluting with hexane gave, in fractions 2–3, 25.5 mg (50.3%

isolated yield) of **3b**. The spectral data of isolated **3b** was identical to that of 3-deuterio-2-phenylbenzo[*b*]furan (**3b**) obtained during photolysis of **1d** in methanol or benzene. A similar photolysis of **1a** in benzene–D_2O gave only **3**.

Photolysis of Desyl Diethyl Phosphate (1a) in CH_3OD. A solution of 139.3 mg (0.400 mmol) of desyl diethyl phosphate (**1a**) in 15 mL of methanol-*O*-*d* (CH_3OD) was deaerated with nitrogen for 30 min and irradiated with 12 × RPR 3500-Å lamps for 110 min. Isolation of major product **3**, using the same chromatography procedure as previously described, yielded 21.6 mg of **3** (55.1% isolated yield). The spectral data of **3** was the same as that for 2-phenylbenzo[*b*]furan (**3**) obtained during photolysis of **1a** in methanol.

Photolysis of 2a in *tert*-Butyl Alcohol and Methanol. To two 13- × 100-mm Pyrex test tubes were added 93.8 mg (0.311 mmol) and 91.5 mg (0.303 mmol) of **2a**, then 90.3 mg (3.763 mmol) and 41.6 mg (1.733 mmol) of isoheptadecane, and, finally, 10.0 mL of methanol and 5.0 mL of *tert*-butyl alcohol. The solutions were deaerated for 15 min with argon and photolyzed with 16 × RPR 3000-Å lamps, as previously described. The quantum efficiencies measured for the three reactions are shown in Table IV.

Competitive Quenching Study of 2a with Naphthalene. To a 10-mL volumetric flask were added 112.3 mg (0.372 mmol) of *p*-methoxyphenacyl diethyl phosphate ester **2a**, 19.0 mg (0.792 mmol) of *n*-heptadecane, and methanol to fill. To six Pyrex tubes was added 1 mL of the above phosphate solution. To five of these tubes were added, respectively, 20.0 (0.197 mmol), 40.0 (0.39 mmol), 60.0 (0.590 mmol), 80.0 (0.787 mmol), and 120.0 μL (0.118 mmol) of a naphthalene stock solution (9.8 mM) in methanol. The volume in each test tube was adjusted to 1.2 mL with the addition of methanol. The tubes were deaerated for 20 min with argon at room temperature and photolyzed using the 16 × RPR 3000-Å lamps; the reactions were monitored by GLC. A linear least-squares analysis was performed on the data obtained. The results are listed below for **2e** and **6** (The asterisk indicates that the lifetimes were calculated assuming diffusion-controlled quenching with an estimated rate of diffusion in methanol[17] of 1.26 × 10^{10} M^{-1} s^{-1}. Error limits were estimated to be ±10%):

naphthalene × 10^4, M	quantm yld of **6b**	quantm yld of **2e**
0.00	0.20	0.071
1.64	0.16	0.057
3.28	0.10	0.027
6.56	0.057	0.017
9.80	0.04	
16.4		0.008
	6b	**2e**
slope (10^3K_{sv}), M^{-1}	4.2 ± 0.4	4.9 ± 0.5
(τ)*, μs	0.33	0.41

Kinetic Isotope Study on 2a. To one 10- × 75-mm Pyrex test tube were added 9.6 mg (0.032 mmol) of phosphate **2a**, 8.4 mg (0.035 mmol) of *n*-heptadecane, and 1 mL of methanol. To another 10- × 75-mm Pyrex test tube were added 20.7 mg (0.069 mmol) of **2a**, 11.3 mg (0.047 mmol) of *n*-heptadecane, and 1 mL of methanol-d_4. To a third 10- × 75-mm Pyrex test tube were added 13.4 mg (0.044 mmol) of **2a**, 5.0 mg (0.021 mmol) of *n*-heptadecane, and 1 mL of methanol-*O*-*D*. Each tube was then deaerated with argon for 20 min at 0 °C. The solutions were irradiated with 4 × RPR 3000-Å lamps and monitored by GLC. The results are shown in Table IV.

General Procedure for Photolysis of Desyl Mono- and Dihydrogen Phosphates 1b and 1c at Various pHs. For acidic conditions, the pH in D_2O was adjusted to ~1.8 with perchloric acid. No correction for pD was made. For pH 7.2, a 0.05 M Tris buffer was prepared in D_2O and the pH was adjusted to 7.2 with a NaOH/D_2O solution. For basic conditions, a 0.05 M sodium bicarbonate buffer was prepared in D_2O and the pH was adjusted to ~11.5 with a NaOH/D_2O solution. Each buffer solution was then mixed with an appropriate amount of acetonitrile to form a 60% buffer/40% acetonitrile solvent system. A stock solution of the corresponding phosphate ester, made from the above solvent system, was prepared such that the concentration of the ester was sufficient to insure that practically all the incident light was absorbed. Each tube was sealed with a septum and deaerated with argon for at least 20 min. The desyl mono- and dihydrogen phosphate ester derivatives were irradiated with 4 × RPR 3500-Å lamps. During photolysis, samples were removed at regular time intervals. Prior to HPLC analysis, 0.5 mL from each photolysis tube was mixed with 0.25 mL of an internal standard solution composed of 1,4-diphenyl-1,3-butadiene in acetonitrile. For ^{31}P NMR analysis, 0.5 mL from each photolysis tube was mixed with 0.10 mL of an internal standard solution composed of tetrasodium pyrophosphate in D_2O. An example of this procedure is demonstrated below.

Photolysis of Sodium Desyl Phosphate Ester Salt (Na^+,1c) under Acidic Conditions. Into a 25-mL volumetric flask was placed 220.5 mg (0.658 mmol) of sodium desyl phosphate (Na^+,**1c**). The salt was dissolved in 25 mL of perchloric acid–acetonitrile solution. To each of five 13- × 100-mm Pyrex tubes was added 4 mL of the stock solution. The solutions were deareated with nitrogen and irradiated and aliquots prepared for HPLC and ^{31}P NMR analysis, as previously described. The apparent pH of the solution before and after photolysis was determined to be 1.9. The quantum efficiencies for the disappearance of desyl dihydrogen phosphate (**1c**) Φ_{Dis}, the appearance of 2-phenylbenzo[*b*]furan (**3**) Φ_{App}, and phosphoric acid (**9c**) Φ_{Phos} are shown in Table III.

Phosphorescence of Sodium Desyl Phosphate (Na^+,1c). Into a 5-mL volumetric flask was placed 94.2 mg (0.280 mmol) of sodium desyl phosphate ester, and a solvent mixture composed of 9% H_2O, 45.5% ethanol, and 45.5% diethyl ether was added. A portion of this solution was placed in a quartz phosphorescence tube, cooled in liquid nitrogen (77 K) in a quartz dewar, and placed in the sample compartment of the phosphoroscope. Excitation at 350 nm produced phosphorescence emission maxima at 390, 425, and 450 ± 5 nm. The (0,0) band was at 395 nm, indicating a triplet energy of 73 ± 1 kcal/mol.

Phosphorescence of Desyl Adenosine Cyclic 3′,5′-Phosphate (13). Into a 1-mL volumetric flask was placed 5.5 mg (0.011 mmol) of desyl adenosine cyclic 3′,5′-phosphate (**13**). The salt was diluted to 1 mL using a solvent mixture composed of 9% H_2O, 45.5% ethanol, and 45.5% diethyl ether. A portion of this solution was placed in a quartz phosphorescence tube, cooled in liquid nitrogen (77 K) in a quartz dewar, and placed in the sample compartment of the phosphoroscope. Excitation at 254 nm produced phosphorescence emission maxima at 390, 425, and 450 ± 5 nm. The (0,0) band was 398 nm, indicating a triplet energy of 73 ± 1 kcal/mol.

Phosphorescence of Sodium 2-Naphthalenesulfonate. Into a 50-mL volumetric flask was placed 140.6 mg (0.611 mmol) of sodium 2-naphthalenesulfonate. The salt was diluted to 50 mL using a solvent mixture composed of 20% H_2O, 40% ethanol, and 40% methanol. A portion of this solution was placed in a quartz phosphorescence tube, cooled in liquid nitrogen (77 K) in a quartz dewar, and placed in the sample compartment of the phosphoroscope. Excitation at 274 nm gave phosphorescence emission maxima at 485, 515, 445, and 595 ± 5 nm. The (0,0) band was at 485 nm, yielding a triplet energy of 60 ± 1 kcal/mol.

Stern–Volmer (SV) Quenching Study of 1c with 2-Naphthalenesulfonic Acid. To a 25-mL volumetric flask was added 350.1 mg (1.04 mmol) of sodium desyl phosphate (Na^+,**1c**). The salt was diluted to 25 mL using a solvent mixture composed of 40% acetonitrile and 60% perchloric acid (0.05 M, pH = 1.5). A stock solution of 2-naphthalenesulfonic acid (0.176 M) was prepared with the same solvent mixture. To each of nine 13- × 100-mm Pyrex tubes was added 2 mL of the stock solution of the desyl salt. To eight of the tubes were added 0.15 (0.026 mmol), 0.30 (0.053 mmol), 0.60 (0.10 mmol), 0.90 (0.16 mmol), 1.20 (0.21 mmol), 1.5 (0.26 mmol), 1.8 (0.32 mmol), and 2.00 mL (0.35 mmol) of the 2-naphthalenesulfonic acid stock solution. The total volume of each of the nine tubes was brought to 4 mL by adding an appropriate amount of the 40% acetonitrile and 60% aqueous perchloric acid solution. The solutions were deareated with argon for 20 min at room temperature and irradiated for 15 min using 4 × RPR 3500-Å lamps. Prior to HPLC analysis, 0.5 mL from each photolysis mixture was added to 0.25 mL of a 1,4-diphenyl-1,3-butadiene/acetonitrile stock solution for use as an internal standard. Analysis was carried out as described in the general procedure section. The lifetime of the triplet state was derived from K_{sv} for the quenching of the appearance of 2-phenylbenzo[*b*]furan (**3**) by a linear least-squares analysis. SV quenching of **1c** by 2-naphthalenesulfonic acid results [quantum efficiency (concentration of quencher, mM)]: 0.10 (0.00), 0.085 (6.60), 0.073 (13.2), 0.058 (26.0), 0.044 (39.0), 0.034 (57.0), 0.028 (66.0), 0.024 (88.0). K_{sv} = 37 M^{-1}; τ_T = 3.3 ns (k_{diff} = 1.1 × 10^{10} M^{-1} s^{-1}).[21]

SV Quenching Study of Desyl Sodium Isopropyl Phosphate (1b) with 2-Naphthalenesulfonic Acid. Into a 25-mL volumetric flask was placed 376.2 mg (1.056 mmol) of sodium desyl isopropyl phosphate (**1b**). The salt was dissolved in 25 mL using a solvent mixture composed of 40% acetonitrile and 60% aqueous perchloric acid (0.05 M, pH = 1.5). A stock solution of 2-naphthalenesulfonic acid (0.18 M) was prepared in the same solvent mixture. To each of nine 13- × 100-mm Pyrex tubes was added 2 mL of the stock solution of sodium desyl isopropyl phosphate ester salt (**1b**). To eight of these tubes were added 0.15 (0.026 mmol),

0.30 (0.053 mmol), 0.60 (0.10 mmol), 1.00 (0.17 mmol), 1.20 (0.21 mmol), 1.5 (0.26 mmol), 1.8 (0.32 mmol), and 2.00 mL (0.35 mmol), respectively, of the 2-naphthalenesulfonic acid stock solution. The total volume of each of the nine Pyrex tubes was brought to 4 mL by addition of an appropriate amount of the 40% acetonitrile and 60% acid solution. The solutions were deaerated for 20 min with argon at room temperature prior to irradiation for 15 min using 4 × RPR 3500-Å lamps. Prior to HPLC analysis, 0.5 mL from each photolysis mixture was added to 0.25 mL of a 1,4-diphenyl-1,3-butadiene/acetonitrile internal standard stock solution. HPLC conditions are given in the section on general procedures. The lifetime of the triplet state was derived from K_{sv} for the quenching of the appearance of 2-phenylbenzo[*b*]furan by a linear least-squares analysis. The results are as follows [quantum efficiency for quenching of **3** (2-naphthalenesulfonic acid, mM)]: 0.12 (0.00), 0.10 (6.8), 0.089 (13.5), 0.059 (27.0), 0.044 (45.0), 0.036 (54.0), 0.029 (68.0), 0.024 (81.0). K_{sv} = 49 M^{-1}; τ_T = 4.4 ns (k_{diff} = 1.1 × 10^{10} M^{-1} s^{-1}).[21]

Photolysis of Desyl Adenosine Cyclic 3′,5′-Phosphate (13) at pH 7.0. Into a 5-mL volumetric flask was placed 42.8 mg (0.032 mmol) of a diasteriomeric mixture of desyl adenosine cyclic 3′,5′-phosphate (**13a/13b**). The cyclic triester was diluted to 5 mL with 1:1 Tris buffer/dioxane solution. To each of five 10- × 75-mm Pyrex tubes was added a 1-mL aliquot of the stock solution. The solutions were deareated with nitrogen, irradiated, and prepared for HPLC and ^{31}P NMR analysis as previously described. The apparent pH of the solution before and after photolysis was measured to be 7.2. The quantum efficiencies for the disappearance of desyl adenosine cyclic 3′,5′-phosphate (**13**) Φ_{Dis}, the appearance of adenosine cyclic 3′,5′-phosphate (**11**) Φ_{App}, and the appearance of 2-phenylbenzo[*b*]furan (**3**) Φ_{App} are shown in Table V.

In a separate experiment, 85.6 mg (0.16 mmol) of desyl adenosine cyclic 3′,5′-phosphate (**13 ax/13 eq**) was dissolved in 10 mL of a 1:1 mixture of dioxane:0.05 mM Tris (in D_2O, pH adjusted to 7.0 with NaOH/D_2O). Into a series of NMR tubes was placed 1.0 mL of the desyl cAMP solution which was then deareated with nitrogen and photolyzed in the merry-go-round apparatus with 4 × RPR 3500-Å lamps. Sample tubes were removed periodically and examined by ^{31}P NMR (see Figure 1). Chemical shifts are reported relative to 85% H_3PO_4 as an external standard.

Photolysis of Desyl cAMP (13) at Various pHs. Cyclic triester **13** (50.3 mg, 0.10 mmol) was dissolved in 3.0 mL of dioxane. Into each of six 10- × 75-mm Pyrex tubes was placed 0.5 mL of the desyl cAMP (**13**) stock solution and the volume brought to 1.0 mL by the addition of 0.5 mL of one of the following buffer solutions: 0.05 M phosphate buffer (pH = 7, H_2O), 0.05 M phosphate buffer (pH = 7, D_2O), 0.05 M Tris buffer (pH = 7.2, H_2O), 0.05 M Tris buffer (pH = 7.2, D_2O), or 0.05 M perchloric acid (pH 1.8, D_2O). The pH of each final solution was determined. The solutions were deareated with argon for 20 min and irradiated for 10 min with 4 × RPR 3500-Å lamps. Prior to HPLC analysis, 0.5 mL from each photolysis mixture was added to 0.25 mL of a solution containing 1,4-diphenyl-1,3-butadiene for use as an internal standard. Analysis was carried out as described in the general procedure section. The quantum efficiencies are shown in Table V.

Competitive Quenching Study of Desyl cAMP (13) with 2-Naphthalenesulfonic Acid. The triester (38.7 mg, 0.074 mmol) was dissolved in 2 mL of a solvent mixture composed of 50% aqueous Tris buffer (0.05 M, pH = 7.2). A stock solution of 2-naphthalenesulfonic acid (0.18 M) was prepared with the same solvent mixture. To five 10- × 75-mm Pyrex tubes was added 0.4 mL of the desyl cAMP (**13**) stock solution. To four tubes were added 0.09 (0.016 mmol), 0.15 (0.027 mmol), 0.25 (0.046 mmol), and 0.35 mL (0.064 mmol) of the 2-naphthalenesulfonic acid stock solution. The total volume was brought to 1 mL by adding an appropriate amount of 50% dioxane and 50% Tris aqueous buffer solution to each of the five Pyrex tubes. The solutions were deareated with argon for 20 min at room temperature and irradiated for 15 min using 4 × RPR 3500-Å lamps. Prior to HPLC analysis, 0.5 mL from each photolysis mixture was added to 0.25 mL of a 1,4-diphenyl-1,3-butadiene/acetonitrile solution. Analysis was carried out as described in the general procedure section. The lifetime of the triplet was derived from K_{sv} for the appearance of 2-phenylbenzo[*b*]furan (**3**) by a linear least-squares analysis. The results are as follows [quantum efficiency for quenching of **3** (2-naphthalenesulfonic acid, mM)]: 0.17 (0.00), 0.14 (16.4), 0.10 (27.3), 0.08 (45.5), 0.071 (63.7). K_{sv} = 23 ± 2 M^{-1}; τ_T = 0.52 ns (k_{diff} = 4.4 × 10^{10} M^{-1} s^{-1}).[21]

Half-life Measurements $t_{1/2}$ for Desyl cAMP (13). Cyclic triester **13** (31.8 mg, 0.059 mmol) was dissolved in 2.0 mL of dioxane. To each of five 10- × 75-mm Pyrex tubes was added 0.5 mL of the cAMP stock solution. Each tube was brought to 1.0 mL by the addition of either a 0.05 M Tris buffer (pH = 7.2, D_2O), 0.05 M Tris buffer (pH = 7.2, H_2O), 0.05 M phosphate buffer (pH = 7.0, H_2O), 0.05 M phosphate buffer (pH = 7.0, D_2O), or 0.05 M acetate buffer (pH 2.0, D_2O). The pH was determined, and the solutions were placed in the dark at room temperature and monitored by HPLC at various time intervals spanning several days. The results are shown in Table VI.

Competitive Quenching Study of 1a with Naphthalene. To 33 mL of benzene were added 264.0 mg (0.758 mmol) of desyl diethyl phosphate (**1a**) and 28.3 mg (0.118 mmol) of *n*-heptadecane, which comprised stock solution A. To 20 mL of benzene was added 111.6 mg (0.871 mmol) of naphthalene, to make up stock solution B. Six separate samples containing 0, 1, 2, 3, 4, and 5 mL of stock B and 5 mL of stock A (each sample was diluted to 10 mL with benzene) were placed in Pyrex tubes, deaerated with nitrogen, and irradiated with 12 × RPR 3500-Å lamps. The concentration of **1a** in all irradiated samples was 11.5 mM, whereas the concentrations of naphthalene varied from 4.35 to 21.8 mM. The reactions were monitored by GLC. A linear least-squares analysis was performed on the data obtained. K_{SV} = 46.2 ± 8 M^{-1} and τ_T = 4.6 × 10^{-9} s for the appearance of **3a**, and K_{SV} = 26.8 ± 10 M^{-1} and τ_T = 2.7 × 10^{-9} s for the disappearance of **1a** were obtained (k_{diff} = 10^{10} M^{-1} s^{-1} for benzene at 40 °C).[22]

Competitive Quenching Study of 1a with *trans*-1,3-Pentadiene. Two stock solutions, one containing 198.7 mg (0.570 mmol) of **1a** and 25.0 mg (0.104 mmol) of *n*-heptadecane in 26 mL of benzene (stock A) and a second containing 55.3 mg (0.812 mmol) of *trans*-piperylene in 10 mL of benzene (stock B), were prepared. Six separate samples containing 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of stock B and 4 mL of stock A plus added benzene to make the total volume of each sample equal to 7 mL were placed in Pyrex tubes, deaerated with nitrogen, and irradiated with 8 × RPR 3500-Å lamps. The concentration of **1a** was 12.5 mM for each tube, whereas the concentration of quencher varied from 5.80 to 29.0 mM. Aliquots were removed for GLC analysis after 10 and 18 min of irradiation. SV plots were determined, and the slopes K_{sv} and lifetimes are as follows: K_{SV} = 56 ± 31 M^{-1} and τ_T = 5.6 ns for the appearance of **3a**, and K_{SV} = 65 ± 31 M^{-1} and τ_T = 6.5 ns for the disappearance of **1a** (k_{diff} = 10^{10} M^{-1} s^{-1} at 40 °C).[22]

Phosphorescence of Desyl Diethyl Phosphate Ester and Benzoin. Two solutions, one of 15.6 mg (44.8 μmol) of **1a** and the other of 9.8 mg (46.2 μmol) of benzoin (recrystallized five times from ethanol), were prepared with 10 mL of a solution of ether, isopentane, and ethanol (EPA; 5:5:2, v:v:v), and emission spectra were recorded at 77 K at excitation wavelengths of 340 and 360 nm. The phosphorescence emission maxima were at 392, 418, and 442 nm for **1a** and 391, 417, and 440 nm for benzoin with the onset at 390 ± 5 nm corresponding to the triplet energy of 73.3 ± 0.9 kcal/mol for both **1a** and benzoin.

Acknowledgment. Generous support from the Petroleum Research Fund, administered by the American Chemical Society (17541-AC4), the NSF OSR 9255223, the state of Kansas, and the General Research Fund of the University of Kansas is gratefully acknowledged. L.W.K. thanks the R. J. McElroy Foundation of Waterloo, IA, for a graduate fellowship.