agents, including isopropyl iodide, a facile reaction occurred. The monoalkylated products were isolated in good yield (Table I). Yields have not been optimized.

Table I. Alkylation of Dianion from $(CH_3O)_2P(=O)CH_2COCH_3$

R–X	Yield of **2**,[a,b] %	Bp of **2**, °C (*P*, mm)
CH_3I	71	68–70 (0.1)
$CH_3CH_2CH_2CH_2I$	70	88–89 (0.1)
$CH_3CH_2CH_2CH_2Br$	70	87–89 (0.1)
$(CH_3)_2CHI$	65	74–76 (0.07)
$CH_2{=}CHCH_2Br$	75	84–85 (0.1)
$C_6H_5CH_2Cl$	70	120–122 (0.5)

[a] All substances exhibited nmr, ir, and analytical data in accord with the assigned structures and were further identified by comparison with authentic samples prepared by alternate routes. [b] Yields refer to distilled products. Crude yields were on the order of 90%.

It was evident from the nmr spectra that alkylation occurred exclusively at the γ carbon. Furthermore, spectral analysis of the crude reaction mixture failed to give any evidence of alkylation at the α carbon, dialkylation, or O-alkylation. The nmr spectra of **2**[4] have a two proton doublet (J_{HP} = 23 Hz) at δ 3.13 due to the α-methylene protons. The absence of a three proton singlet at *ca.* δ 2.30 further indicated that alkylation occurred only on the γ carbon.

We have also alkylated γ-substituted β-keto alkylphosphonates (eq 3). Starting with dimethyl 2-oxo-

$$\underset{\mathbf{2}}{(CH_3O)_2\overset{O}{\overset{\|}{P}}CH_2COCH_2R} \longrightarrow \underset{\mathbf{5}}{(CH_3O)_2\overset{O}{\overset{\|}{P}}CH_2COCHRR'} \quad (3)$$

propylphosphonate (**1**), it is possible to generate the dianion **3**, alkylate with RX, generate the dianion of this alkylated product with an additional equivalent of *n*-butyllithium, and add a second alkylating agent (R′X) to yield **5**; for example, phosphonate **5** (R = *n*-Bu, R′ = benzyl) could be obtained in low yield from **1** in this manner. One can, however, obtain high yields of **5** if the monoalkylated product **2** was isolated and purified before proceeding with the second alkylation (Table II).

Table II. Alkylation of Dianion from Dimethyl 2-Oxoheptylphosphonate

R–X	Yield of **5**,[a,b] %
CH_3I	71
$CH_3CH_2CH_2CH_2I$	73
$CH_2{=}CHCH_2Br$	70
$C_6H_5CH_2Cl$	67

[a] Yields refer to pure product after purification on silica gel. [b] All substances exhibited nmr, ir, and analytical data in accord with the assigned structures.

The following procedure for the preparation of dimethyl 2-oxoheptylphosphonate (**2**) (R = *n*-Bu) is representative. A dry 100-ml flask equipped with septum inlet and magnetic stirrer containing 0.44 g of sodium hydride (57%, washed with hexane to remove mineral oil) was flushed with nitrogen and maintained under a positive pressure of nitrogen. Approximately 25 ml of freshly distilled anhydrous THF was added followed by the dropwise addition (*via* syringe) of dimethyl 2-oxopropylphosphonate (10 mmol, 1.7 g). The reaction mixture was stirred at room temperature for 1.5 hr to allow for formation of the monoanion (white precipitate). Then, 11 mmol (6.6 ml of 1.66 *M*) of *n*-butyllithium in hexane was added dropwise (0°) and the resultant solution was stirred for 20 min. The white precipitate of the monoanion disappeared immediately upon addition of the *n*-butyllithium. Butyl iodide (12 mmol, 2.2 g) was added (0°) and the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched by the addition of 5% aqueous HCl and the product was isolated by extraction with chloroform. After drying the combined organic extracts, the solvents were removed under reduced pressure and the crude product was distilled to yield 1.6 g (70%) of dimethyl 2-oxoheptylphosphonate which was identical (nmr, ir, ms, glc) with an authentic sample.

The specific alkylation at γ carbon of **1** *via* dianion **3** makes dimethyl 2-oxopropylphosphonate a useful reagent in organic synthesis and provides a general high-yield synthesis of β-keto phosphonates for use in the Horner–Emmons modification of the Wittig olefin synthesis. The preparation of dimethyl 2-oxoheptylphosphonate (**2**)[5] (R = *n*-Bu) as illustrated above provides a new route to a key prostaglandin reagent.[6] Furthermore the reaction sequence allows for eventual modification of the alkyl portion of the C_8 side chain found in prostaglandins.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(4) The nmr spectrum of dimethyl 2-oxopropylphosphonate has the following signals: δ ($CDCl_3$) 2.30 (s, 3 H, COMe), 3.00 (d, 2 H, J_{HP} = 23 Hz, PCH_2), 3.72 [d, 6 H, J_{HP} = 11 Hz, $(MeO)_2PO$].

(5) Previously prepared from ethyl hexanoate and dimethyl α-lithiomethanephosphonate: E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5654 (1966). The preparation of **2** (R = *n*-Bu) and similar keto phosphonates is usually impractical by the Michaelis–Arbusov reaction: B. A. Arbusov, *Pure Appl. Chem.*, **9**, 307 (1964).

(6) For some recent uses of **2** (R = *n*-Bu) in prostaglandin synthesis, see E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf, and R. K. Varma, *J. Amer. Chem. Soc.*, **93**, 1491 (1971); E. J. Corey and P. A. Grieco, *Tetrahedron Lett.*, 107 (1972); P. Crabbé and A. Guzmán, *ibid.*, 115 (1972); H. L. Slates, Z. S. Zelowski, D. Taub, and N. L. Wendler, *J. Chem. Soc., Chem. Commun.*, 304 (1972).

Paul A. Grieco,* C. S. Pogonowski
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213
Received December 27, 1972

Photochemical Formation of Oxazolidines from Aryl Ketones and Aliphatic Imines

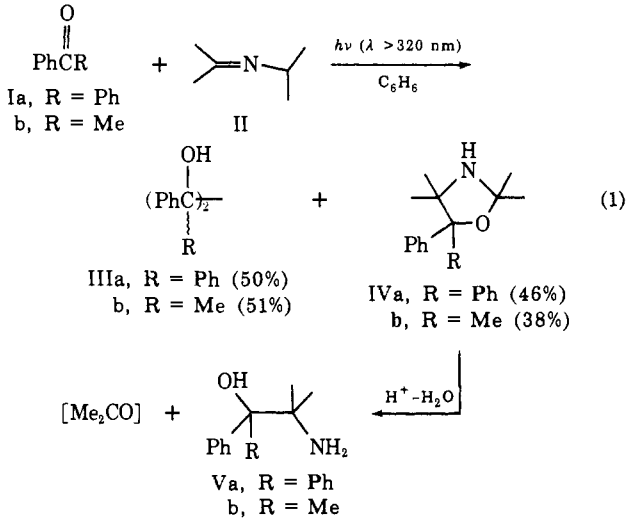
Sir:

As part of a broadly based study of the interaction between electronically excited reagents and nitrogen-containing systems,[1] we have investigated the photochemical reaction of aryl ketones with aliphatic Schiff bases. Here we report the novel, synthetically useful formation of substituted oxazolidines from irradiation

(1) A. A. Baum, L. A. Karnischky, D. McLeod, Jr., and P. H. Kasai, *J. Amer. Chem. Soc.*, **95**, 617 (1973).

of aryl ketones in the presence of aliphatic imines, and also the generation of an example of a new class of ambident radicals: 2-azaallyls.

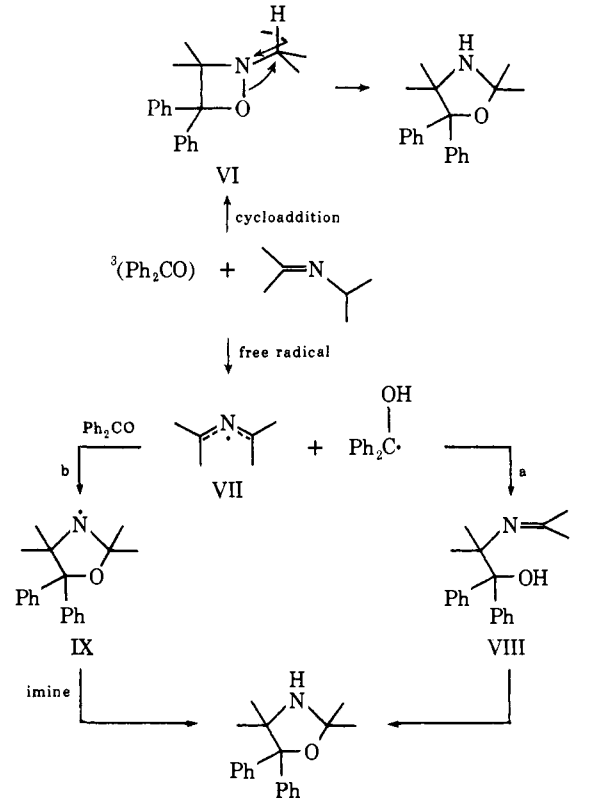
A nitrogen-purged solution of benzophenone (Ia) (3.0 g) and isopropylidineisopropylamine (II) (6.0 g) in 250 ml of benzene was irradiated through a uranium-glass filter with a 450-W medium-pressure mercury lamp for 3.5 hr. Glpc analysis of the crude photolysis solution revealed that no diisopropylamine was formed. Evaporation of solvent and excess imine left a crystalline residue which was readily separated into two components by chromatography on silica gel. The material first eluted was identified as benzopinacol (IIIa) (50% based on the benzophenone consumed) by comparison with an authentic sample. The second component (46% based on benzophenone) was assigned the 2,2,4,4-tetramethyl-5,5-diphenyloxazolidine structure (IVa) shown in eq 1 on the basis of its spectral and analytical properties.[2] This assignment was supported by the observation that IVa was quantitatively converted into 1,1-diphenyl-2-amino-2-methylpropanol[3] (Va) when heated at reflux with aqueous methanolic HCl. Irradiation of a benzene solution of acetophenone (Ib) and II as above afforded another 1:1 adduct (IVb). The 2,2,4,4,5-pentamethyl-5-phenyloxazolidine structure was assigned to IVb on the basis of its spectral properties and chemical behavior.[2] These results are summarized in eq 1.



(1)

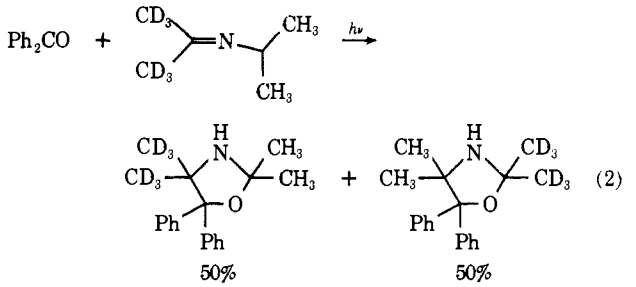
We have considered two mechanistic pathways as *a priori* possibilities for explaining the formation of oxazolidines in the above reactions. The first of these involves cycloaddition of the triplet[4] excited carbonyl compound across the carbon–nitrogen double bond of the imine followed by rearrangement of the azaoxetane[6] intermediate (VI) as shown in Scheme I

Scheme I. Possible Mechanisms for Oxazolidine Formation



("cycloaddition" path). This mechanism requires that pinacol be formed in a separate reaction between excited ketone and imine. Alternatively, oxazolidine formation could follow either free radical path shown in Scheme I. Thus, tetramethyl-2-azaallyl (VII) formed by dehydrogenation of imine by triplet[4] excited ketone could either couple with protonated ketyl (path a), or enter into a 3 + 2 radical cycloaddition reaction with ketone (path b). The hydroxyimine (VIII) formed in path a would be expected to cyclize to the oxazolidine;[7] the neutral amino species (IX) formed in b could give oxazolidine by hydrogen abstraction from another molecule of imine.

Distinction between the cycloaddition and free radical pathways was made on the basis of a labeling experiment. When benzophenone was irradiated in the presence of isopropylidineisopropylamine containing 80% deuterium in the allylic methyl positions, the oxazolidine isolated had deuterium equally distributed between the methyls at C-2 and C-4 as determined by nmr spectroscopy (eq 2). Since the recovered imine



(2)

was completely unscrambled, this result strongly suggests that the symmetrical 2-azaallyl radical is an intermediate. That the formation of oxazolidine is the

(2) The infrared, nmr, uv, and mass spectra of the 1:1 adduct are consistent only with the cyclic structure shown and not the acyclic hydroxyimine tautomer. Details will be presented in our full paper.

(3) H. M. Kissman, D. S. Tarbell, and J. Williams, *J. Amer. Chem. Soc.*, 75, 2959 (1953).

(4) Since the singlet lifetime of benzophenone is *ca.* 6 psec,[5] it would be impossible for 0.2 *M* imine to efficiently intercept this excited state by diffusion. Since at this imine concentration benzophenone disappears with $\phi \sim 0.3$, and since ultraviolet spectroscopy reveals no ground state complex formation, the triplet state must be responsible for these reactions.

(5) P. M. Rentzepis and C. J. Mitschele, *Anal. Chem.*, 42 (14), 20A (1970).

(6) Of the two possible azaoxetanes, the one shown in Scheme I is the one most likely to rearrange under the reaction conditions.

(7) E. D. Bergmann, *Chem. Rev.*, 53, 309 (1953).

result of coupling of this radical with a protonated ketyl (path a), and not a 3 + 2 radical cycloaddition reaction (path b) follows from yield *vs.* concentration studies. In the latter case, the yield of oxazolidine would be expected to increase with increasing ketone concentration.[8] The coupling mechanism predicts the oxazolidine yield to be essentially independent of ketone concentration. In fact, when the initial benzophenone concentration was varied from 0.02 to 0.09 *M*, the yield of oxazolidine IVa remained constant at 46% showing that the coupling mechanism is operative.

The failure of imine II to undergo 2 + 2 photocycloaddition with excited aryl ketones is noteworthy. Irradiation of benzophenone and 2,4-dimethyl-2-pentene, the hydrocarbon analog of II, gives a mixture of the two possible oxetanes in 94% yield;[9] thus, the azomethine nitrogen of II is exerting the controlling influence.

Other investigators have shown that irradiation of alcohol solutions of aryl ketones and *diaryl-N*-alkylimines results in reduction of imine.[10] The protonated ketyl derived from ketone by hydrogen abstraction from solvent presumably delivers a hydrogen atom to the azomethine double bond of the imine, and the resulting α-aminoalkyl radical gives amine by disproportionation.[10] In the present case the α-aminoalkyl radical formed would not benefit from aryl stabilization, and it is perhaps not surprising that reduction of the imine double bond does not compete favorably with the self- or cross-coupling reactions of the ketyl radical. Competition between reduction and coupling with 2-azaallyl (*i.e.*, cross coupling) is further complicated by the fact that the latter reaction may well be occurring within the initial solvent cage.[11]

(8) Only ~50% of the imine consumed forms oxazolidine suggesting radical VII is being partitioned between "oxazolidine" and "non-oxazolidine" pathways. The latter does not involve benzophenone since all the consumed benzophenone can be accounted for in terms of IIIa + IVa.

(9) A. A. Baum, unpublished results.

(10) (a) M. Fischer, *Chem. Ber.*, **100**, 3599 (1967); (b) A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2653 (1969).

(11) See, for example, S. A. Weiner, *J. Amer. Chem. Soc.*, **93**, 425 (1971).

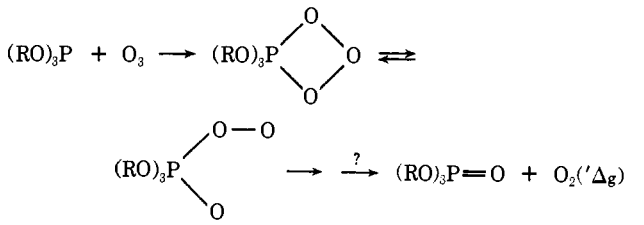
Anthony A. Baum,* Linda A. Karnischky
Union Carbide Corporation, Tarrytown Technical Center
Tarrytown, New York 10591
Received January 16, 1973

Mechanisms in Phosphite Ozonide Decomposition to Phosphate Esters and Singlet Oxygen

Sir:

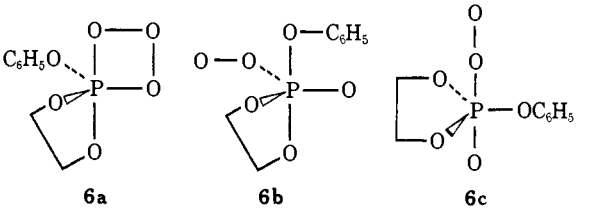
Phosphite ozonides[1-6] represent a particularly convenient and readily accessible source of singlet excited molecular oxygen, a synthetically useful intermediate with potential environmental and biological importance.[7-9] We wish to report here evidence for the involvement of two mechanisms in the decomposition of these ozonides to phosphate esters and oxygen. The data[10] presented below indicate that ozonides derived from phosphites with small rings or bicyclic structures decompose by simple extrusion of oxygen from the adduct without rearrangement about phosphorus. The decomposition of these phosphite ozonides shows virtually no substituent sensitivity, as is evident by the similarity in the decomposition rates of compounds **1-8** ($k = 1.4 \pm 0.4 \times 10^{-4}$ sec^{-1} at $-5°$ in CH_2Cl_2). On the other hand, those phosphite ozonides without geometrical constraints appear to decompose by a much lower energy pathway and display substantial substituent sensitivity consistent with a requirement for prior rearrangement *via* pseudorotation.

Previous work on these ozone adducts may be interpreted to support an overall mechanism for the decomposition reaction as shown below. Thompson's ^{31}P



nuclear resonance data[1] provide strong evidence for pentacovalent phosphorus intermediates. Evidence for a rapid preequilibration of ring-closed and ring-opened ozonides is derived from thermochemical analyses of Benson and Shaw,[12] which indicate a maximum oxygen–oxygen bond strength of 2 kcal/mol compared with activation energies in the decomposition step of ~15 kcal/mol.[2,3] Our results add to this simple description and indicate that the decomposition step is deceptively complex and best described in terms of two mechanisms.

The similarity of the rates of decomposition for phosphite ozonides **1-8** suggests that one mechanism is operative in these cases. Support for this idea may be obtained by noting that the five-membered ring and the bicyclic phosphites are constrained to decompose from a limited range of geometries. Pseudorotations of the ozonides of phosphites **2-8** lead to several chemically distinguishable species, illustrated for compound **6**.



6a **6b** **6c**

Of these species, only **6a** or an ozonide ring opened

(1) Q. E. Thompson, *J. Amer. Chem. Soc.*, **83**, 845 (1961).

(2) (a) R. W. Murray and M. L. Kaplan, *ibid.*, **91**, 5358 (1969); (b) *ibid.*, **90**, 537 (1968).

(3) E. Koch, *Tetrahedron*, **26**, 3503 (1970).

(4) (a) E. Wasserman, R. W. Murray, M. L. Kaplan, and W. A. Yager, *J. Amer. Chem. Soc.*, **90**, 4160 (1968); (b) R. W. Murray and M. L. Kaplan, *ibid.*, **90**, 4161 (1968).

(5) (a) P. D. Bartlett and G. D. Mendenhall, *ibid.*, **92**, 210 (1970); (b) P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 6055 (1970).

(6) M. E. Brennan, *Chem. Commun.*, 956 (1970).

(7) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

(8) A. M. Trozzolo, *Ann. N. Y. Acad. Sci.*, **171** (1970).

(9) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(10) Phosphites not commercially available were prepared by standard methods.[11] Ozonides were prepared by addition of phosphite to solutions of ozone in methylene chloride maintained at $-78°$. All ozonides have been shown to produce singlet oxygen (presumably $^1\Delta_g$) by the characteristic bleaching effect on rubrene.

(11) (a) G. M. Kosolopoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950; (b) W. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, *J. Amer. Chem. Soc.*, 72, 5491 (1950); (c) P. C. Crofts, J. H. H. Markes, and H. N. Rydon, *J. Chem. Soc.*, 4250 (1958).

(12) S. Benson and R. Shaw, *Org. Peroxides*, **1**, 105 (1970).