been verified.[23] With the exception of the rhodium complex **1a**, the other active catalysts[15,24] are known to form complexes with molecular oxygen. It is significant that the iridium chloride complex **1b** is a poor catalyst for the autoxidation in benzene solution, but the analogous iodide complex **8** is an effective catalyst. Apparently, olefins such as cyclohexene displace oxygen from the coordination sphere in **1b**, and the resulting olefin complex is less likely to coordinate with oxygen. It is probable that a prerequisite for this oxidation is prior coordination of molecular oxygen. The iodide **8** is known to form a much more stable oxygen adduct than the chloride **1b**.[2b,15]

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[23] Such an intermediate has been suggested in the autoxidation of olefins catalyzed by iron phthalocyanine: A. H. Cook, *J. Chem. Soc.*, 1774 (1938).

[24] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect. A*, 1711 (1966).

[25] Author to whom inquiries should be addressed: Department of Chemistry, Stanford University, Stanford, Calif. 94305.

[26] National Science Foundation Science Faculty Postdoctoral Fellow, 1966–1967.

James P. Collman,[25] Mitsuru Kubota,[26] John W. Hosking
Venable Laboratory, University of North Carolina
Chapel Hill, North Carolina

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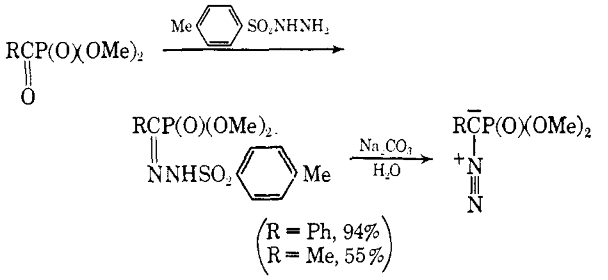
Novel Diazoalkanes and the First Carbene Containing the $(MeO)_2P(O)$ Group

Sir:

The preparation of diazoalkanes containing heteroatom substituents, *e.g.*, $(RS)_2CN_2$,[1] $(PhSO_2)_2CN_2$,[2] $ROCH_2CHN_2$,[3] and RSO_2CHN_2,[4] their preparative utilization, and their decomposition to carbenes have been of current interest. Diazoalkanes containing phosphorus substituents, $Ph_2P(O)C(Ph)N_2$[5] and $R_2P(O)CHN_2$ (R = Ph, $PhCH_2$),[6] have been reported also.

We have prepared $(MeO)_2P(O)C(Ph)N_2$ (I) and $(MeO)_2P(O)C(Me)N_2$ (II) because we felt that they would serve excellently, *via* the great variety of reactions diazoalkanes and the carbenes (or carbenoids) derived from them are capable of undergoing, in the introduction of organophosphorus functionality into diverse organic and inorganic compounds. We felt that I and II would be more useful than the $Ph_2P(O)$-substituted diazoalkanes since their methoxy groups represent reactive phosphorus functionality which would be useful in further synthetic steps.

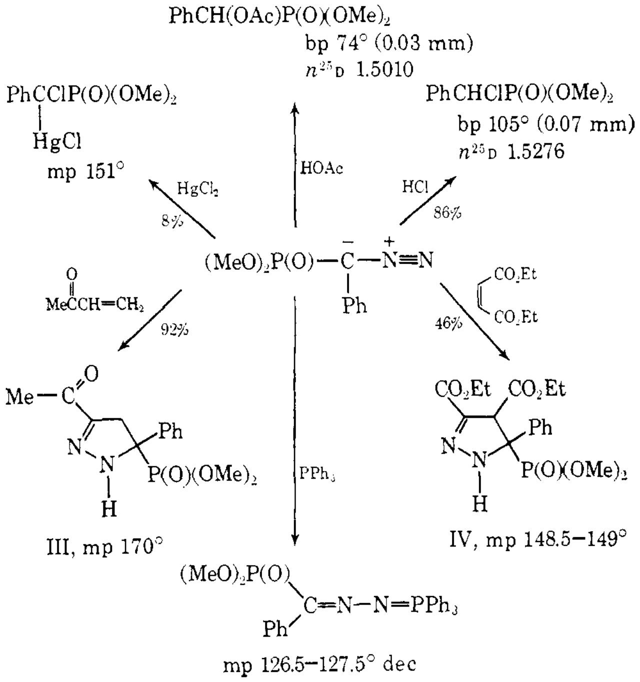
Compounds I and II were synthesized as shown in eq 1. Compound I is an orange-red, crystalline solid, mp 44–44.5°, which could be distilled at reduced pressure and which appears to be stable indefinitely at room temperature. Compound II is a yellow, distillable liquid, bp 37–38° (0.13 mm), $n^{25}D$ 1.4583, which decomposes slowly at room temperature but is quite stable on storage at 0°. Both compounds show infrared bands characteristic of the diazo group, I at 2080 and II at 2075 cm^{-1}, as well as P–O absorption at 1260 cm^{-1}.



(1)

The unusually high stability of $Ph_2P(O)$- and $(MeO)_2P(O)$-substituted diazoalkanes is noteworthy and may be a consequence of C → P π bonding. Compounds I and II have proved to be versatile reagents, undergoing the usual diazoalkane reactions and also showing carbenoid reactivity on treatment with copper powder. Scheme I summarizes reactions of I, Scheme II reactions of II. The products of 1,3-dipolar addition of I and II to activated vinyl compounds appear to be 2-pyrazolines as shown; where two modes of addition are possible, the isomer involving Michael addition of the diazo carbon is favored. All 1,3-dipolar adducts showed strong N–H infrared absorption at ~3200 cm^{-1} and a broad downfield singlet in the nmr spectrum, which was assignable to the N-*H* proton. Adducts to methyl vinyl ketone and ethyl acrylate showed carbonyl absorption corresponding to α,β unsaturation: $\nu_{C=O}$ (cm^{-1}): III, 1660; V, 1655; VI, 1725. The diethyl maleate adduct IV showed two distinct C=O peaks at 1725 and 1735 cm^{-1}, demonstrating the presence of conjugated and unconjugated carbonyl groups.[7] Of special interest in Scheme II is the reaction of II with phenyl(bromodichloromethyl)mercury in refluxing ben-

Scheme I. Reactions of $(MeO)_2P(O)C^-(Ph)N_2^+$



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[1] U. Schöllkopf and U. Wiskott, *Ann. Chem.*, **694**, 44 (1966).

[2] J. Diekmann, *J. Org. Chem.*, **28**, 2933 (1963).

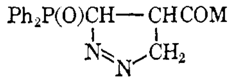
[3] C. Grot, E. Pfeil, E. Weinrich, and O. Weissel, *Ann. Chem.*, **679**, 42 (1964).

[4] A. M. Van Leusen, R. J. Mulder, and J. Strating, *Rec. Trav. Chim.*, **86**, 225 (1967), and earlier publications of this research group.

[5] L. Horner, H. Hoffmann, H. Ertel, and G. Klahre, *Tetrahedron Letters*, 9 (1961).

[6] N. Kreutzkamp, E. Schmidt-Samoa, and A. K. Herberg, *Angew. Chem.*, 77, 1138 (1965).

[7] Kreutzkamp, *et al.*,[6] reported that additions of $Ph_2P(O)CHN_2$ to methyl vinyl ketone and dimethyl maleate give 1-pyrazolines, *e.g.*, i,

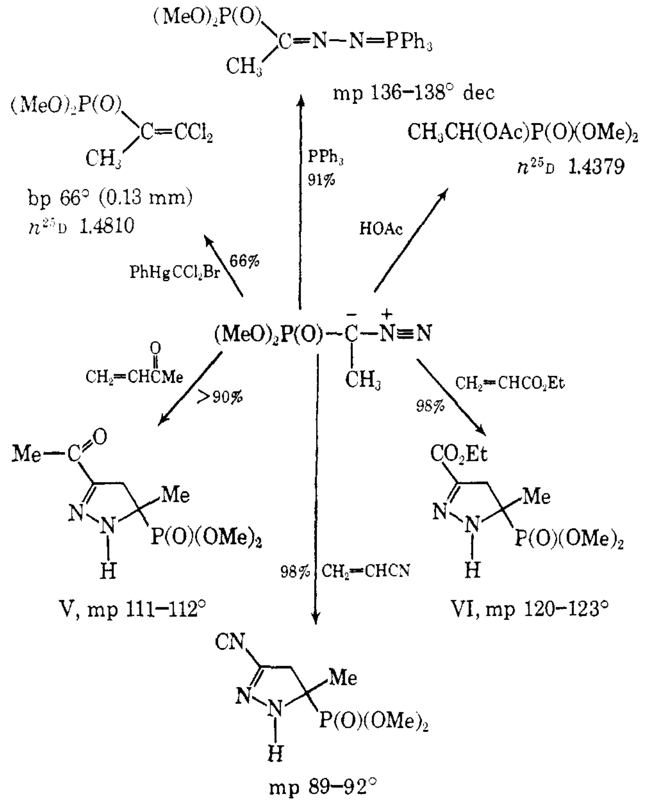


$$\begin{array}{c} Ph_2P(O)CH{-}CHCOMe \\ N{=}N{-}CH_2 \end{array}$$

i

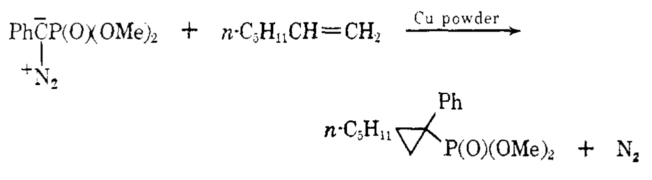
but unfortunately provided no spectroscopic evidence in support of their structural assignments, so that their correctness cannot be assessed.

Scheme II. Reactions of $(MeO)_2P(O)C^-(CH_3)N_2^+$

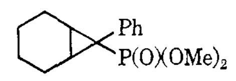


zene. Dihalocarbene–diazoalkane reactions have been reported previously by Reimlinger,[8] and this represents the first application of this mercurial reagent in such a reaction. Notable also is the stability of I and II toward carboxylic acids. On a 10-mmole scale, a ~15-hr period of reflux of I in ethereal acetic acid (100% excess) was required for the evolution of nitrogen to be completed. I was inert to benzoic acid under the same conditions.

While a solution of I in benzene could be boiled for 48 hr without perceptible decomposition, the addition of copper powder to a benzene solution of I, followed by a 19-hr reflux period, resulted in evolution of nitrogen and a color change from orange to yellow. When a mixture of 6 mmoles of I, 60 mg-atoms of copper powder, and 100 ml of 1-heptene was heated at reflux for 12 hr, this same color change was observed. Filtration through Celite, evaporation of unconverted olefin, and distillation at reduced pressure gave 1.29 g (73%) of dimethyl 1-phenyl-2-*n*-amylcyclopropylphosphonate, bp 108° (0.04 mm), n^{25}_D 1.5025. A similar reaction



with cyclohexene gave VII (stereochemistry unknown), mp 117–118°, in 65% yield. Another recrystallization from cyclohexane raised the melting point to 120–120.5°. No addition of $PhCP(O)(OMe)_2$ to tetramethylethylene or *cis*-1,2-dichloroethylene was observed. In these cases the $PhCP(O)(OMe)_2$-derived product was $(MeO)_2P(O)C(Ph){=}C(Ph)P(O)(OMe)_2$, mp 187.5–188.0°. These reactions thus provide the first examples of the generation and trapping of a phosphorus-substituted carbene.



VII

All compounds mentioned in this communication gave combustion analyses and infrared and/or nmr spectra in agreement with the structures indicated. Our efforts in this general area are continuing.

Acknowledgment. The authors are grateful to the National Institutes of Health (Grant CA 08278) for support of this work. This investigation also derived support from Public Health Service Fellowship 2-F1-GM-32,679-01 (to R. S. M.).

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[8] H. Reimlinger, *Chem. Ber.*, **97**, 339, 3503 (1964).

[9] Alfred P. Sloan Foundation Fellow, 1962–1966.

[10] Postdoctoral Research Associate, 1965–1966.

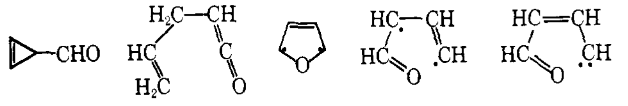
[11] National Institutes of Health Predoctoral Fellow, 1966–1967.

Dietmar Seyferth,[9] Peter Hilbert,[10] Robert S. Marmor[11]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received June 9, 1967

Structures of the Excited States of Furan Produced on Mercury ($^3P_1$) Photosensitization

Sir:

In an earlier communication[1] it had been reported that the principal reaction that was observed on sensitization of furan vapor with Hg($^3P_1$) atoms was decarbonylation to give a mixture of propyne and cyclopropene.[2] In an attempt to elucidate the mechanism of this reaction, the influence of a number of factors on the photosensitized reactions of furan has been studied. Evidence is presented here for the intermediacy of I and II in this system, and on this basis the structures III, IV, and V are proposed for the excited states of furan. Only one electronically excited state is possible in this system—the triplet—if the spin conservation rule is applicable. This state should possess considerable vibrational energy as well. III, IV, and V are resonance structures but their unique behavior generates considerable doubt that they are equivalent in any way in this system. IV may be an electronically excited state and III a vibrationally excited ground state formed by internal conversion. The origin of V is obscure.



I II III IV V

Reaction of Hg($^3P_1$) atoms with furan at pressures which ranged from 0.2 to 1.0 atm[3] gave two compounds of formula C_7H_8O and a compound of formula $C_8H_8O_2$.[4] The first two which were presumably adducts of furan and C_3H_4 were isolated by vpc. In the infrared spectra of this pair the only absorptions that could be attributed to an oxygen function were a series of intense bands

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[1] R. Srinivasan, *J. Am. Chem. Soc.*, **89**, 1758 (1967).

[2] The small amount of allene that was observed is believed to come by a secondary process, possibly photochemical.

[3] None of the products reported here are to be observed on direct irradiation of furan in solutions.

[4] The molecular weights and formulas of all of the compounds reported here were determined by analytical mass spectrometry using an AEI MS-9 instrument.