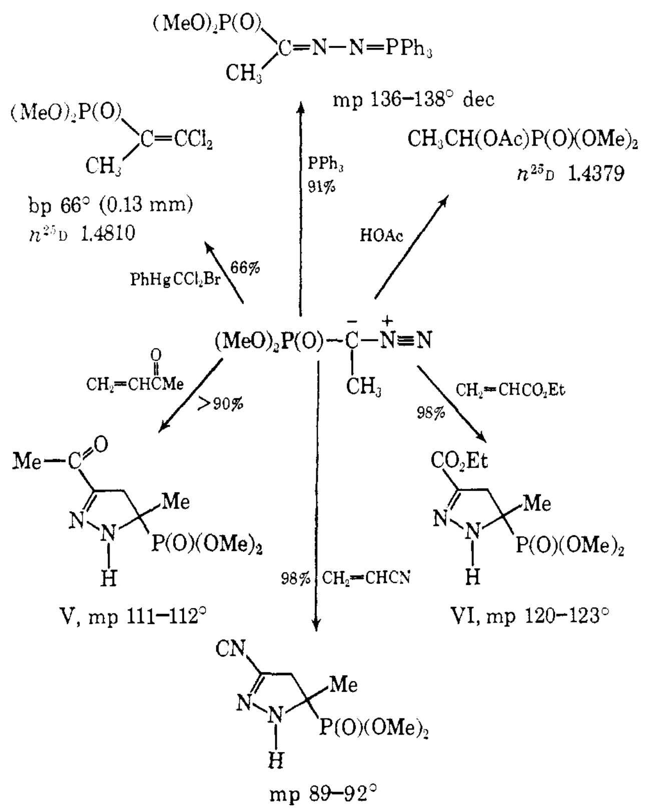
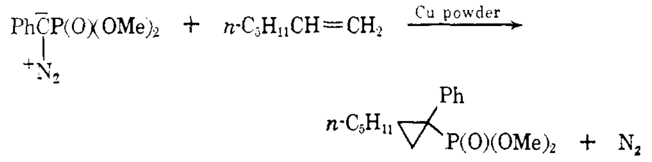
Scheme II. Reactions of $(MeO)_2P(O)C^-(CH_3)N_2^+$

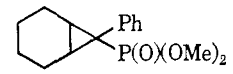


zene. Dihalocarbene–diazoalkane reactions have been reported previously by Reimlinger,[8] and this represents the first application of this mercurial reagent in such a reaction. Notable also is the stability of I and II toward carboxylic acids. On a 10-mmole scale, a ~15-hr period of reflux of I in ethereal 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.

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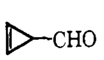
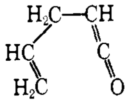
Structures of the Excited States of Furan Produced on Mercury ($^3P_1$) Photosensitization

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.

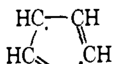


I

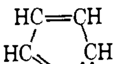


II

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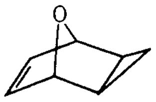
[1] R. Srinivasan, *J. Am. Chem. Soc.*, 89, 1758 (1967).

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

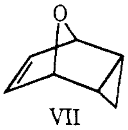
[3] None of the products reported here are to be observed on direct irradiation of furan in solutions.

[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.

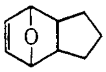
from 1000 to 700 cm^{-1} much as in the spectrum of furan itself. The nmr spectra of these two compounds were very similar and consisted of a narrow multiplet at τ 3.63 (2 H) due to a pair of olefinic protons and another narrow multiplet at τ 5.4 ± 0.1 (2 H) which could be attributed to a pair of allylic protons situated α to an oxygen atom. The remaining four protons gave rise to a complex pattern from τ 8.4 to 9.4 in one case and 9.0 to 10.0 in the other. The chemical shifts of these protons especially in the latter instance indicated that they were located in a cyclopropyl ring. From the similarity of these spectra to those of the Diels–Alder adducts of furan that have been reported[5] it was deduced that these products have the structures VI and VII.



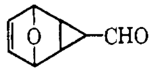
VI



VII



VIII



IX

It has already been reported[5a] that the Diels–Alder addition of furan lacks the stereospecificity of cyclopentadiene so that the formation of both VI and VII is not surprising. The identification of one from the other was hindered by poorly resolved nmr spectra.

Since furan undergoes Diels–Alder addition to even an activated double bond only slowly, the possibility that this reaction is also photosensitized was considered. Photosensitization of furan in the presence of cyclopentene gave not only VI and VII but in addition a new product of the formula $C_9H_{12}O$ (infrared spectrum similar to that of VI and VII from 1000 to 700 cm^{-1}; nmr spectrum: τ 3.75 (2 H), narrow multiplet; 5.55 (2 H), multiplet; 7.9–8.7 (8 H), complex; ultraviolet λ_{max} 3000 A (ϵ_{max} 71);[6] reduction with hydrogen and Adams catalyst—uptake 1.2H_2) which was identified as the Diels–Alder adduct VIII of unknown stereochemistry. The fact that the addition of cyclopentene (18.9 mm) to furan (76.6 mm) diminished by 20% but did not scavenge the formation of CO and C_3H_4 indicated that the excited state of furan which underwent Diels–Alder addition (which is most likely to be III) was not the precursor for the decarbonylation reaction. The observed decrease can be reasonably explained by the quenching of some of the Hg($^3P_1$) atoms by cyclopentene instead of by furan.

The product of formula $C_8H_8O_2$ was isolated by column chromatography over silica gel. It showed an intense absorption in its infrared spectrum at 1710 cm^{-1} and a weak absorption at 2750 cm^{-1} which indicated that it was an aldehyde. The presence of a doublet at τ 0.93 (1 H; J = 7 cps) in the nmr spectrum confirmed that there was a -CHO group with a $\gg$CH adjacent to it. The rest of the spectrum consisted of a narrow multiplet at τ 3.80 (2 H), a broad multiplet at 4.95 (2 H), and two complex absorptions at 7.41 (2 H) and 8.05 (1 H), respectively. The characteristic patterns at τ 3.80 and 4.95 indicated that the product was a Diels–Alder adduct of furan to a C_4H_4O fragment which had the structure $C_2H_2{>}CH{-}CHO$. The shift of the carbonyl frequency by about 20 cm^{-1} to longer wavelength showed a conjugation of the >C=O vibration to the rest of the molecule. The only protons that were not accounted for occurred in a pair at τ 7.41. This suggested structure IX which demonstrates that 2-cyclopropenecarboxaldehyde (I) is an intermediate in this system.[7] It is proposed that I is formed from an excited state of structure IV[8,10] and that I gives rise to cyclopropene and carbon monoxide by an intramolecular rearrangement, since oxygen decreases the yield of cyclopropene but does not eliminate it.

The possibility had been suggested[1] that furan on photosensitization may also rearrange to vinylketene II. When furan (137 mm) is allowed to react with Hg($^3P_1$) atoms in the presence of methanol (37 mm) the quantum yields for CO and cyclopropene were reduced by 13%, which decrease can be wholly attributed to the deactivation of some of the mercury atoms by methanol. At the same time the formation of a new product was observed. From spectral data this was identified as the methyl ester of vinylacetic acid, $CH_2{=}CHCH_2COOCH_3$ (X). Obviously, furan on photosensitization has undergone addition to methanol. The product from the addition of CH_3OD to furan under the same conditions was examined by nmr spectroscopy. In X, the absorptions at τ 4.17 (1 H), 4.76 (2 H), 6.33 (3 H), and 7.00 (2 H) can be attributed to the -CH-, terminal methylene, methyl, and allylic protons. In the monodeuterated ester the absorptions at these τ values corresponded to 0.98, 2.01, 3.00, and 1.10 protons, respectively. The adduct must therefore be $CH_2{=}CHCHDCOOCH_3$ (XI). If the ester is formed from vinylketene II by the addition of CH_3OD this distribution of deuterium would be readily explicable. An alternative mechanism in which the excited-state structure III reacts with methanol would predict an incorrect distribution of deuterium. It would appear that furan is capable of transiently forming vinylketene II and the probable excited state (V) which is the precursor for this reaction is not the same as III or IV.

It is important to point out here that decarbonylation is the significant photosensitized process in furan and that the products formed by the other pathways have a quantum yield of one-fifth to one-tenth of this value. However, the identification of these alternate pathways helps to understand the mechanism of the decarbonylation reaction.

Acknowledgment. The author wishes to thank Mr. Fred Hetzel for the nmr spectra and Dr. Harold Shechter for much useful advice and many helpful discussions.

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[5] (a) F. A. L. Anet, *Tetrahedron Letters*, 1219 (1962); (b) M. P. Kunstmann, D. S. Tarbell, and R. L. Autrey, *J. Am. Chem. Soc.*, **84**, 4115 (1962); (c) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

[6] There is no obvious explanation for this ultraviolet absorption. Both VI and VII also display ultraviolet absorption maxima at 3020 (ϵ_{max} 340) and 3050 A (ϵ_{max} 350) which are consistent with the formulation of their structures as being related to VIII.

[7] The dimethyl derivative corresponding to the aldehyde I (actually a methyl ketone) has recently been isolated from the 2,5-dimethylfuran–Hg($^3P_1$) system. It has a half-life of about 3 days at −10°.

[8] It is noteworthy that such a ring contraction has been reported before in the photochemistry of 3,5-diphenylisoxazole.[9] In this case, the initial isomerization leads to a phenyl ketone which was actually isolated.

[9] E. F. Ullman and B. Singh, (*J. Am. Chem. Soc.*, **88**, 1844 (1966).

[10] Although such ring contractions have not been observed in thiophene, H. Wynberg and his co-workers (*ibid.*, **88**, 5047 (1966)) have indicated that a similar mechanism may be used to explain certain photoisomerizations in that system.

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