

(95%) of **41b** as a white powder: $^1\text{H NMR}$ ($\text{Me}_2\text{SO}-d_6$) δ 7.5 (q, 4 H, ArH), 6.0 (br s, 2 H, NH), 2.3 (s, 6 H, ArCH_3 , HetH); crystallized from DMF-95% ethanol, does not melt $<300^\circ\text{C}$.

Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_6\text{O}_2\text{S}$: C, 49.0; H, 4.4; N, 26.4. Found: C, 48.9; H, 4.2; N, 26.0.

2,8-Diaminopurine Hydrochloride (7·HCl), 41a (3.04 g, 10 mmol) was treated with HF as before for 3 h. Ion exchange salt conversion on Bio-Rad AG-50 resin of the crude HF salt gave 1.9 g (100%) of 7·HCl as a yellowish powder: $^1\text{H NMR}$ (D_2O , external Me_4Si) δ 8.3 (s); crystallized from aqueous ethanol, does not melt $<360^\circ\text{C}$.

Anal. Calcd for $\text{C}_5\text{H}_7\text{N}_6\text{Cl}$: C, 32.2; H, 3.8; N, 45.0. Found: C, 32.5; H, 3.8; N, 44.8.

2,8-Diamino-6-methylpurine Hydrochloride (37·HCl), 41b (15.0 g, 47.2 mmol) was treated with HF as before for 3 h. Ion exchange on Bio-Rad AG-50 resin gave 9.5 g (100%) of 37·HCl: $^1\text{H NMR}$ (D_2O , external Me_4Si) δ 2.65 (s); crystallized from 95% ethanol-ether, does not melt $<300^\circ\text{C}$.

Anal. Calcd for $\text{C}_6\text{H}_9\text{N}_6\text{Cl}$: C, 35.9; H, 4.5; N, 41.9. Found (hygroscopic): C, 35.6; H, 5.0; N, 41.5.

Registry No.—7 HCl, 62743-10-6; 8, 60914-37-6; 11 2HCl, 62743-11-7; 11 sulfate, 62743-13-9; 11 dipicrate, 62743-14-0; 12 2HCl, 62743-15-1; 12 sulfate, 62743-17-3; 16, 62743-18-4; 17, 24571-53-7; 18, 62778-08-9; 20, 2973-83-3; 21, 62743-19-5; 22, 62743-20-8; 23, 62743-21-9; 24, 62743-22-0; 25, 62743-23-1; 27 HCl, 54897-59-5; 28, 2651-15-2; 29, 62743-24-2; 30, 62743-25-3; 31, 62743-26-4; 32, 62743-27-5; 32 4-aminomethyl derivative, 62743-28-6; 33, 62743-29-7; 34, 62743-30-0; 37, 60914-60-5; 37 HCl, 33704-87-9; 39a, 3546-50-7; 39b, 60914-71-8; 40a, 62743-31-1; 40b, 62743-32-2; 41a, 62743-33-3; 41b, 62778-09-0; A' 2HCl epimer 1, 62743-34-4; A' 2HCl epimer 2, 62743-35-5; A' sulfate epimer 1, 62743-37-7; A' sulfate epimer 2, 62743-39-9; B' 2HCl epimer 1, 62743-40-2; B' 2HCl epimer 2, 62743-41-3.

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Photochemistry of Phospholenes. 6. Photochemical Polar Addition of Alcohols Involving Participation by Trivalent Phosphorus¹

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Irradiation of 1-phenyl-3-methyl-2-phospholene (**1**) in methanol-xylene solution afforded a mixture of the photoethers **2** and **3** (20%) and the exocyclic isomer **4** (50%). The addition was found to proceed completely regiospecifically. Thus, phenylphospholene **12** afforded 3-methoxyphospholane as a mixture of geometrical isomers upon similar irradiation. However, 2-methyl derivatives **19** were almost completely inert to photoaddition under similar conditions. Labeling studies with methanol-*O-d* showed that each of the products was formed in an ionic process involving photoprotonation at C-2. Deuterium was also found to be incorporated at the exo position of **4**, probably via a photochemical 1,3-phosphoryl shift. Investigation of the photoreactions of other phospholenes in alcohol revealed that the presence of trivalent phosphorus adjacent to the double bond is a necessity for the photoprotonation. The photoprotonation of **1** and **12** is therefore interpreted in terms of a reactive excited state displaying charge-transfer character resulting from the interaction of the double bond with the lone pair of electrons.

Simple cyclic isolated olefins, which have difficulty adopting a twisted configuration, undergo a variety of reactions from their excited state, including dimerization and various addition reactions. An example of the latter which has recently received considerable attention is the photosensitized polar addition of alcohols to six- and seven-membered olefins.^{2,3} These reactions are believed to proceed through initial protonation of highly strained trans cycloalkenes or orthogonal triplet. In striking contrast, cyclopentene and other highly constrained cyclic olefins exhibit radical behavior on irradiation under similar conditions,^{2,4} apparently due to the inability of these olefins to undergo *cis* \rightarrow *trans* isomerization; the radical-type behavior exhibited in those cases probably originates from intermolecular reaction by the 3 (π , π^*) excited

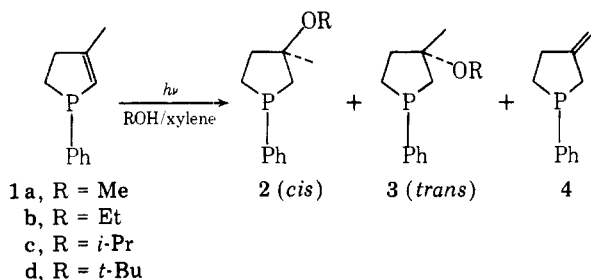
state itself. More recently, it has been shown⁵ that the direct irradiation of the tri- and, particularly, tetrasubstituted cyclopentenes in hydroxylic media yielded unsaturated as well as saturated ethers. This photochemical behavior appears to involve the nucleophilic trapping of the π , R (3s) Rydberg excited state.

In the course of our studies^{1,6} on the photochemistry of phospholenes, we have found^{1b} that even five-membered cyclic olefins, in which double bonds are conjugated with trivalent phosphorus, gave the ethers and exocyclic isomer with direct and/or sensitized irradiation in alcohols. While a large number of simple cyclic olefin systems have been examined as mentioned above, there is little known⁷ concerning the role that α -heteroatoms may have on the photochemical polar

addition. Accordingly, we have studied this addition reaction in more detail to explore the exact nature of the reaction and now wish to present new data concerning the scope of the reaction.

Results and Discussion

Photoproducts. On irradiation in degassed methanol-xylene (1:10) solution, 1-phenyl-3-methyl-2-phospholene (**1**) underwent rapid disappearance. After ca. 70% of the starting material was consumed, the reaction mixture was separated by silica gel chromatography into three principal components under rigorously inert atmosphere. Isolation of the first component afforded a colorless liquid which was ultimately identified as an unresolved mixture of the starting olefin **1** and exo isomer **4**. The presence of two isomers was revealed by GC as well as NMR which displayed a broad singlet at δ 4.82 characteristic of exocyclic methylene protons in addition to



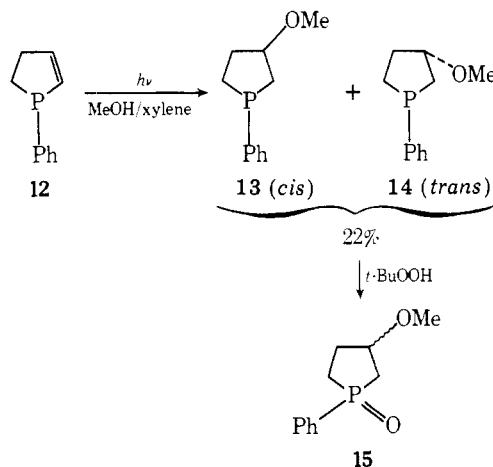
the vinyl proton doublet at δ 5.68 with large coupling ($J_{PH} = 42$ Hz) characteristic of starting olefin. Attempts to isolate **1** and **4** by several passes through the column were unsuccessful. The separation was easily achieved, however, by the chromatography after oxidation of the mixture with *tert*-butyl hydroperoxide to the corresponding phosphine oxides. The oxide of the exo isomer, indicating the methylene protons at δ 5.05, consumed 1 molar equiv of bromine rapidly to give an isomeric dibromide.

Isolation of the second chromatographic component afforded a colorless oil which was readily characterized as a methyl ether (**2a**) by the presence of a three-proton singlet at δ 3.02 in the NMR spectrum and by the appearance of a parent ion at m/e 208 in the mass spectrum. The third component

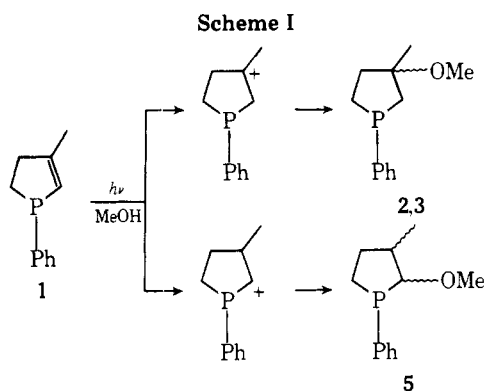
was assigned the stereoisomeric structure **3a**, since it exhibited an NMR and mass spectrum similar to those of the ether **2a**, except for downfield shift of 0.13 ppm of methoxy protons. A priori, ionic addition of methanol to **1** might be expected to afford two sets of the ethers **2**, **3**, and **5**, as shown in Scheme I. However, since the photoethers exhibited no NMR bands attributable to either a proton adjacent to a methoxy group or secondary methyl protons, a structure such as **5** was clearly precluded.

Further proof for the correct assignment and isomeric relationship of **2a** and **3a** was easily provided by the chemical reaction of the ethers, as outlined in Scheme II and the Experimental Section. Thus, the 1-benzylphospholanium bromide of pure geometric isomers **6a** and **7a** were prepared and subjected to treatment with aqueous sodium hydroxide at room temperature. This resulted in the formation of the isomeric phospholane 1-oxides **8a** and **9a** with retention of configuration as previously observed⁸ for other phospholane systems. The NMR spectra of the isomeric **8a** and **9a** were identical with those of the oxides **8a** and **9a** obtained by oxidation of **2** and **3** with *tert*-butyl hydroperoxide, a reaction also known⁹ to occur with retention of configuration at phosphorus. The same reaction mixture of 2- and 3-phospholene oxide (**10** and **11**, respectively) was obtained from both isomers by base-induced elimination of methanol. The treatment of the benzyl bromide salts **6** and **7** with refluxing aqueous alkali resulted in the same reaction products. Apparently, 3-phospholene 1-oxide was formed by the base-induced isomerization¹⁰ of **10** which should be the initial elimination product of **8** and **9**.

The regioselective introduction of the methoxy group at the C-3 position to the exclusion of other positional isomers was also observed in the irradiation in methanol of unsubstituted phospholene **12** which lacks the directive influence of the



3-CH₃ group. Thus, on irradiation in methanol-xylene solution, **12** was found to undergo relatively slow conversion to a mixture of two methyl ethers in 22% yield. The two photoethers were easily assigned the diastereomeric structures



Scheme II

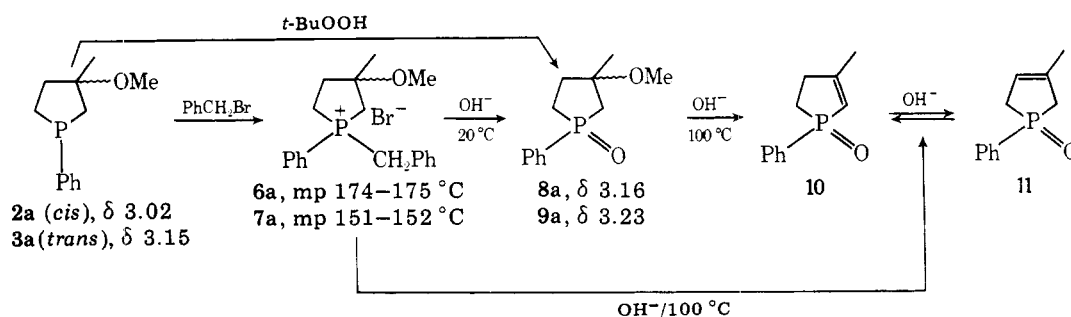


Table I. Irradiation^a of 1-Phenyl-3-methyl-2-phospholene (1)

[MeOH], M	% convn ^b	% yield ^b		
		2 + 3	4	4/(2 + 3)
0 ^c	18		0	
0 ^d	11		37	
0.15	23	8	43	5.4
0.75	26	14	66	4.7
1.5	31	20	54	2.7
1.5 ^e	27	25	50	2.0
4.5	33	23	36	1.6
7.5	36	27	33	1.2
15	39	27	21	0.8
Neat	40	23	14	0.6

^a Irradiations were carried out as described in the Experimental Section in a quartz tube of 5.0-mL capacity under nitrogen for 5 h using 5.0-mL xylene solutions containing 0.28 mmol of 1. ^b Determined by GC analysis of aliquots removed from the irradiation mixture. ^c Dry xylene was used. ^d Xylene saturated with water. ^e Contained 0.1 N NaOMe.

13 and 14, predominantly 14, based on the NMR and mass spectra. The assignment was further supported by direct comparison of the oxide of one of the ethers with a specimen of 1-phenyl-3-methoxyphospholane 1-oxide prepared independently by catalytic hydrogenation of corresponding 1-phenyl-3-methoxy-2-phospholene 1-oxide¹¹ (vide infra).

Stereochemical assignment of the photoethers was based on their NMR spectra. One isomer (i.e., 2a or 13) eluting faster than the other isomer from the column showed the methoxy protons resonating at higher field than those of the other isomer (i.e., 3a or 14). This chemical-shift difference is attributable to the orientation of the methoxy and phenyl groups. The conformation of the five-membered ring is usually discussed in terms of an envelope or twisted-envelope shape and these forms are flexible and undergo rapid pseudorotation. It has been shown^{12a} that the parent phospholane ring is reasonably depicted in the same manner. Inspection of a model for the photoether in the twisted-envelope conformation reveals that the methoxy protons cis to the phenyl ring are located in a position such that they should resonate upfield due to the anisotropic effect of the phenyl substituent. The phenyl substituent should have little effect on the shifts of the methoxy protons trans to the substituent. Therefore, those methoxy protons shifted upfield in 2a and 13 are assigned to those cis to the phenyl ring.^{12b} The similar upfield shift of a methyl group by an analogous 1,3-anisotropic effect of a *cis*-phenyl group is noted¹³ in the five-membered cyclic phosphites. The assignment was further supported by the finding that the 3-methyl signal of the oxide 8a of the *cis* isomer showed a deshielding effect¹⁴ by a P=O group to be operative on this group: the 3-CH₃ signal of 8a is deshielded by 0.19 ppm relative to that of the oxide 9a of the *trans* isomer. The same kind of deshielding effects of the ring alkyl substituents have been found¹⁵ with five-membered ring phosphates.

The present stereochemical assignment to the phospholane system provided additional insight into the stereochemistry of catalytic hydrogenation. 3-Methoxy-1-phenylphospholane 1-oxide (15) obtained by hydrogenation of 3-methoxy-1-phenyl-2-phospholene 1-oxide in the presence of palladium-on-carbon catalyst, a reaction known¹⁶ to occur completely stereospecifically, showed methoxy protons at 3.37 ppm, identical with the oxide 15 of the *cis* isomer of the photoether. Thus, it might be concluded that the reduction product arose from *cis* addition of hydrogen in the direction containing the P=O group across the double bond.

Additional insight into the present reaction was afforded by a series of irradiations conducted with 1 under a variety of

Table II. Irradiation^a of 1 in Various Alcohols

Registry no.	Alcohol	% convn ^b	% yield ^b		
			2 + 3 (3/2)	4	4/(2 + 3)
67-56-1	MeOH	31	20 (1.2)	54	2.7
64-17-5	EtOH	32	14 (1.1)	46	3.3
67-63-0	<i>i</i> -PrOH	28	13 (1.2)	42	3.2
75-65-0	<i>t</i> -BuOH	25	10 (1.3)	36	3.6

^a Irradiations were carried out in a quartz tube of 5.0-mL capacity under nitrogen for 5 h using 0.15 M alcohol in xylene solution containing 0.28 mmol of 1. ^b Determined by GC analysis of aliquots removed from the irradiation mixture.

conditions, as summarized in Tables I and II. Neither the isomerization nor the ether formation reaction was inhibited noticeably by the addition of sodium methoxide. Furthermore, dark control in the presence of a small amount of acid showed no formation of the products. These observations eliminate the possibility that acidic products, known^{5a} to be generated in the photolysis of methanol, might induce the present reaction.

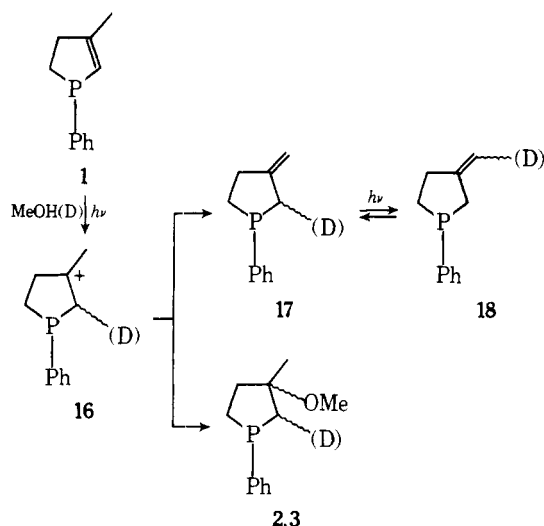
The ratio of *exo* isomer to the ether was significantly dependent on the concentration of methanol, favoring the ether formation with increasing concentration. This suggested the intervention of a common carbonium ion to both *exo* isomer and the ether. A priori, the *exo* isomer could be formed via intramolecular hydrogen shift. This was shown, however, not to be the case, since irradiation of 1 in dry xylene showed no formation of *exo* isomer, while similar irradiation in wet xylene resulted in a gradual built-up of *exo* isomer. Thus, initial protonation is shown to be a necessary step for the formation of both ether and *exo* isomer.

The substitution of other alcohols for methanol again afforded the ethers along with the isomerization product 4, although the reaction was less efficient. This is in marked contrast, however, to the photochemical behavior of cyclohexene in alcohol, in which only isomerization was observed in the irradiation with *tert*-butyl alcohol even in the presence of acid. The marked enhancement in basicity of the excited state of 1 compared to that of cyclohexene apparently implies that species which undergo protonation in the present reaction should be essentially different in nature. The slight increase of the ratio of isomerization to ether formation in going from methanol to *tert*-butyl alcohol might be related to nucleophilicity and steric bulk of the alcohols.^{16a}

Labeling Studies. From the foregoing experimental data it might be concluded that the 2-phospholene undergoes photochemical reaction in alcohols via an ionic process to yield *exo* isomer and ethers. In order to get more convincing support for the common carbonium ion mechanism as outlined in Scheme III, labeling studies were undertaken.

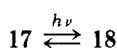
Irradiation of 1 in methanol-*O-d*-xylene solution again afforded the ethers and *exo* isomer. In the NMR spectrum of the resulting ether, the intensity of unresolved multiplet attributable to ring methylene at δ 1.45 ~ 2.40 was greatly reduced and the coupling patterns were significantly simplified as expected for the presence of deuteration at the ring carbon, although the exact position of deuteration was not clear because of its complexity. Likewise, analysis of the NMR spectrum of the recovered starting material clearly displayed the presence of some deuteration on the vinyl proton even in an irradiation interrupted at only partial conversion (10%), as has been observed^{2,3} previously for other olefins which exhibit ionic photobehavior, and the gradual build-up of deuterium was observed as the reaction proceeded (Table III). Deuterium atom was also found to be incorporated at the ring carbon of the *exo* isomer. These observations suggest that both the ethers and *exo* isomer arise via an initial selective protonation

Scheme III



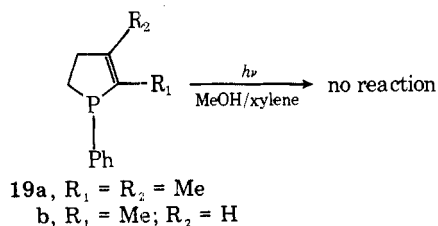
at C-2 of 1 to form common carbonium ion 16, which in turn undergoes three competing reactions: (a) nucleophilic capture by solvent to afford the ethers, (b) elimination to exo cyclic olefin, and (c) deprotonation to regenerate the starting olefin 1, as depicted in Scheme III.

Surprisingly, however, a marked attenuation of the doublet at δ 5.60 of exo isomer was noted, indicating substantial deuterium incorporation occurred at exo-methylene carbon. Control studies showed that the exo isomer is photolabile but does not afford any of the methyl ethers or endo olefin on irradiation in methanol: this precludes the possibility that the light-induced protonation on 4 is involved in this marked incorporation of deuterium at the exo position. The reversible 1,3-hydrogen shift was also precluded from the foregoing results. We tentatively propose a rapid reversible photochemical 1,3-phosphoryl shift



to explain the observed scrambling. The exact nature of this reaction is not clear at present and is the subject of continued study.

Methyl Substituent Effect. The unsubstituted phospholene 12 was shown to undergo photoprotonation to give 1-phenyl-3-methoxyphospholanes on irradiation in methanol. However, attempts to extend the reaction to 2-methyl derivatives 19 in order to learn the stereochemistry of the addition reaction lead to some surprising results. Thus, direct or pho-



tosensitized irradiation of 19 in methanol under conditions in which the 3-methyl derivative 1 was completely converted to the mixture of the ethers and exo isomer resulted in almost total recovery of the starting olefins. In neither case was there any appreciable formation of exo isomer or an ionic- or radical-type addition product.

Photoreactions of Other Phospholenes in Alcohols. In contrast to the efficient photoprotonation of 1, irradiation of 2-phospholene 1-oxide 10 in methanol leads to substantially different results. The only volatile product detected by GC was 3-methylphospholane 1-oxides 20, as a 1:1 mixture of geometrical isomers, which was easily prepared by the re-

Table III. Deuterium Distribution^a of the Oxides of 1 and 4

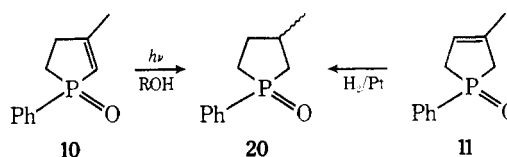
% convn	Oxide of 1 vinyl	Oxide of 4	
		Exo methylene	Ring methylenes
10	0.13 ± 0.01 D	0.47 ± 0.05 D	0.44 ± 0.06 D
21	0.20	0.52	0.53
44	0.44	0.64	0.86

^a Calculated by relative NMR peak area to aromatic protons as standard.

Table IV. Irradiation^a of 10 in Alcohols

Alcohol	% convn ^b	21, % yield ^b
MeOH	18	2
EtOH	33	23
<i>i</i> -PrOH ^c	44	35
<i>t</i> -BuOH	17	0.7

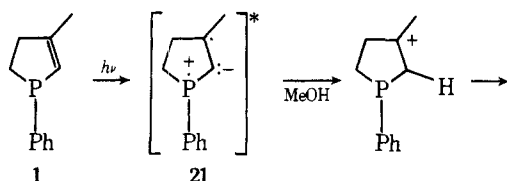
^a Irradiations were carried out in a quartz tube of 5.0-mL capacity under nitrogen for 3 h using a 5.0-mL alcohol solution of 0.25 mmol of 10. ^b Determined by GC. ^c Acetone was detected by GC.



duction of the 3-phospholene 1-oxide 11. No trace of the ethers 8 and 9 or exo isomer was detected even by GC. The yield of 20 increased in going from methanol to isopropyl alcohol, as indicated in Table IV, and acetone was detected in the irradiation with the latter solvent. The reduction was efficiently quenched by 1,3-pentadiene to yield linear Stern-Volmer plots with a slope of 14 M⁻¹ (in isopropyl alcohol). The results suggest that the oxide 10 undergoes a similar radical type of reaction via excited triplet state, as has been observed⁴ previously for cyclopentene. It has been reported^{6c} that irradiation of 1-phenyl-3-methyl-3-phospholene in methanol was rapidly transformed into a complex mixture of products without any detectable formation of the ethers; the main reaction pathway was photochemical cleavage into isoprene and phenylphosphinidene, as has been observed^{1a,6a} for the corresponding 3-phospholene oxides. These results strongly imply that the presence of trivalent phosphorus adjacent to the double bond is required for photoprotonation.

Reactive Excited State. It seems quite clear from foregoing data that photochemical reactions of 2-phospholenes in alcohol involve a common carbonium ion arising from photoprotonation at C-2 of the phospholene. There remains then the important question of what is the reactive intermediate which is undergoing protonation. The intervention of *trans*-olefin or orthogonal triplet state was clearly precluded because of a large distortion inherent in such a olefin. The radical type of reaction shown by 2-phospholene 1-oxide supports the assumption.

Weiner et al.¹⁷ have observed the single major band above 220 nm in the UV spectra of vinylphosphine and assigned it to an electron-transfer type of transition, in which an electron is removed from the nonbonded orbital on trivalent phosphorus and transferred to the empty π^* orbital of the vinyl group. The necessity of the lone pair of electrons to the observed transition is demonstrated by the effective disappearance of any maximum above 200 nm in the spectrum of the vinylphosphine oxide. In accordance with their observation, 2-phospholenes 1 and 12 showed the strong single band at 256 nm in the UV spectra, whereas the corresponding



phosphine oxide showed weak absorption with vibrational fine structure, indicating the lack of interaction between phosphorus and the double bond.¹⁸ Thus, the excited state of 2-phospholene should be polarized as in 21, in which there is an increase of electron density on the α carbon atom relative to the ground state. Such charged character of $2p^*$ clearly explains the following facts: (a) regioselective protonation on C-2, (b) the enhanced basicity of the excited state of 1 compared to the photochemical behavior of cyclohexene, and (c) the necessity of trivalent phosphorus adjacent to the double bond.

Interestingly, the UV spectra of 2-methyl derivatives 19 show only weak absorption with unresolved vibrational fine structure similar to that of 2-phospholene oxide. This implies that the failure of these derivatives to undergo photoprotonation under irradiation in methanol is attributable to their inability to obtain an electron from the adjacent phosphorus and hence possess a polarized double bond in the lowest excited state. An electron-releasing α -methyl group might probably raise the energy of this reactive state to an upper level by destabilizing the negative charge on the α carbon.

Attempts to explore the multiplicity of the reactive excited state of phospholene were unsuccessful, since irradiation of 1 with quencher (1,3-pentadiene) or sensitizer (benzophenone) resulted in a complex mixture of the products including the ethers and exo isomer, probably arising from the possible reaction of 1 with quencher or sensitizer.¹⁹

The observation that complete absence of the ether or exo isomer in the acid-catalyzed reaction of 1 in methanol in the dark is in marked contrast to other simple olefins which undergo acid-catalyzed protonation in the absence of light. The major single band at 256 nm of 1 in methanol changed²⁰ gradually by the addition of diluted acid (HCl) in the dark to the weak band with vibrational fine structure similar to that of 2-phospholene 1-oxide, suggesting that protonation of the lone-pair electrons is probably occurring on phosphorus rather than on the double bond. There is, thus, a fine balance between the acidity of the solvent and basicity of phospholene in various states, with ground-state phospholene being protonated only by strong acid on phosphorus in the dark, while the excited-state phospholene is being protonated by weak acid like alcohol on the α carbon under irradiation.

Synthetically, the present photoreaction provides a method for selectively protonating a 2-phospholene system to afford the product which is not easily prepared in the dark reaction.

Experimental Section

General. All melting and boiling points were uncorrected. Infrared spectra were determined on a JASCO IR-G recording spectrometer. Proton magnetic resonance spectra were determined on a JEOL JNM-MH-100 NMR spectrometer; chemical shifts are reported in units of δ (part per million) downfield from Me_4Si . Mass spectra were obtained on a Hitachi RMS-4 spectrometer. Ultraviolet and fluorescence spectra were measured with a Shimadzu UV 250 recording spectrometer and a Hitachi MPF-2A spectrofluorometer, respectively. GC analyses were performed on a Yanagimoto instrument Model G-80 using a 2.0 m \times 5.0 mm column packed with 10% SE-30 and 13% Apiezon L on 60–80 mesh Diasolid L. Woelm silica gel (activity III) was always used for column chromatography.

Materials. Phospholene 1-oxides were prepared by cycloaddition of dienes and phosphonous dihalides, followed by hydrolysis of the resulting adducts according to the general procedure of Quin.¹⁰ 1-Phenyl-2-phospholenes were prepared by reduction²¹ of diene-

phenylphosphonous dichloride adducts with Mg and distilled prior to irradiations.

Irradiations. Unless otherwise indicated, all irradiations were conducted using a Halos 300-W high-pressure mercury lamp and a water-cooled quartz immersion well. A commercial mixture of *o*-, *m*-, and *p*-xylene was employed. The solution was purged with nitrogen 5–10 min before irradiation. Vigorous stirring during irradiation was effected by a magnetic stirring bar. The progress of photochemical reactions was monitored by GC analysis of aliquots removed periodically. For product identification the irradiation mixtures were concentrated on a rotary evaporator, and individual components were isolated by silica gel column chromatography and characterized either as described below or by comparison with authentic specimens. The irradiations outlined in Tables I, II, and IV were conducted in a sealed quartz tube of 5.0-mL capacity strapped to an immersion well. Control runs showed that no reaction occurred in the absence of light.

Irradiation of 1-Phenyl-3-methyl-2-phospholene (1). (A) **In Methanol-Xylene.** In a typical run, a 270-mL xylene solution containing 30 mL of methanol and 2.0 g of freshly distilled phospholene 1 was irradiated under nitrogen for 6 h. Isolation of the first major component (1.26 g) by column chromatography using petroleum ether (bp 40–60 °C) with an increasing amount of diethyl ether afforded a colorless liquid with strong phosphine odor, which was identified as an unresolved mixture of the starting olefin 1 and exo isomer by GC and NMR. Attempts to separate 1 and 4 by several passes through the column resulted in two poorly resolved pairs of isomers. The mixture was treated with a slight excess of *tert*-butyl hydroperoxide in xylene, followed by the column chromatography using ethyl ether as eluent. The first fraction (0.58 g, 42%) was identified as the oxide of exo isomer 4: NMR (CDCl_3) 1.97–3.08 (m, 6 H, $-\text{CH}_2-$), 5.60 (d, $J = 9.0$ Hz, 2 H, $=\text{CH}_2$), and 7.30–7.95 (m, C_6H_5).

The dibromide, prepared in chloroform and recrystallized from benzene, had mp 136–137 °C. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{Br}_2\text{OP}$: C, 37.53; H, 3.72. Found: C, 37.67; H, 3.54.

The second fraction (0.68 g) was identified as the oxide of 1 by comparison of its IR and NMR with those of an authentic sample.

Similar isolation of the second and third product components afforded *cis*- and *trans*-1-phenyl-3-methoxyphospholane (0.314 g, 19%), respectively. The NMR and mass spectra of each isomer are recorded in Table V. Benzyl bromide salts were prepared for each isomer in benzene and recrystallized from ethyl acetate. Analytical data and melting points for the salts are given in Table V.

(B) **In Methanol-*O-d*-Xylene.** A 280-mL xylene solution containing 10 mL of methanol-*O-d* (Merck and Co., Inc., 99.5 + atom % D) and 2.0 g of 1 was irradiated under nitrogen. Each of the components was isolated as described in part A. The oxides of recovered olefin 1 and exo isomer were found by NMR analysis to have the deuterium composition outlined in Table III. Control experiment showed that no deuterium exchange was observed in the separation step described above. The photoethers 2a and 3a exhibited the NMR spectra similar to those of materials obtained as described in part A, except for an attenuation of the bands at δ 1.45–2.40 to an integration corresponding to 1.0 ± 0.1 proton.

(C) **In Other Alcohol-Xylene.** A 270-mL xylene solution containing 30 mL of each alcohol and 2.0 g of 1 was irradiated and the irradiation mixtures were separated into individual components as described in part A. The NMR and mass spectra of each photoether are recorded in Table V together with melting points and analytical data for the benzyl bromide salts.

Irradiation of 1-Phenyl-2-phospholene (12). Irradiation of a 270-mL xylene solution containing 30 mL of methanol and 2.0 g of freshly distilled phospholene under nitrogen for 6 h followed by isolation of the product in the usual manner afforded the photoethers 13 and 14 in 10 and 12% yields, respectively.

The NMR and mass spectra of each isomer are given in Table V together with the melting points and analytical data of the benzyl bromide salts.

Irradiation of 1-Phenyl-3-methyl-2-phospholene 1-Oxide (10). Irradiation of the phospholene oxide 10 (2.1 g) in isopropyl alcohol (250 mL) under nitrogen for 7 h followed by isolation of the major product by column chromatography eluted with diethyl ether-methanol (9:1) afforded 1-phenyl-3-methylphospholane 1-oxide as a 1:1 mixture of geometrical isomers (655 mg, 39%), which was identical in all respects with an authentic specimen prepared²² by catalytic hydrogenation of 1-phenyl-3-methyl-3-phospholene 1-oxide. GC analysis of the reaction mixture showed the presence of acetone.

For quenching experiments, the solutions of 50 mM 10 in 5.0 mL of isopropyl alcohol with or without piperylene were placed in closed quartz tubes. The tubes were irradiated simultaneously on a merry-go-round apparatus at room temperature for 3 h, and the amount of

Table V. 3-Alkoxyphospholanes and Their Benzyl Bromide Salts

Registry no.	Compd	¹ H NMR ^a , δ, ppm (J, Hz)			Mass (m/e) ^b	mp, °C	Benzyl bromide salt Formula	Carbon, %		Hydrogen, %	
		C-CH ₃	C-OR	-CH ₂ -				Calcd	Found	Calcd	Found
52561-64-5	2a	1.29 ^c	3.02 ^c	1.50-2.30 ^d	208, 195, 178, 177, 176, 161, 138, 109, 108,	174-175	C ₁₉ H ₂₄ BrOP	60.17	59.66	6.38	6.40
52561-65-6	3a	1.29 ^c	3.15 ^c	1.45-2.40 ^d	107, 91, 78, 77	151-155			59.79		6.39
62726-78-7	2b	1.16 ^c	0.87(6.1) ^e 3.09(6.1) ^f	1.28-2.78 ^d	222, 177, 178, 138, 123, 109,	167-171.5 ^g	C ₂₀ H ₂₆ BrOP	61.08	60.91	6.66	6.65
62726-79-8	3b	1.08 ^c	0.97(6.1) ^e 3.12(6.1) ^f	1.10-2.72 ^d	108, 107, 91, 78, 77						
62726-80-1	2c	1.22 ^c	1.09(6.9) ^h 3.42(6.9) ⁱ	1.15-2.70 ^d	236, 209, 193, 178, 176, 138,	172-177 ^g	C ₂₁ H ₂₈ BrOP	61.92	60.14	6.93	7.02
62726-81-2	3c	1.21 ^c	1.19(6.9) ^h 3.48(6.9) ⁱ	1.18-2.72 ^d	109, 108, 107, 78, 77						
62726-82-3	2d	1.22 ^c	1.09 ^c	1.35-2.70 ^d	250, 210, 178, 177, 176, 138,	181-188 ^g	C ₂₂ H ₃₀ BrOP	62.71	62.93	7.18	7.08
62726-83-4	3d	1.21 ^c	1.19 ^c	1.34-2.50 ^d	78, 77						
62726-84-5	13	j	3.17 ^c	1.50-2.50 ^d	194, 164, 163, 162, 109, 108,	78-79 ^g	C ₁₈ H ₂₂ BrOP	59.19	58.54	6.07	6.10
62726-85-6	14	j	3.23 ^c	1.50-2.40 ^d	107, 78, 77						

^a CD₃OD solution with internal standard. ^b m/e values reported include the parent ion and other significantly large peaks appearing above m/e 70. ^c Singlet. ^d Complex multiplet. ^e Triplet. ^f Quartet. ^g A mixture of cis and trans isomers. ^h Doublet. ⁱ Septet. ^j Complex multiplet at δ 3.80-4.15 attributable to CH-OMe.

consumed 10 was determined by GC. Five concentrations of piperlene in addition to blanks were used for the Stern-Volmer plot.

Base-Induced Reactions of Oxides and Benzyl Bromide Salts of 1-Phenyl-3-methyl-3-methoxyphospholanes. (A) Oxides 8 and 9. To pure 2a (150 mg) in 5 mL of benzene at 5 °C was added 100 mg of *tert*-butyl hydroperoxide. The mixture was allowed to stand overnight and then concentrated, and the residue was chromatographed to yield 8a: NMR (CDCl₃) 1.32 (d, *J* = 1.7 Hz, 3 H, C-Me), 1.52-2.73 (m, 6 H, -CH₂-), 3.23 (s, 3 H, OCH₃), and 7.23-8.07 (m, 5 H, C₆H₅).

Oxide 9a was similarly prepared: NMR (CDCl₃) 1.41 (d, *J* = 1.3 Hz, 3 H, C-Me), 1.52-2.56 (m, 6 H, -CH₂-), 3.12 (s, 3 H, OCH₃), and 7.36-8.10 (m, 5 H, C₆H₅).

Two milliliters of 1.0 N NaOH was pipetted into a 5-mL flask containing 70 mg of either 8a or 9a and the resulting solution heated at reflux for 40 min. After cooling, the reaction mixture was neutralized, the aqueous layer was extracted with small portions of chloroform, and the extract was dried, concentrated, and chromatographed to yield 10 (48 mg, 80%) and 11 (10 mg, 16%).

(B) Benzyl Bromide Salts 6 and 7. Two milliliters of 1.0 N NaOH was added into a 5-mL flask containing 152 mg of either 6a or 7a and the resulting solution heated at reflux for 2 h. Toluene was detected by GC. Cooling and neutralization followed by chromatography afforded 10 (58 mg, 76%) and 11 (10 mg, 13%).

One milliliter of 1.0 N NaOH was added into a 5-mL flask containing 76.4 mg of 6a and the resulting mixture was stirred vigorously at room temperature for 10 min. Isolation of the product in the above procedure gave 90% yield of the oxide, which displayed an NMR spectrum identical with that of 8a obtained in part A.

Independent Preparation of 1-Phenyl-3-methoxyphospholane 1-Oxide. 1-Phenyl-3-methoxy-2-phospholene 1-oxide was prepared from chloroprene and phenylphosphonous dichloride followed by treatment with sodium methoxide in methanol, according to the literature¹¹ procedure for the P-methyl derivative, and recrystallized from PhH: mp 95-96 °C; IR (CHCl₃) ν 1588 (C=C), 1440 (P-Ph), 1188 (P=O), and 1108 cm⁻¹ (COC); NMR (CDCl₃) 1.84-3.03 (m, 4 H, -CH₂-), 3.69 (s, 3 H, -OMe), 4.91 (d, *J*_{PH} = 16.0 Hz, 1 H, C=CH), and 7.25-7.91 (m, 5 H, -C₆H₅). Anal. Calcd for C₁₁H₁₃O₂P: C, 63.46; H, 6.29. Found: C, 63.25; H, 6.10.

To 1.35 g of 1-phenyl-3-methoxy-2-phospholene 1-oxide in 5 mL of absolute ethanol was added 0.5 g of 5% palladium-on-carbon, the mixture was hydrogenated for 6 h at 7 to ~8 kg/cm², the solution was filtered, and the solvent removed to give a yellow oil, which showed no vinyl proton but rather methoxy protons at δ 3.36, identical with

that of the oxide obtained by oxidation of *cis*-1-phenyl-3-methoxyphospholane (13) with *tert*-butyl hydroperoxide.

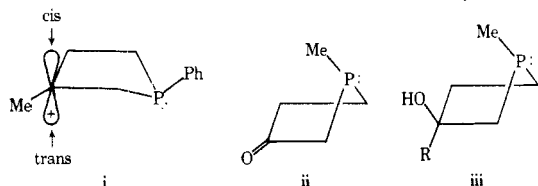
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Registry No.—1, 1445-83-6; 4, 52561-63-4; 4 dibromide oxide, 52561-66-7; 4 oxide, 62726-86-7; 6a, 62726-70-9; 6b, 62726-71-0; 6c, 62726-72-1; 6d, 62726-73-2; 7a, 62726-74-3; 7b, 62726-75-4; 7c, 62726-76-5; 7d, 62726-77-6; 8a, 62726-87-8; 9a, 62726-88-9; 10, 707-61-9; 12, 28278-55-9; 13 benzyl bromide, 62726-68-5; 14 benzyl bromide, 62726-69-6; 1-phenyl-3-methoxy-2-phospholene 1-oxide, 62726-89-0.

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Photochemical Rearrangements of 4,7-Dimethyl-3-chromanone and Related Compounds¹

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Photorearrangement reactions are described for 4,7-dimethyl-3-chromanone (8), 4,7-dimethyl-3-methoxychromene (25), and 1-phenyl-2-methoxy-3,4-dihydronaphthalene (34). Irradiation of 8 in basic methanol produces 2-hydroxy-3-methoxy-2,3,6-trimethyl-2,3-dihydrobenzofuran (9). The formation of 9 is readily explicable in terms of a photoinduced ring opening of the enol of 8 to give an *o*-quinoneallide intermediate (17) followed by 1,4-addition of methanol. Evidence for the proposed sequence was obtained by studying the photobehavior of the closely related 4,7-dimethyl-3-methoxychromene (25) system. Irradiation of 25 in methanol produced a mixture of 2,3-dimethoxy-3-(2-hydroxy-4-methylphenyl)-1-butene (26) and 2-methoxy-3-(2-hydroxy-4-methylphenyl)-1,3-butadiene (27). When the irradiation of 25 was carried out in benzene, a mixture of 27, 2,6-dimethyl-2-methoxy-3-methylene-2,3-dihydrobenzofuran (29), and 1-methoxy-2-oxa-5,7-dimethylbenzobicyclo[3.1.0]hexene (30) was obtained. These products are most readily derived from an *o*-quinoneallide intermediate (31) formed by a photoinduced ring opening of the 3-chromene ring. The excited state behavior of the closely related 1-phenyl-2-methoxy-3,4-dihydronaphthalene (34) system was also studied and it was found to undergo a similar rearrangement.

In earlier reports from this laboratory,²⁻⁴ evidence was presented which demonstrated that the enol content can be an overriding factor in determining the excited-state behavior of a carbonyl group. As part of our studies in this area, we investigated the photochemical rearrangement of several 4-substituted 3-chromanones (1) to 4-substituted dihydrocoumarins (5)^{2,5} and found that the reaction involves the prior conversion of 1 into its enol tautomer 2, which is subsequently converted to 5 on exposure to UV light in alcoholic solvents. When the irradiation was carried out in a nonpolar solvent, where the concentration of the enol form was negligible, photorearrangement from the keto tautomer occurred resulting in the formation of a rearranged 3-chromanone (i.e., 7).⁶ The unusual richness of the photochemistry of this system, which is a sensitive function of reaction conditions, including the choice of solvent, provides a useful probe for determination of reaction mechanism. The distribution of products and the ability to trap a cyclopropanone intermediate (i.e., 4) with furan have permitted elucidation of the nature and sequence of intermediates involved in this photochemical system. We now wish to report that replacement of the 4-phenyl or carbomethoxy substituent with a methyl group markedly alters the outcome of the rearrangement. The present publication describes our findings with the 4,7-di-

methyl-3-chromanone (8) system and delineates the significant role played by an *o*-quinoneallide intermediate in the overall photochemistry of this ring system.

Results and Discussion

4,7-Dimethyl-3-chromanone (8) was conveniently prepared by the series of reactions outlined in Scheme I. Its physical and spectroscopic properties are in excellent agreement with those previously reported by Still and Goldsmith.⁷ The NMR spectrum of 8 in deuteriochloroform indicates that this system exists exclusively as the keto tautomer [60 MHz, τ 8.56 (d, 3 H, $J = 7.0$ Hz), 7.72 (s, 3 H), 6.52 (q, 1 H, $J = 7.0$ Hz), 5.67 (AB q, 2 H, $J = 17.0$ Hz), and 2.9-3.3 (m, 3 H)].

Irradiation of 8 in methanol resulted in a very slow and messy reaction; no characterizable products could be obtained. When a catalytic quantity of sodium methoxide was added to the solution, however, a very fast and clean reaction occurred upon irradiation. Under these conditions a high yield (75%) of 2-hydroxy-3-methoxy-2,3,6-trimethyl-2,3-dihydrobenzofuran (9) was obtained. The NMR spectrum of this compound showed that it consisted of a 79:21 equilibrium mixture of 9a [(60 MHz, CDCl₃) τ 8.54 (s, 6 H), 7.68 (s, 3 H), 6.89 (s, 3 H), 4.85 (s, 1 H, exchanged with D₂O), and 2.8-3.5 (m, 3 H)] and 3-methoxy-3-(2-hydroxy-4-methylphenyl)-2-