

THE PHOTOCHEMICAL ADDITION OF ALCOHOLS TO 1-PHENYL-3-METHYL-2-PHOSPHOLENE

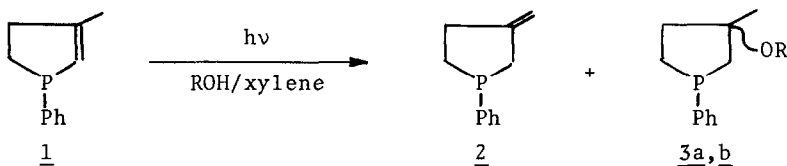
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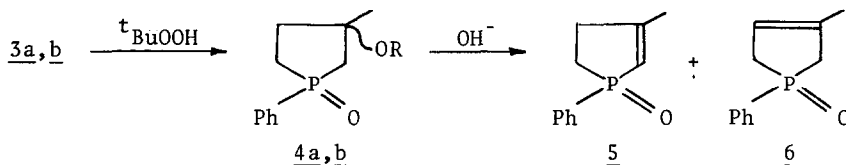
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Reported examples of photochemical ionic addition of water and alcohols to cyclic olefins have been restricted to the case where double bond was contained within a six-eight-membered ring^{1a,b} and smaller cyclic olefins participate in radical addition reactions due to their stereochemical rigidity.^{1a} In the present communication we wish to report exceptions to this generality; five-membered cyclic olefin containing trivalent phosphorous adds alcohols in a polar fashion in the absence of added acid.

The irradiation² of 0.04M solution of 2-phospholene (1) in methanol-xylene (1:10) was monitored by gas chromatography, which revealed a gradual buildup of at least three products. Silica gel chromatography of the reaction mixture after ca. 70% of starting material was consumed provided 54% of exocyclic olefin (2)³, $\delta(\text{MeOH-d}_4)$ 4.82 (broad s, =CH₂), and 20% of methyl ethers (3a,b) as a 1:1.2 mixture of geometrical isomers,⁴ predominantly 3b, $\delta(\text{MeOH-d}_4)$, 3a 1.29 (s, -CH₃), 3.15 (s, -OCH₃), $\delta(\text{MeOH-d}_4)$, 3b 1.29 (s, -CH₃), 3.02 (s, -OCH₃). Exo isomer was separated as phosphine oxide, $\delta(\text{CDCl}_3)$ 5.05 (d, J_{PH} 9 Hz, =CH₂) which consumed one mole of bromine rapidly to give isomeric pure dibromide, m.p. 136-137° (C₆H₆), $\delta(\text{CDCl}_3)$ 4.06 (s, -CH₂Br). Although further assignment of which methoxy is cis or trans to the phenyl group in the ethers (3) is under investigation, chemical proof for their isomeric relationship is easily provided by the formation of the same products, phospholene oxides (5 and 6), from phosphine oxide (4a,b) of both isomers by base-induced elimination of methanol.

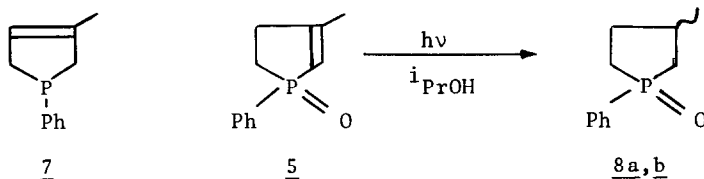


| R | <u>2</u> , % | <u>3</u> , % | <u>2/3</u> |
|-------------|--------------|--------------|------------|
| Me | 54 | 20 | 2.7 |
| Et | 46 | 14 | 3.3 |
| <i>i</i> Pr | 42 | 13 | 3.2 |
| <i>t</i> Bu | 36 | 10 | 3.6 |



Dark control with and without added acid showed the reactions are truly photochemical. Similar reactions took place in other alcohols although decrease in over all rate of the reactions and increase in 2:3 ratio in going from methanol to *t*-butyl alcohol were observed. These results suggest the dependence of the reaction upon acidity and nucleophilicity of the medium. Through control experiments the exo isomer (2) were found to be stable to the irradiation, affording neither endocyclic isomer (1) nor the ethers (3). Moreover, little 2 can be detected by gas chromatography after prolonged irradiation of 1 in dry xylene, suggesting that the presence of the hydroxy proton is also needed for the isomerization reaction.

In contrast to the above addition, irradiation of isomeric 3-phospholene (7) afforded no detectable amounts of alcohol addition products nor exo isomer. More intriguing are the results of irradiation of 2-phospholene oxide (5) in alcohols, which has no lone pair electrons on phosphorous. 5 was photoreduced



best in isopropyl alcohol to give isomeric mixture of phospholanes (8a,b) and no trace of adducts (4a,b) were detected even in the reaction with methanol.⁶

Apparently, the fact that the addition occurs only to C=C adjacent to the trivalent phosphorous suggests that the excited state involves a polarized double bond, presumably derived from an electron transfer from the nonbonded orbital on phosphorous to the empty π^* orbital on C=C.⁷ Thus, initial protonation at C-2 of the polarized excited state to form carbonium ion followed by nucleophilic attack of alcohol and elimination of proton at methyl group to exocyclic olefin explain the foregoing results.

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References and Footnotes

- (a) P. J. Kropp, *J. Amer. Chem. Soc.*, 91, 5783 (1969); 89, 3650 (1967); 88, 4091 (1966).
(b) J. A. Marshall, *Accounts Chem. Res.*, 2, 33 (1966), and references cited therein.
- All irradiations were carried out under N_2 in an immersion apparatus using a quartz well and a 300 watt high pressure Hg lamp.
- All new compounds showed satisfactory mass spectra and their benzyl bromide salts gave satisfactory elemental analysis results.
- Stable cis and trans forms of five-membered cyclic phosphines have been known and separated⁵ owing to the configurational stability of trivalent

phosphorous.

5. (a) A. Bond, M. Green and S. C. Pearson, *J. Chem. Soc. (B)*, 929 (1968).
(b) K. L. Marsi, *J. Amer. Chem. Soc.*, 91, 4724 (1969).
(c) L. D. Quin and T. P. Barket, *Ibid.*, 92, 4303 (1970).
6. H. Tomioka, Y. Hirano and Y. Izawa, unpublished results.
7. M. A. Weiner and G. Pasternack, *J. Org. Chem.*, 32, 3707 (1967).