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SYNTHESIS AND PHOTOCHEMICAL REACTION OF DIELS-ALDER ADDUCT OF PHOSPHOLE OXIDE AND CYCLOPENTADIENE(1)

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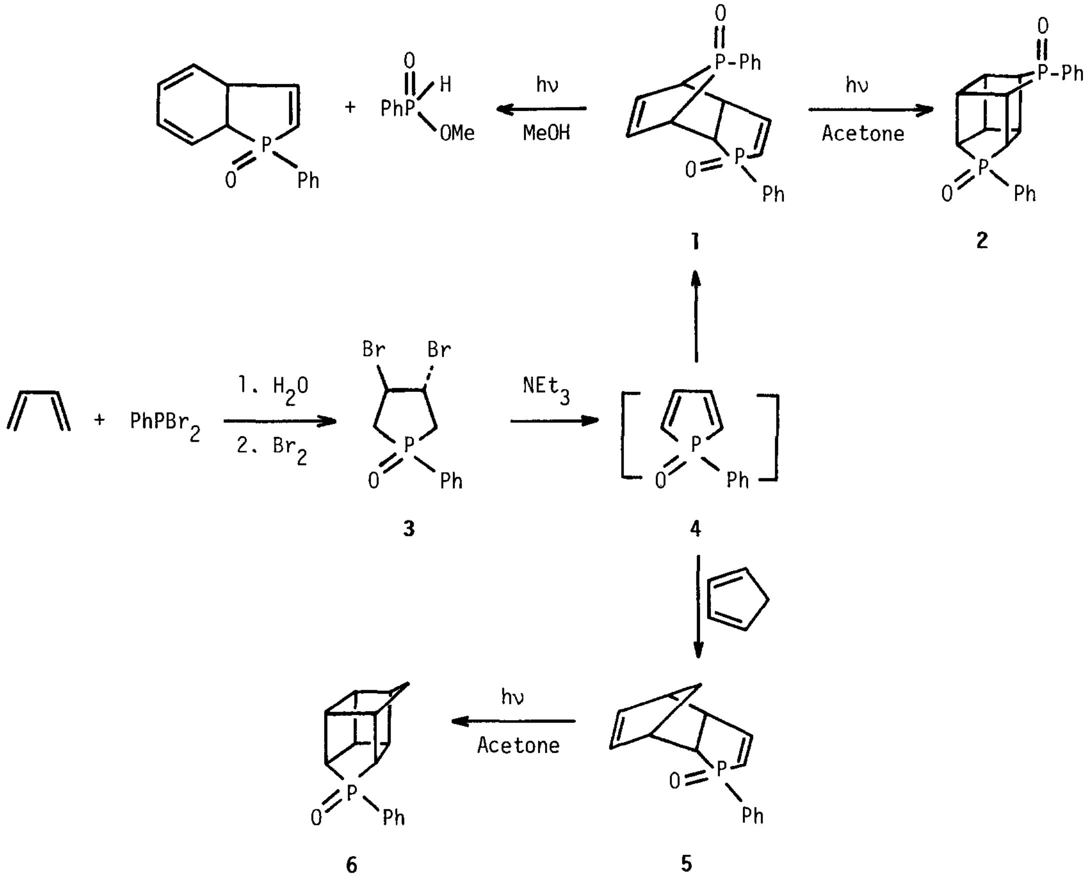
Summary: Irradiation of 1-phenylphosphole oxide-cyclopentadiene adduct gave a caged product, whereas similar irradiation of 1,2,5-triphenylphosphole oxide-cyclopentadiene adduct afforded a cleavaged product.

Previous studies[2)] from this laboratory showed that the Diels-Alder dimer of 1-phenylphosphole oxide (**1**) underwent an interesting photochemical conversion. Thus, direct irradiation of the dimer (**1**) resulted in an efficient extrusion of Ph-$\ddot{P}$=O bridge, while the sensitized irradiation produced a caged product (**2**) as a result of intramolecular [2 + 2] cycloaddition. The former reaction is a useful method to generate the reactive phosphorus intermediate,[1,3)] analogous to carbene and nitrene, and has recently been employed[4)] to build a new phosphorus heterocycles. The latter, on the other hand, has recieved much attentions as one of efficient energy storage system. Thus, as an extension of this study, we have prepared the Diels-Alder adducts of phosphole oxide with cyclopentadiene and examined their photochemical reactivities.

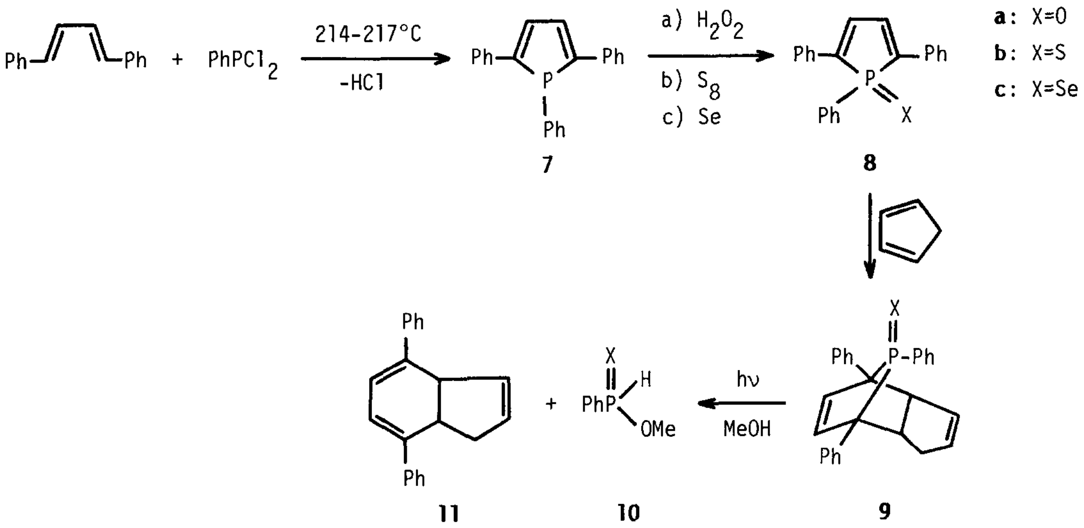
When 3,4-dibromophospholane oxide (**3**), easily available[5)] from the cycloaddition of 1,3-butadiene and phenyldibromophosphine followed by bromination, was dehydrobrominated with 2-molar excess of triethylamine in cyclopentadiene at 20°C, the readily self-dimerizable phosphole oxide (**4**) generated was trapped by cyclopentadiene to give Diels-Alder adduct (**5**)[6,7)] in 67.6% yield as an oil after silica gel chromatography. Structure of **5**, where phosphole oxide is reacting as a dienophile, was assigned mainly based on its NMR spectra which displayed complicated vinyl protons signal centered at δ 7.00 and 6.52 ppm characteristic of 2-phospholene vinyl protons. Further proof for the correct assignment of **5** was obtained by the photochemical reaction of the adduct. Thus, when **5** was irradiated in acetone for 24 h, a caged product (**6**) was isolated in 71.9% yield as a sole isolable product by silica gel chromatography. The NMR of **6** showed no vinyl protons but eight methine protons at δ 2.50 ∿ 3.60 ppm. Direct irradiation of **5** in methanol, on the other hand, resulted in almost total recovery of the starting material even after prolonged irradiation. Methyl phosphinate was not detected in the reaction mixture, suggesting that Ph$\ddot{P}$=O was not generated.



Scheme I

Since phosphoryl groups at bridging position are known[3,4] to be extruded easily upon irradiation, the observation supports the structure **5**.

When 1,2,5-triphenylphosphole oxide was reacted with cyclopentadiene, however, it was found that the phosphole oxide acted as a diene, instead of dienophile. Thus, triphenylphosphole oxide (**8a**), prepared according to the procedure of Campbell et al,[8] was refluxed in benzene in the presence of 2 molar excess of cyclopentadiene for 4 h, during which time portion of 2 molar excess of the diene was added every 2 h. Evaporation of the solvent gave adduct (**9a**)[6] as a white needles (acetone, mp 161-163°C) in 40% yield. The structure of **9a** was easily ascertained by its NMR spectra which showed the presence of four well-separated olefinic protons, in addition to two methine protons, while three olefinic and three methine protons are expected for the other possible adduct similar to **5**. The correct assignment of **9a** was further confirmed again by its



Scheme II

photochemical reactivities. Thus, irradiation of **9a** in methanol resulted in almost exclusive formation of dihydroindene derivative (**11**) in 90% yield along with equal amount of methyl phosphinate (**10a**). Moreover, similar irradiation in acetone also gave **11**. No caged product was isolated in the irradiation mixture. These results strongly support the structure 9.[9] It is quite probable that two phenyl groups attached at bridge-head carbons facilitate the extrusion of the bridging phosphoryl group.

The reaction of cyclopentadiene with phosphole sulfide (**8b**) and selenide (**8c**) also gave similar adducts (**9b** and **c**)[6] in 40 and 35% yields, respectively. Irradiation of these adducts in methanol also gave thio- (**10b**) and selenophosphinate (**10c**) in about 50% yields. The results suggest that not only $Ph\ddot{P}{=}S$ but also previously unreported $Ph\ddot{P}{=}Se$ can be generated in the irradiation of the cyclopentadiene adducts with corresponding phosphole derivatives.

The present study showed that, in their reaction with cyclopentadiene, phosphole oxides can act either as a diene or as a dienophile depending on the substituents to give two kinds of Diels-Alder adducts and that one of the adducts serves as a useful starting point for construction of a caged phosphorus compound while the other as a sueful source to generate reactive phosphorus intermediates.

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References and Notes

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6) **5** (oil): δ ($\mathrm{CDCl_3}$) 1.5 (m, 2H), 2.55 (m, 2H), 3.2 (m, 1H), 3.6 (m, 1H), 5.86 (m, 1H), 6.1 (m, 1H), 6.52 (m, 1H), 7.00 (dd, 1H), and 7.40-7.72 (m, 5H).
6 (oil): δ ($\mathrm{CDCl_3}$) 1.68 (br. s, 2H), 2.5-3.0 (m, 8H), and 7.38-7.64 (m, 5H).
9a (m.p. 161-163°C): δ ($\mathrm{CDCl_3}$) 2.1-2.4 (m, 2H), 4.06 (dt. 1H), 4.4 (dd, 1H), 5.44 (dd, 1H), 5.64 (m, 1H), 6.48 (dd, 2H), 7.06-7.50 (m, 15H).
9b (m.p. 169-171°C): δ ($\mathrm{CDCl_3}$) 1.98-2.40 (m, 2H), 4.24 (-d, 1H), 4.60 (m, 1H), 5.46 (m, 1H), 5.64 (m, 1H), 6.60 (dd, 2H), and 6.98-7.7 (m, 15H).
9c (m.p. 148-150°C): δ ($\mathrm{CDCl_3}$) 1.92-2.28 (m, 2H), 4.3 (m, 1H), 4.6 (m, 1H), 5.44 (m, 1H), 5.62 (m, 1H), 6.60 (m, 2H), and 6.96-7.72 (m, 15H).

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