

PRESERVATION OF THE β -PHOSPHOLENE NUCLEUS IN REACTIONS OF
DIENE-METHYLPHOSPHONOUS DICHLORIDE ADDUCTS*

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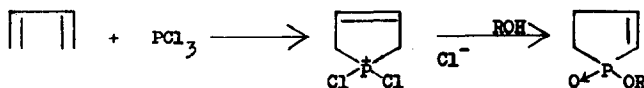
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The Diels-Alder reaction between dienes and phosphorus trihalides has recently been reported (1). The adducts with phosphorus trichloride (but not the tribromide) were found to undergo double-bond migration on subsequent treatment with a variety of reagents, e.g., alcohols.



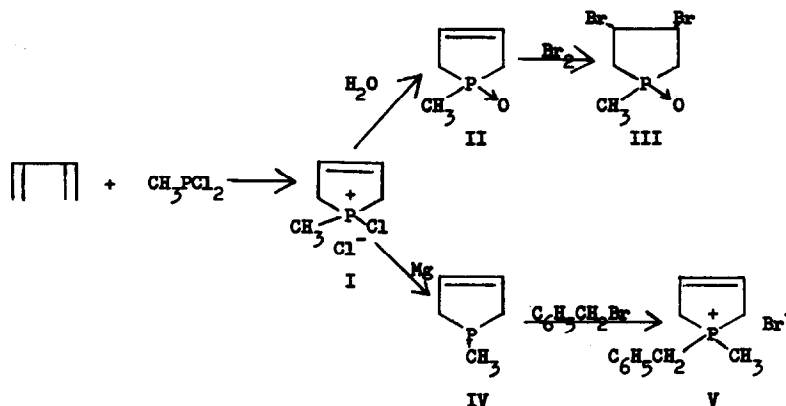
It has further been stated (2) that proton nmr and infrared spectral data show certain adducts with phenylphosphonous dichloride (3) to undergo a similar rearrangement on hydrolysis to the tertiary phosphine oxide, although adequate supporting data have not yet been published. This observation may cast doubt on the structure of a considerable number of compounds in the literature as β -phospholene derivatives. We are

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therefore prompted to present some evidence that shows methylphosphonous dichloride adducts (4) not to rearrange on either hydrolysis or reduction (dehalogenation).

A cyclohexane solution of butadiene and methylphosphonous dichloride containing copper stearate as a polymerization inhibitor gave, after standing for three months, a 72% yield of crystalline 1-methyl-3-phospholene-1,1-dichloride (I). This adduct was hydrolyzed in 80% yield to the oxide (II), b.p. 59° (0.16 mm.), a deliquescent solid, which was analyzed as the dibromide (III), m.p. 145-146°. Reduction (4) of I with magnesium in carefully dried tetrahydrofuran gave a 7% yield of the phospholene (IV), b.p. 114-115°, which was analyzed as its benzyl phosphonium salt (V), m.p. 185-186.5°.



The pmr spectrum (Varian A-60 Spectrometer) of the oxide II (in CDCl_3) consisted of three 1:1 doublets: methyl, $\tau = 8.39$ ppm, $J = 12.8$ cps (3H); methylene, $\tau = 6.69$ ppm, $J = 10.9$ cps (4H); vinyl, $\tau = 4.17$ ppm, $J = 27.2$ cps (2H). This spectrum is in accord only with the 3-phospholene structure. The 2-isomer would have two non-equivalent methylene groups and two non-equivalent vinyl protons. The spectrum of the neat phospholene IV showed a 1:1 doublet at $\tau = 9.19$ ppm, $J = 3.4$ cps (3H),

a complex multiplet at $\tau = 7.25-8.25$ ppm (4H) and a 1:1 doublet at $\tau = 4.28$ ppm, $J = 6.5$ cps (2H). The phosphonium salt V (in CDCl_3) gave a spectrum consisting of four 1:1 doublets and a phenyl multiplet: $\tau = 7.60$ ppm, $J = 14.3$ cps (3H); $\tau = 6.68$ ppm, $J = 9.9$ cps (4H); benzyl, $\tau = 5.40$ ppm, $J = 16.5$ cps (2H); vinyl, $\tau = 4.17$ ppm, $J = 28.0$ cps (2H); $\tau = 2.33-2.75$ ppm (5H). The spectrum of the dichloride I (in CDCl_3) consisted of three doublets: $\tau = 6.13$ ppm, $J = 14$ cps (3H); $\tau = 5.53$ ppm, $J = 8$ cps (4H); $\tau = 3.18$ ppm, $J = 36$ cps (2H). Double resonance experiments (P^{31} decoupling) confirmed the observed couplings in II, IV and V to be P^{31} -H couplings. Thus, irradiation of the P^{31} nucleus in V gave a spectrum consisting of four singlets, $\tau = 7.62$ (3H), 6.65 (4H), 5.38 (2H) and 4.19 ppm (2H) and a phenyl multiplet.* The pmr spectral data are consistent only with the presence of the 3-phospholene nucleus in the entire series of compounds.

The extraordinarily large vinyl proton- P^{31} coupling was common to all the phospholenes with the exception of the phosphine IV. A similar trend has been noted within families of acyclic phosphorus compounds and these also show greater P^{31} -H couplings for β - than for α -protons (5). The large magnitude of these coupling constants has been associated with the positive charge on phosphorus in phosphine oxides, phosphonium salts and halophosphoranes. Thus, support for the contention (4) that the chlorophosphorane (I) is a compound of quaternary, rather than pentavalent, phosphorus may be obtained from the pmr data. Trends for the chemical shifts also support this assignment. There is a pronounced downfield shift for α -proton signals for all derivatives of IV; this shift reaches the remarkable value of 3.06 ppm for the P-methyl protons of the dichloride I as compared to the

*We are indebted to Mr. F. E. Dickson (NMR Specialties, Inc. New Kensington, Pa.) for carrying out the double resonance experiments.

parent IV. This phenomenon has also been associated with positive charge on the phosphorus atom (5).

Derivatives of the adducts from 2,3-dimethylbutadiene and from isoprene have been shown similarly to possess the 3-phospholene nucleus. Full details will be published elsewhere.

The partial rearrangement of the oxide (II) to 1-methyl-2-phospholene-1-oxide (VI) has been accomplished by heating at 280-300° for twenty hours or by refluxing in 3N sodium hydroxide for twenty four hours. The yield of mixed isomers in each case exceeded 90%; glc analyses showed the ratio (II:VI) for the two methods to be about 4:5 and 2:3 respectively. The 2-phospholene oxide (VI) was obtained by distillation, b.p. 90° (0.55 mm.); it formed a dibromide (VII), m.p. 145.5-147° whose infrared spectrum differed considerably from that of III. The spectrum of VI had the expected (2) intensification of the C=C absorption and shift to lower frequency (II, $\nu_{C=C} = 1621 \text{ cm.}^{-1}$; VI, 1589 cm.^{-1}). The pmr spectrum of VI was quite different from that of the 3-isomer (II). The vinylic protons were extensively split ($\tau = 2.2-3.6 \text{ ppm}$) and two complex multiplets ($\tau = 7.1, 7.6 \text{ ppm}$) were observed for the non-equivalent methylene groups.

Heating in 3N hydrochloric acid was not effective for rearranging II to the 2-isomer, but did rearrange 1,3-dimethyl-3-phospholene-1-oxide to 1,3-dimethyl-2-phospholene-1-oxide (90% conversion). Acid catalysis must therefore be taken into consideration as an alternative to base catalysis (2) in interpreting the behavior of diene-phosphorus trichloride adducts on solvolysis, since the reaction medium becomes quite acidic upon solvolysis.

Since it now appears that bond mobility in the 3-phospholene series is to some extent dependent on the structural organization on phosphorus, it is obvious that each family of derivatives must be subjected to a determination of the location of the double bond. Thus, the 1-aryl-3-

phospholenes reported previously (4) are presently being re-examined.

Compounds III, V and VI gave satisfactory analyses for C, H, and P.

REFERENCES

1. V. Hasserodt, K. Hunger, and F. Korte, Tetrahedron 19, 1563 (1963).
2. K. Hunger, Vs Hasserodt, and F. Korte, Tetrahedron 20, 1593 (1964).
3. W. B. McCormack, U. S. Patents 2,663,736-8 (1953).
4. L. D. Quin and D. A. Mathewes, J. Org. Chem. 29, 836 (1964).
5. J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, Tetrahedron 20, 499 (1964).