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GEOMETRICAL ISOMERS FROM THE DIELS-ALDER SYNTHESIS OF 3-PHOSPHOLENE DERIVATIVES*

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The 3-phospholene ring system may be formed by the condensation of 1,3-dienes with tricovalent phosphorus halides, a reaction first observed by McCormack for phosphonous dihalides (1). The initial adducts in this particular case may be hydrolyzed to produce phosphine oxides (1) or reduced to form phosphines (2). It has not previously been recognized that geometrical isomers may result from these reactions. Thus, when piperylene is used as the diene, it is theoretically possible to produce _cis_ and _trans_ forms of both the oxides (e.g., II from methylphosphonous dichloride) and the phosphines (III), since the phosphorus atom in both situations is configurationally stable (3).

We have found that for both of these products geometrical isomers are indeed present. In addition to their potential value in the development of the Diels-Alder route to cyclic phosphorus compounds, these results are of stereochemical interest; they provide a demonstration of the not unexpected existence of geometrical isomerism among cyclic phosphine oxides, and, more importantly, a second example of trivalent phosphorus

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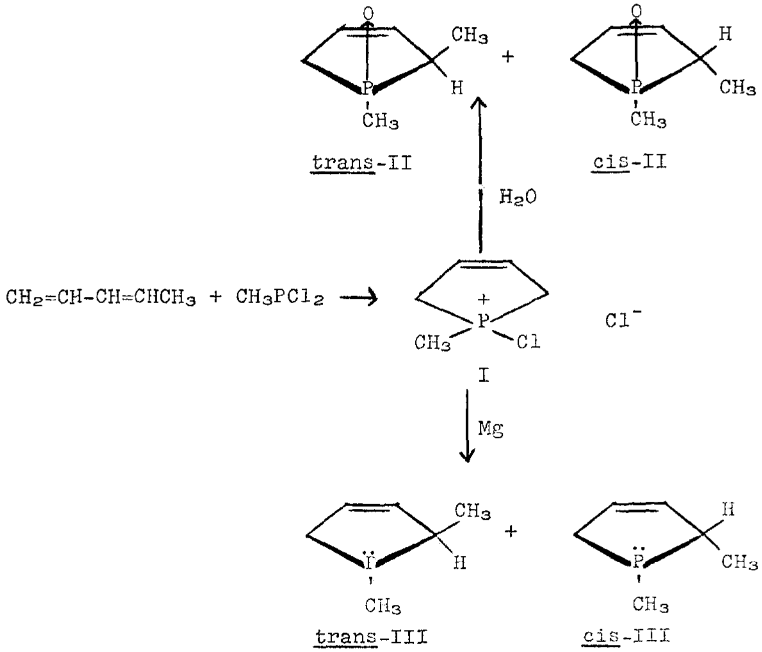
effecting a similar isomerism in a monocyclic compound. The other example was provided in the preceding paper (4), and was encountered as the result of the addition of a Grignard reagent to a phosphorinanone. It seems likely that stereoisomerism will prove to be of general occurrence among properly substituted cyclic phosphines, and should receive the same consideration in developing the chemistry of such compounds as is accorded carbocyclic compounds. The products of some earlier investigations where 1-substituted dienes were condensed with phosphorus halides may well prove to be mixtures of geometrical isomers.



Commercial cis, trans-piperylene was condensed with methylphosphonous dichloride at room temperature in heptane, with copper stearate as polymerization inhibitor. After several months' standing, some of the adduct (I) was removed, washed with heptane, and hydrolyzed by addition to water. After neutralization the mixture was extracted with chloroform. The extract on distillation gave the oxide II, b.p. 58-64° (0.17-0.25 mm.), 62% yield. This product showed two peaks on gas chromatography (GC), that one eluted first (IIa) having twice the area of the second (IIb). IIa was obtained free of IIb by preparative GC (2 m. by 1 cm. column of polyethylene glycol 20,000 on 30-60 mesh Chromosorb P, 1:4, 195°). Anal. Calcd. for $C_6H_{11}OP$:C, 55.38; H, 8.52; P, 23.80. Found:C, 55.40; H, 8.46; P, 23.87. IIb was difficult to separate from thermal rearrangement products (5); it was obtained in crude form by distillation of II with a spinning band column. After one fractionation, a mixture of 85% IIb, 8% IIa and 7% of a rearrangement product was obtained.. Anal. Found:C, 55.21; H, 8.40; P, 24.02.

The infrared spectra of IIa and IIb were very similar. The C = C stretching bands (1610 and 1613 cm.$^{-1}$, respectively) indicated both compounds to have the double bond similarly situated, since appreciable differences are common between $\Delta^{2,3}$ and $\Delta^{3,4}$ isomers (5,6). Their proton magnetic resonance (pmr) spectra (Table I) were almost identical. Nevertheless, the pmr spectrum of a neat mixture of IIa and IIb showed two distinct sets of signals. The spectra confirm the structures assigned to the individual products, and also eliminate the possibility of the isomerism being due to location of the double bond (5,6). Thus, the presence of two olefinic hydrogens, and of splitting of C-CH_3 by one proton (and by P^{31}, giving four peaks) may be cited in support of II.

TABLE I

Pmr Spectra of 1,2-Dimethyl-3-Phospholenes and Their Oxides[1]

	P-CH_3 (J_{PCH})[2]	HC=CH(J_{PCCH})	C-CH_3(J_{PCCH}) (J_{HCCH})[3]
IIa	1.84 (12.5)	6.01 (26.0)[4]	1.43 (14) (7)
IIb	1.83 (12.5)	6.24 (25.5)[2]	1.54 (16) (7)
IIIa	1.12 (3.5)	5.85 (6.5)[2]	1.34 (18) (8)
IIIb	1.01 (3.5)	5.82[5]	1.36 (10) (7.5)

[1] Taken with a Varian A-60 spectrometer on neat samples. Values are ppm from tetramethylsilane reference in a sealed capillary. Parenthetical values are coupling constants in cps. [2] Doublet. [3] Four-line pattern. [4] Doublet, each peak further split by 1 cps. [5] Complex multiplet.

Reduction of I with magnesium in tetrahydrofuran gave the phosphine III (2), b.p. 130-134°, in 54% yield. The pmr spectrum again suggested the presence of isomers, and this was confirmed by GC. The isomers were easily separated by preparative GC, using the above column at 100°. The products were trapped in 6N hydrochloric acid, and were recovered on making the solutions basic. The retention time ratio of IIIa to IIIb was 0.67 :1; the area ratio was about 3:1. Pmr spectra (Table I) again support the assigned 3-phospholene structure. The spectra show certain differences which appear dependent on the orientation of the ring substituents. The coupling constant of the C-methyl protons with phosphorus in IIIa (18 cps) is considerably larger than in IIIb (10 cps), and in fact is abnormally large for a phosphine (7). Pending further study in related compounds, this effect may prove of value in making an assignment of cis and trans structures to the isomers. Infrared spectra were similar yet characteristic. Both had a C=C stretching band at 1615 cm.$^{-1}$. The benzyl bromide salt of IIIa had m.p. 200-201°; that of IIIb, 202-203° (mixed m.p. 183-185°; a value of 158-158,5° has been reported (2) for a different composition). Anal. Calcd. for $C_{13}H_{18}BrP$:P, 10.86. Found for IIIa; P, 10.43. Found for IIIb; P, 10.46.

When the cis, trans mixture of III was exposed to dry air for several hours, a crude oxide mixture, with resemblance to that from the hydrolysis of I, was obtained; GC showed peaks for IIa and IIb in the expected ratio, and the infrared spectra of the two mixtures were similar. Subjecting phosphine IIIa individually to atmospheric oxidation gave oxide IIa, as determined by GC. Similarly, oxide IIb was formed from IIIb. The stereochemistry of oxidation of phosphines by oxygen is not yet known, but if this occurs with retention, as does hydrogen peroxide oxidation (8), then the same geometry is established for IIa and IIIa, and for IIb and IIIb.

The rough agreement between the ratio of IIa to IIb (2:1) and IIIa to IIIb (3:1) may suggest that the original adduct I also consists of cis, trans isomers in this approximate ratio, and that the reactions providing II and III from I are stereospecific. It is furthermore possible that trans- and cis- piperylene react stereospecifically, although at different rates (1), to provide a particular isomer of I, as suggested by the resemblance of the ratio (2.7:1) of these isomers in the commercial piperylene used to the product ratios. These relations are being examined by subjecting the individual piperylenes to the conversions described herein.

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