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GEOMETRICAL ISOMERISM OF 4-ETHYL-1-METHYL-4-PHOSPHORINANOL*

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The configurational stability of the trivalent phosphorus atom is sufficient to permit optically active derivatives to exist (1-3). It follows that suitably substituted cyclic compounds with trivalent phosphorus should exist in cis and trans isomeric forms. Goldwhite (4) has presented evidence from the NMR spectra of substituted 1,3,2-dioxaphospholanes that this may be the case; both the 2-chloro-4-methyl- and the 2-methoxy-4-methyl- derivatives showed the presence of two kinds of C-methyl groups. This effect also was noted for the 2-chloro-4,4,5,5-tetramethyl derivative. However, the only case of separation of isomers whose existence depends on the configuration at phosphorus is that described by Davis and Mann (5), who have isolated two crystalline isomers of the tricyclic compound 5,10-diethyl-5,10-dihydrophosphanthrene. No individual geometric isomers have previously been isolated for monocyclic trivalent-phosphorus compounds**, and nothing is known about the stereochemical

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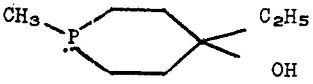
**Henderson, Epstein, and Seichter (6), have proposed that two isomeric forms of tetraphenylcyclotetraphosphine may be stereoconformers where one has a planar, and the other a puckered, P_4 ring, or that they may differ in configuration on phosphorus (and thus could be considered as geometric isomers).

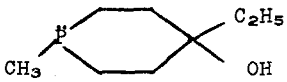
consequences of the presence of such a function in a simple ring system.

It is the purpose of this and the following paper to show that geometrical isomerism can be an important feature of the chemistry of simple monocyclic phosphines, and should be taken into account in work with compounds theoretically capable of possessing this property. We describe here the separation of geometrical isomers of a derivative of the phosphorinane system, and in the next paper the separation of isomers of a derivative of the 3-phospholene system.

4-Ethyl-1-methyl-4-phosphorinanol (I) possesses the requisite structure for geometrical isomerism.



cis-I



trans-I

Its synthesis was accomplished by a Grignard addition to 1-methyl-4-phosphorinanone (b.p. 57-58° at 0.7 mm. Anal. Calcd. for $C_6H_{11}OP$: C, 55.38; H, 8.52; P, 23.80. Found: C, 55.68, H, 8.58; P, 23.73) which was prepared in 60% yield by application of the Thorpe method (7) to methyl-bis-(2-cyanoethyl)phosphine (8). The ketone was reacted with 2 moles of ethylmagnesium bromide to provide I (b.p. 45-62° at 0.2 mm.) in 56% yield. Gas chromatography (1 m. by 8 mm. column of polypropylene glycol on Chromosorb P, 1:3, at 168°) revealed (in addition to some of the ketone) the presence of two compounds in this sample (at 70 ml. of helium per min., Ia at 6.8 min., Ib at 8.0 min.; area of Ia: Ib, 1.33). The sample was fractionated on a spinning band column, whereupon fractions enriched in Ia and Ib were obtained. Two re-fractionations provided gas chromatographically homogeneous specimens of Ia (b.p. 62° at 0.55 mm.) and Ib (b.p. 68-69° at 0.6 mm.), each of which had the correct P content (Calcd. for $C_8H_{17}OP$: P, 19.33. Found: for Ia, 19.42; for Ib, 19.01). The separation was also accomplished by preparative-scale gas chromatography.

The proton magnetic resonance spectra (Varian A-60 spectrometer, benzene solution with tetramethylsilane internal standard) were very similar and in accord with the assigned structure. Compound Ia had a P-CH_3 doublet (J = 2.5 cps.) at 0.95 ppm., overlapping part of a $CH_2\underline{CH_3}$ triplet (J = 6 cps.) at 0.83 ppm. The two methyl signals were more in overlap for Ib, giving a multiplet centered at about 0.89 ppm. For both compounds, a complex multiplet (10 H) for the CH_2 groups was located at 1.0-2.0 ppm. The appearance of the multiplet was different for each isomer, but decoupling seems required to make this region interpretable. The infrared spectra of Ia and Ib (neat) were almost identical. The O-H stretching band for each appeared at 3350 cm.$^{-1}$. There was only a minor difference in the C-O stretching band; Ia had a single peak at 1105 cm.$^{-1}$, while Ib had a peak at 1100 cm.$^{-1}$ showing a weak shoulder near the maximum. That there were no major differences near this region of the spectra may suggest that the hydroxy group is in a similar conformational situation in both isomers, as significant differences in C-O stretching are common for axial and equatorial alcohols (9). Detailed assignment of geometrical features to the ring must, however, await the results of further experimentation.

The isomers were further characterized by quaternization with benzyl bromide, and then conversion of the salts to the perchlorates. Ia gave a salt (needles) of m.p. 199-200° from water-methanol (Anal. Calcd. for $C_{15}H_{24}ClO_5P$: C, 51.36; H, 6.90; P, 8.33. Found: C, 51.14; H, 6.73; P, 8.89), while Ib gave a more soluble salt (leaflets) of m.p. 166-168° (Found: C, 51.35; H, 6.82; P, 8.83).

1,4-Diethyl-4-phosphorinanol, prepared similarly, has also been found to give two peaks on gas chromatography. Individual isomers have not been isolated.

Considerable configurational stability of phosphorus in the phosphorinanol system was demonstrated when no change in the ratio of Ia to Ib, in a sample enriched in the latter by distillation, occurred on refluxing for 64 hr. in benzene, or 28 hr. in toluene.

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