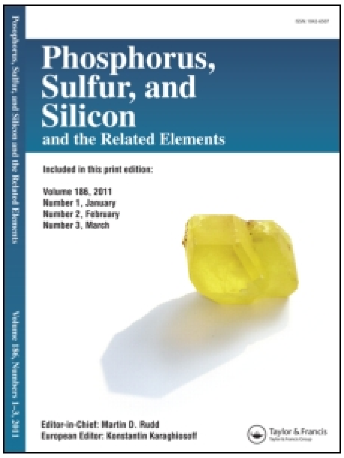

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Robertson, A. J.(1987) 'Chiral Phosphines: The Effect of Asymmetric Carbon Centers α or β to Phosphorus on the ^{31}P NMR Spectra', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 265 — 268
To link to this Article: DOI: 10.1080/03086648708080573
URL: http://dx.doi.org/10.1080/03086648708080573

Phosphorus and Sulfur, 1987, Vol. 30, pp. 265–268
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CHIRAL PHOSPHINES: THE EFFECT OF ASYMMETRIC CARBON CENTERS α OR β TO PHOSPHORUS ON THE ^{31}P NMR SPECTRA

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ABSTRACT Chiral alkylphosphines containing asymmetric carbon centers either alpha or beta to the phosphorus are formed from the free radical addition of phosphine to prochiral olefins. The phosphorus NMR spectra of the primary phosphines have only one signal for the enantiomeric pair while the spectra of the secondary phosphines have three signals in a 1:2:1 ratio. This is the statistical ratio expected for the enantiomeric pair and two meso forms. Four enantiomeric pairs of tertiary phosphines can be formed from one prochiral olefin. One pair has alkyl groups of the same configuration while the remaining pairs have mixed configurations. The phosphorus NMR spectra show two signals in a 1:3 ratio. Dilution of the secondary phosphines with a polar solvent results in only one signal in the phosphorus NMR spectra. The chemical shifts and diluent effect can be explained in terms of the gamma shielding effect (1).

INTRODUCTION

Addition of phosphine to prochiral internal olefins such as cis/trans butene-2 produce chiral alkylphosphines with asymmetric carbon centers α to phosphorus while branched terminal olefins suchα-methylstyrene and 2,4,4' trimethylpentene-1 yield alkyl groups in which the asymmetric carbon β to phosphorus.

An enantiomeric pair of mono sec-butylphosphine having configurations L and D (Figure 1) are formed from the addition of phosphine to cis/trans butene-2. They are expected to have identical physical properties, including phosporus NMR chemical

$$\underset{L}{C} - C - \overset{C}{\underset{H}{C}} - PH_2 \qquad \underset{D}{C} - C - \overset{H}{\underset{C}{C}} - PH_2$$

Figure 1 - Enantiomeric Mono sec-butylphosphines

shifts. Here are, however, four di sec-butylphosphine conformational isomers making up an enantiomeric pair in which the phosphorus atoms are also asymmetric and two meso forms. They are illustrated as their Fisher and Newman projections in Figure 2. The two meso forms are expected to have different physical properties than the enantiomeric pair. There are eight possible tertiary alkyl phosphine isomers forming four enantiomeric pairs. One pair has all three alkyl groups in either the D or L configuration and in addition has an asymmetric phosphorus. The remaining three pairs contain two of the three alkyl groups in either the D or L configuration.

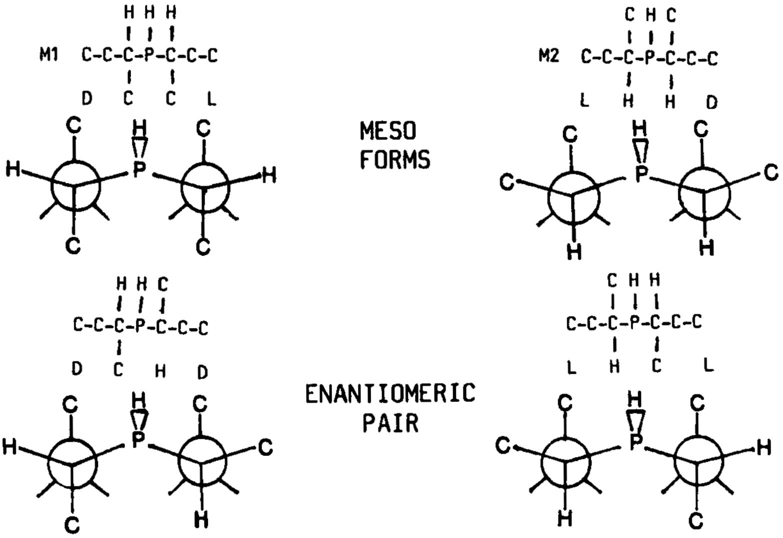

Figure 2 - Fisher and Newman projections of di sec-butylphosphines

Results

As expected the phosphorus NMR spectra of the primary phosphines show only one signal at -114.50, -147.86 and -151.28 Hz respectively, for primary phosphines derived from cis/trans butene-2, α-methylstyrene and 2,4,4' trimethylpentene-1. On the other hand the chiral secondary phosphines have three signals in a 1:2:1 ratio (Figure 3) and the chiral tertiary phosphines have only line signals in a 1:3 ratio.

An interesting phenomenon occurs when the racemic mixtures of chiral secondary phosphines are diluted with a small amount of polar solvent such as chloroform. The three signals are reduced to one and on further dilution are shifted slightly down field. However, on dilution with a non-polar solvent such as benzene, the three signals remain unchanged. A similar 1:2:1 signal pattern is also found for the corresponding secondary phosphine oxides and the salts of their respective monothiophosphinic acids.

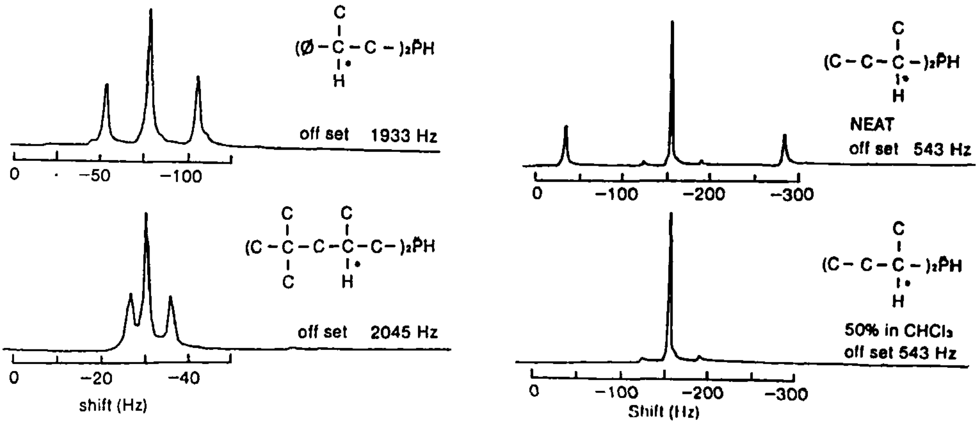

Figure 3 - Phosphorus NMR spectra of chiral dialkylphosphines

Discussion

Changes in phosphorus NMR chemical shifts are due to a combination of change in Pi bonding, changes in electronegativity of the substituents or changes in the R-P-R sigma bond angle (2). In this case only the later applies. An increase in the R-P-R bond angle of the trivalent phosphorus compounds results in a de-shielding of the phosphorus or a down field shift in the resonance signal (3). Inspection of the Newman projections of the four conformers of di sec-butylphosphine indicate that one meso (M-1) wherein both 2-methyl groups are adjacent would have the largest R-P-R bond angle and the other meso form (M-2), the smallest R-P-R bond angle. The bond angle for the enantiomeric pair should be the same and somewhere between those of the two meso forms. On this basis, the signal further downfield can be assigned to M-1 and the upfield signal to M-2.

The proposed changes in R-P-R bond angle cannot account for the effect of polar solvents on the NMR signal. Quinn and Breen (1) have reported that within a family of aliphatic phosphorus compounds changes in R-P-R bond angle alone cannot account for the chemical shift differences. Shielding by gamma carbons gauche to the phosphorus is also involved. They developed an emperical formula (eq.1) relating the chemical shift Δ P to the chemical shift of a parent compound of a homologous series and the number of beta and gamma carbons present. In equation (1) α and β

$$\Delta P = \sigma \text{ (Parent)} + M\alpha + N\beta \quad (1).$$

are the number of α and β carbons while M and N are constants for a given class of aliphatic phosphorus compounds.
M is a positive value (deshielding) while N is negative

(shielding). The parent compound for dialkylphosphines is dimethylphosphine which has a σ (parent) value of -99.0 PPM. The values for M and N are +22 and -10 respectively. Inserting the values in equation (1) for di sec-butylphosphine results in a predicted chemical shift of -31.0 PPM. This is in excellent agreement with the observed shifts -23.81, -28.87 and -34.20 PPM for the di sec-butylphoshphine isomers. The gamma carbons are shown gauche to phosphorus in all four isomers in Figure 3. However, in reality, the bulky adjacent methyl groups in M-1 cause rotation along the C1-C2 bond axis forcing the gamma carbons away from the phosphorus. This effect is minimal in M-2 and somewhere in between for the enantiomeric pair. In other words, M-1 should have the least gamma shielding and the phosphorus resonance signal should be further downfield which is in agreement with the change in R-P-R bond angle theory.

The addition of a polar solvent molecule at the lone pair will displace the gamma carbons and nullify any changes in gamma shielding. This reduces the differences in chemical shift of the four isomers considerably and results in only one signal being observed instead of three. In theory the three signals should still be observed but chemical shift changes due solely to any change in R-P-R bond angle are too small to be resolved.

Experimental

The alkylphosphines were prepared by the free radical addition of phosphine to the corresponding olefins according to Rauhut et al(4) using 2,2' -azobis - (2-methylbutyronitrile) as the free radical initiator. The phoshorus NMR spectra were proton decoupled and were determined on a Bruker WP80 NMR spectrometer on which the resonance signal for 85% of H_3PO_4 is 24.288 MHz. Upfield shifts are negative with respect to 85% H_3PO_4 in accordance with the 1976 IUPAC convention (5).

Acknowledgement

The author wishes to thank Mr. T. Jones (Brock University, St.Catharines) for determining the phosphorus NMR spectra.

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