Conformational Equilibrium around the Phosphorus–Carbon Bond in Dichlorophosphines

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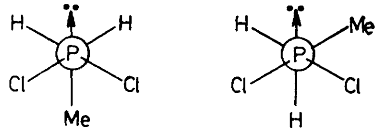
Summary It is shown by ^{1}H, ^{13}C, and ^{31}P n.m.r. spectroscopy that the preferred conformation of ethyldichlorophosphine and isopropyldichlorophosphine around the P–C bond is that in which a methyl group and the phosphorus lone pair are *trans* to each other.

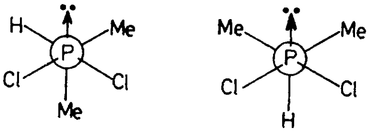
A great deal of information on intermolecular interactions can be obtained from studies of conformational equilibria around single bonds. There have been numerous studies on the conformation and rotation barrier around the C–C bond in halogenated hydrocarbons,[1] but relatively few on the conformation around the P–C bond in halogenophosphines.[2] Recent n.m.r. studies reported the height of the rotational barrier around the P–C bond in halogenophosphines existing in only one conformation.[3]

We report here results of low-temperature ^{1}H, ^{13}C, and ^{31}P n.m.r. studies on the dihalogenophosphines (**1**) and (**2**) which can exist as a mixture of different conformations.†



(A) (B)

(1)



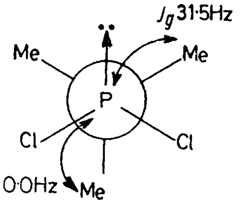
(A) (B)

(2)

At room temperature the $\{^{1}H\}^{31}$P n.m.r. spectrum of (**2**) shows only a single peak, which broadens on cooling to -140 °C, and eventually is resolved into two peaks of unequal intensity (10:1) at 202·2 and 192·0 p.p.m. respectively.‡ The existence of these two peaks at low temperature indicates that (**2**) exists in two conformations which interconvert slowly on the n.m.r. time scale at -140 °C. From the intensities of the signals the ΔH difference between conformers (A) and (B) is 1·7 kJ mol^{-1} at 130 K.

In order to assign the stronger peak to conformation (A) (symmetry C_1) or (B) (C_s), we examined the ^{2}J(P–C–C) coupling constant which is known to be highly dependent upon the bond orientation around phosphorus.[4] In PBu^{t}Cl$_2$ (**3**) at low temperature (-140 °C) the $\{^{1}H\}^{13}$C n.m.r. spectrum shows two different methyl carbon resonances at 24·2 and 21·2 p.p.m. respectively,‡ owing to slow rotation about the P–C bond.[3] The corresponding ^{2}J(PC) coupling constants are quite different: ^{2}J(PC) is 31·5 Hz for Me *gauche* to the phosphorus lone pair (J_g); ^{2}J(PC) is 0 for Me *trans* to the phosphorus lone pair (J_t). At room temperature, $^{2}J(PC) = 21{\cdot}4$ Hz = *ca.* $(2J_g + J_t)/3$.

Assuming that for a similar disposition with respect to the phosphorus lone pair, ^{2}J(PC) is similar in (**2**) and (**3**), the ^{2}J(PC) value measured in (**2**) (J_e) allows the relative population X $[= (J_g - J_e)/(2J_e - J_t - J_g)]$ of conformations (A) and (B) to be determined. The value measured at room temperature (J_e 17·5 Hz) indicates that (A) is the predominant conformation at room temperature (X *ca.* 4). The monotonic slight variation with temperature observed for ^{2}J(PC) (decrease from 17·5 to 14 Hz) and for ^{2}J(PH) (increase from 17·1 to 20 Hz),[5] on recording the ^{13}C and ^{1}H n.m.r. spectra from 40 to -130 °C§ shows that (**2**) is enriched in conformation (A) as the temperature decreases.



On the same basis, comparison of the ^{2}J(PC) values measured for (**1**) at room temperature (13·6 Hz) and for (**3**) at -140 °C, shows that (A) is the preferred conformation of (**1**). The relative population of conformations (A) and (B) $[X = 2(J_g - J_e)/(J_e - J_t)]$ should be 2·6.

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† (**1**) and (**3**) were commercially available (Strem chemicals) while (**2**) was prepared by reduction of the AlCl$_3$–PCl$_3$–Pr^{i}Cl complex in diethyl phthalate by antimony (B. J. Perry, J. B. Reesor, and J. L. Ferron, *Canad. J. Chem.*, 1963, **41**, 2299).

‡ The ^{31}P chemical shifts are given in p.p.m. downfield with respect to external 85% H$_3$PO$_4$. The ^{13}C chemical shifts are given in p.p.m. downfield with respect to internal Me$_4$Si.

§ At low temperature (-140 °C), in the ^{13}C n.m.r. spectrum separate signals for the two conformers of molecule (**1**) have not been observed, as was possible in the ^{31}P spectrum. This is due to the fact that the chemical shift differences expected between the different methyl carbons are smaller than that observed between the two ^{31}P signals (320 Hz). As a consequence hindered rotation would be observed at a lower temperature in the ^{13}C spectrum than in the ^{31}P spectrum.

For comparison it is interesting that in $O{=}PCl_2Et$ the less symmetric conformation ($P{=}O$ and C–Me bonds *gauche* to each other) predominates in the liquid phase. In the solid state, the symmetric form C_s becomes more abundant. In 1,1-dichloro-2-methylpropane, the *gauche* conformation is the more stable.[6]

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