Nuclear Magnetic Resonance Investigation of Diastereoisomerism in the Unsymmetrical Tetra-alkyldiphosphanes $R^1R^2PPMeEt$ (R^1R^2 = Bu^{t}Pr^i, Bu^{t}Et, Bu^{t}Me, Pr^{i}Et, and Pr$^i_2$)

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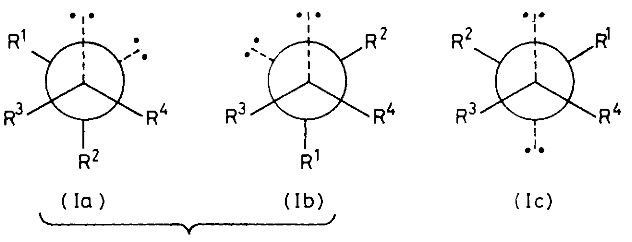
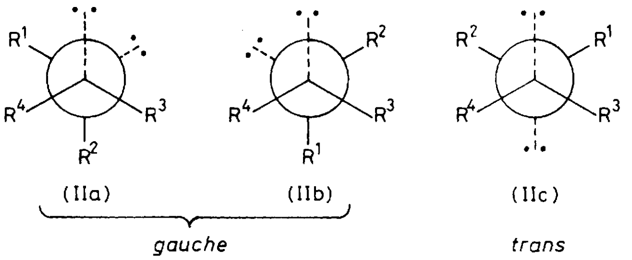
Three new unsymmetrical diphosphanes of type $R^1R^2PPMeEt$ (R^1R^2 = Bu^{t}Pr^i, Bu^{t}Et, Bu^{t}Me, and Pr^{i}Et) and one of type $R_2PPMeEt$ (R = Pr^i) have been prepared by the scrambling reaction between symmetrical diphosphanes in CH_2Cl_2, and characterised *in situ* by ^{31}P n.m.r. spectroscopy. The chemical shifts and $J(PP)$ coupling constants are reported and discussed. The compounds $R^1R^2PPMeEt$ exist in diastereomeric forms, slightly differing in population under the equilibrium conditions employed. They provide clear examples of the variation of n.m.r. parameters with chirality: the more stable form has the lower ^{31}P chemical shift, δ(P), and the larger $|^1J(PP)|$ in each case.

The formation of unsymmetrically substituted diphosphanes by mixing two different symmetric diphosphanes in dichloromethane is well known. McFarlane and McFarlane [1] found that by mixing P_2Me_4 and P_2Ph_4 in CH_2Cl_2 the unsymmetrical diphosphane Me_2PPPh_2 was formed. Harris *et al.*[2] recently reported n.m.r. data for several unsymmetrical diphosphanes obtained by the same mixing procedure. Other reports about unsymmetrical diphosphanes have appeared,[3] but ^{31}P n.m.r. data have been obtained [4-7] for only a few such compounds because of their instability. All the n.m.r. studies reported so far refer to unsymmetrical diphosphanes of formulae $R^1_2PPR^3_2$ or $R^1R^2PPR^3_2$ (R^3 may be the same as R^1 or R^2 for $R^1R^2PPR^3_2$). Compounds of formula $R^1R^2PPR^3R^4$ (but where one of the pair R^1, R^2 may be the same as one of the pair R^3, R^4) have not been investigated previously. This paper reports that a number of unsymmetrical tetra-alkyldiphosphanes of this type may be formed in CH_2Cl_2 by mixing $(EtMeP)_2$ with other diphosphanes $(R^1R^2P)_2$. The ^{31}P n.m.r. spectra of the resultant compounds $R^1R^2PPMeEt$ were obtained and the data are quoted and discussed. Phosphorus-31 n.m.r. data for one other new unsymmetrical tetra-alkyldiphosphane, Pr$^i_2$PPMeEt, are also included herein.

One of the interesting features of the unsymmetrical diphosphanes $R^1R^2PPR^3R^4$ is their possession of two chiral centres (the two phosphorus atoms). In principle, therefore, they can exist in the two stereoisomeric forms (I) and (II) (plus mirror images). For clarity, the structures are drawn here assuming perfectly staggered conformations, although these are unlikely to be realistic.[8,9] Isomers (I) and (II) are not readily interconvertible and should give distinct n.m.r. signals. The proton-decoupled ^{31}P n.m.r. spectrum of a mixture of the two stereoisomers for a given compound should consist of two sets of four lines, *i.e.* two AB patterns. When $R^1 = R^4$ and $R^2 = R^3$ the compound will be of the type $(R^1R^2P)_2$, which exists in the well recognised *racemic* and *meso* forms, corresponding to structures (I) and (II) respectively. Such species have already been reported to give distinct n.m.r. signals.[10,11] Unsymmetrical compounds $R^1R^2PPR^3_2$, on the other hand, have only one chiral centre (the phosphorus atom with the two different alkyl groups), while the other phosphorus atom is prochiral. In such a case, the forms (I) and (II) are identical and give only one set of signals,[2] provided internal rotation about the P–P bond is rapid on the n.m.r. time-scale. However, the two *gauche* conformers are non-equivalent. Structures (I) and (II) are also identical when $R^1 = R^2$ and $R^3 = R^4$, but in this case, the molecule has neither chiral nor prochiral centres, and the two *gauche* conformers are equivalent. In the case of unsymmetrical compounds of type $R^1R^2PPR^3R^1$ (*i.e.* $R^1 \equiv R^4$) isomer (I) may be termed the pseudo-*racemic* form, since like alkyls are *gauche* in the conformer with *trans* lone pairs, while isomer (II) may be referred to as pseudo-*meso*. When there are four different alkyl groups classifications of this sort become meaningless, although distinctions could be made in terms of the relative sizes of the alkyl groups. Clearly, the substituent pattern, as discussed above, should strongly influence the observed n.m.r. spectra, and, conversely, the spectral data should provide evidence for the effects of the substituents on conformation and configuration.



(Ia) (Ib) (Ic)
gauche *trans*
Isomer (I)



(IIa) (IIb) (IIc)
gauche *trans*
Isomer (II)

The present work aimed (*a*) to provide evidence of a wider variety of tetra-alkyldiphosphanes than has been reported to date, (*b*) to investigate the variation of chemical shifts and coupling constants with the nature of the alkyl substituents, and hence (*c*) to obtain evidence regarding both stereoisomerism and conformational preference in these compounds.

Results

Four unsymmetrical tetra-alkyldiphosphanes of formula $R^1R^2PPMeEt$ and one of formula Pr$^i_2$PPMeEt have been studied in CH_2Cl_2 solution. Only the phosphorus-31 n.m.r. spectra (under conditions of proton-noise decoupling) were obtained. These each showed two AB patterns from the two different stereoisomeric forms (I) and (II), as expected. Indeed,

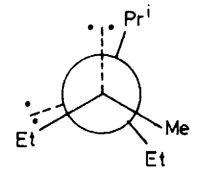
Table. Phosphorus-31 n.m.r. data for the unsymmetric tetra-alkylphosphanes $R^1R^2P_aP_bMeEt$

R^1R^2	θ_c/°C	Isomer[a]	Population ratio[b]	$\lvert {}^1J(P_aP_b)\rvert$/Hz	$\delta(P_a)$/p.p.m.[c]	$\delta(P_b)$/p.p.m.[c]
Bu^{t}Pr^i	36	(I)	lp 1.7	251.2	25.58	−54.20
		(II)	hp	265.0	18.65	−52.64
	−65	(I)	lp 2.0	244.0	21.86	−57.56
		(II)	hp	264.1	13.13	−55.05
Bu^{t}Et	36	(I) pseudo-*rac*	lp 2.2	229.2	10.22	−54.72
		(II) pseudo-*meso*	hp	257.9	0.36	−54.71
	−75	(I) pseudo-*rac*	lp 1.3	234.5	5.03	−57.98
		(II) pseudo-*meso*	hp	265.0	−4.99	−57.16
Bu^{t}Me	−75	(I) pseudo-*rac*	hp 2.2	233.3	−20.05	−58.60
		(II) pseudo-*meso*	lp	196.8	−11.07	−58.15
Pr$^i_2$	36			259.2	3.06	−58.91
	−75			278.0	−4.11	−64.44
Pr^{i}Et	36	(I) pseudo-*rac*	lp 1.5	213.2	−8.58	−52.77
		(II) pseudo-*meso*	hp	226.7	−12.56	−53.91
Et$_2$[d]	−50			204.4	−29.73	−52.30
EtMe[e]	40	*rac*	hp 1.2	[f]	−46.43	
		meso	lp	[f]	−44.59	

[a] See the text for the assumptions on which the stereoisomers are assigned and for the designations of which alkyl groups are labelled R^1, R^2 R^3, and R^4. [b] hp and lp denote the higher and lower population isomers respectively. [c] The chemical shift data are corrected for the minor amount of second-order character shown by the spectra. [d] Data from ref. 2. [e] Data from ref. 10. [f] Not obtained separately, but supposed [10] to be *ca*. 204 Hz.

the form of the spectra provides unequivocal proof for the formation of the unsymmetrical compounds from the scrambling reaction. The populations of the two stereoisomers are unequal in each case, but not dramatically so. The ^{31}P-{^{1}H} spectrum of Bu^{t}Pr^{i}PPMeEt is shown in Figure 1. The phosphorus-31 n.m.r. chemical shifts and J(PP) coupling constants for all the compounds are given in the Table. Assignment of the phosphorus signals to the two stereoisomeric forms (I) and (II) is based on two assumptions. The first is that the molecules exist preferentially in the *gauche* form, although the *trans* conformer cannot be totally excluded, and second, that the stereoisomer which allows the more bulky substituents to be situated *gauche* to the lone pairs is more stable [1] than that with lighter alkyl groups in such positions. (Low-temperature ^{13}C and ^{1}H n.m.r. spectra [12,13] have shown that $P_2Bu^t_4$ is neither *trans* nor symmetrically eclipsed, but *gauche*, although large deviations towards the semi-eclipsed form cannot be excluded.[8])

Of course, for rotamers with *gauche* lone pairs there are three *gauche* interactions between alkyl groups. If the dihedral angles are the same for the two such rotamers of a given stereoisomer, then the only difference in interactions for the rotamers is that between alkyl groups *trans* to the lone pairs, and the most stable conformation is presumably that in which these groups have the smaller bulk (although that may be difficult to decide when comparing, for example, Pr^i–Et and Bu^t–Me interactions). Most conformations can relieve strain by adjustments of the dihedral angle towards the semi-eclipsed form, although the degree of adjustment will depend on the rotamer. In general, the more stable the rotamer, the greater is the optimum adjustment. The semi-eclipsed form for conformation (II) of Pr^{i}EtPPMeEt is shown by (III).



(III)

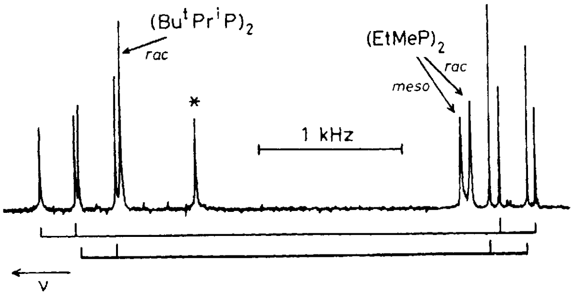


Figure 1. ^{31}P-{^{1}H} n.m.r. spectrum, obtained at 36 °C, just after mixing (Bu^{t}Pr^{i}P)$_2$ and (EtMeP)$_2$ in CH$_2$Cl$_2$. Peaks due to the starting materials are labelled. The peak marked with an asterisk is due to an impurity (see text). The two AB patterns assigned to Bu^{t}Pr^i-PPMeEt are indicated underneath the spectrum

For the compounds Bu^{t}EtPPMeEt, Bu^{t}MePPMeEt, and Pr^{i}EtPPMeEt, we designate the substituents such that the like alkyls are R^1 and R^4. The above assumptions then imply that the pseudo-*racemic* stereoisomer (I) is the more stable for Bu^{t}MePPMeEt [with preferred *gauche* conformer (Ib)] but the pseudo-*meso* form (II) is the more highly populated for Bu^{t}EtPPMeEt and Pr^{i}EtPPMeEt. For Bu^{t}Pr^{i}PPMeEt we designate the groups of similar bulk attached to the different phosphorus atoms as R^1 and R^4 (*i.e.* R^1 = Pr^i, R^4 = Et), and the above assumptions then suggest stereoisomer (II) is more stable than (I), and that (IIb) is the preferred conformer.

On this basis, assignments of the AB spectra to given stereoisomers can be made (as given in the Table), but it must be emphasised that this procedure relies totally on the assumptions given above, which, while reasonable, cannot be unequivocally proved. Caution must also be exercised because none of the population ratios is greater than 2.5.

Discussion

*Phosphorus-*31 *Chemical Shifts.*—The data of the Table enable a number of empirical observations to be made, although detailed interpretation is hindered by the lack of knowledge of molecular geometry (including conformation).

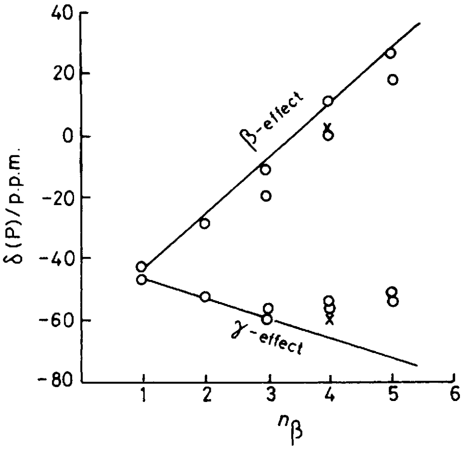


Figure 2. Plot of the ^{31}P chemical shifts for the two phosphorus atoms of tetra-alkyldiphosphanes $R^1R^2PPMeEt$ against the number of β-methyl groups, $n_β$, for the R^1R^2P moiety. The upper line, for P_a, illustrates the β-effect of the methyls for the more stable diastereoisomers whereas the lower line, for P_b, shows the influence of γ-shielding. For clarity the points for $Pr^i_2PPMeEt$ are marked by crosses, and those for $Pr^iEtPPMeEt$ have been omitted

First, substituent bulk clearly substantially increases the chemical shift, δ(P), of the neighbouring phosphorus nucleus. This influence can be described in terms of the number of methyl groups β to the designated phosphorus, and Figure 2 shows there is a roughly linear correlation between δ(P) and $n_β$. Such an effect has been noted before for diphosphanes [10,11] (and, earlier, for phosphanes [14–17]) and may be attributable [18] to changes in the valence angles, CPC. Payne and Stephen [19] have described the situation for monophosphanes accurately using a second-order pairwise additivity scheme for the effects of the substituents. Secondly, increasing substituent bulk causes *shielding* at the remote phosphorus. This is also shown in Figure 2. The methyl groups are now in the γ position with respect to the relevant phosphorus, so this is an example of the well known γ-shielding phenomenon observed for a number of nuclei and first noted by Grant and Paul [20] for ^{13}C. However, Figure 2 shows deviations from linearity of the γ-effect with the bulkiest substituents. Such deviations were noted earlier [11] for the combined β- and γ-effects, and attributed to geometric distortions. The present work allows separate evaluation of the β and γ influences, and shows no discernible deviations for the β-effect, suggesting that the distortions in question relate to dihedral angles rather than valence angles.

General observations can also be made regarding the shift differences between a given pair of stereoisomers. In fact, the stable form always has the lower value of δ(P) for P_a (see Table), as has been previously shown [10,11] to be true for diphosphanes of formula $(R^1R^2P)_2$ for which the *racemic* form is likely to be the stable one. Moreover, for the present systems, of type $R^1R^2P_aP_bMeEt$, the shift difference for P_a between stereoisomers increases as the difference in bulk between R^1 and R^2 increases, although $Bu^tMePPMeEt$ appears anomalous in this respect. Precise comparisons are difficult to achieve because of the temperature dependence of δ(P), which is considerable; previous work [11] has shown remarkable variations in the temperature coefficient of δ(P) between different tetra-alkyldiphosphanes. The limited amount of variable-temperature data for the compounds considered here shows the greatest change (for both phosphorus nuclei) for $Pr^i_2PPMeEt$, which is consistent with the large variation found previously for $P_2Pr^i_4$. No generalisations can be made for the difference between stereoisomers of the chemical shift for P_b. This is, as expected, smaller in magnitude than that for P_a, and ranges from 2.51 to −1.84 p.p.m. (subtracting the shift for the less populated isomer from that of the preferred form). Our tentative conclusion is that since the effects at P_a and P_b differ markedly, population differences between rotamers do not play the dominant role in causing the shift differences between stereoisomers, but that differences in dihedral and/or CPC angles may play a vital role.

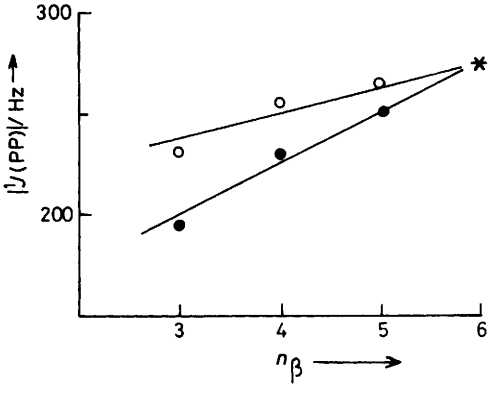


Figure 3. Plot of $|^1J(PP)|$ for the two stereoisomeric forms of the tetra-alkyldiphosphanes $Bu^tRPPMeEt$ against $n_β$, the number of β-methyl groups of the Bu^tRP moiety. The open circles correspond to the more stable stereoisomeric forms, whereas the filled circles are for the less stable forms. The asterisk indicates the projected value for $Bu^t_2PPMeEt$, which is thought to be too low (see text)

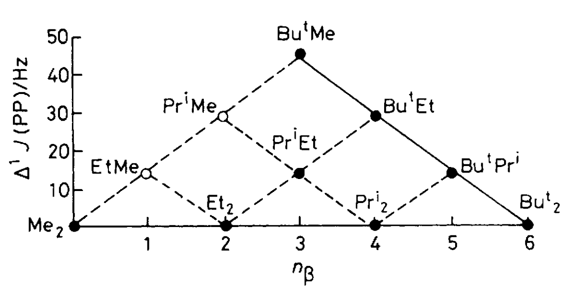


Figure 4. Plot of $|\Delta^1J(PP)|$, the difference in $^1J(PP)$ for the two diastereomeric forms of tetra-alkyldiphosphanes of general formula $R^1R^2PPMeEt$, against $n_β$, the number of β-methyl groups in the R^1R^2P moiety. The open circles indicate projected values rather than observed results

Phosphorus–Phosphorus Coupling Constants and Conformational Considerations.—The values of $|^1J(PP)|$ for $R^1R^2PPMeEt$ (Table) show an increasing trend as the bulk of the substituents R^1 and R^2 increases. This trend is readily apparent if, when $R^1 \neq R^2$, the average values of $|^1J(PP)|$ for the two stereoisomers of a given compound are considered, although the temperature dependence of the coupling constants complicates matters. Such a trend has been reported earlier for other diphosphanes.[2,10,11] If the $|^1J(PP)|$ data for $Bu^tRPPMeEt$ are extrapolated to predict the value for $Bu^t_2PPMeEt$, the figure of *ca*. 285 Hz is obtained whereas for $Bu^t_2PPMe_2$ the value is 320 Hz [2] (and would be expected to be higher for $Bu^t_2PPMeEt$). This result is consistent with previous data,[2] which have shown that the presence of a pair of bulky groups bonded to a given phosphorus raises $|^1J(PP)|$ considerably. Presumably this is a reflection of CPC angle changes and/or variations in conformer populations and/or changes in dihedral angles.

When values for diastereoisomers are compared, it is found that $|^1J(PP)|$ for the more stable form is consistently higher than for the less stable form by substantial amounts (up to 36.5 Hz). Again, this is consistent with earlier data [10,11] on compounds of the type $(R^1R^2P)_2$. The difference in $|^1J(PP)|$ between diastereoisomers for $R^1R^2PPMeEt$ increases as R^1 and R^2 become more different, as is shown in Figure 3. This is as expected since conformer populations will be most heavily biased when R^1 and R^2 differ most. The data are plotted another way in Figure 4, which allows diastereomeric differences in ^1J(PP) to be predicted for, as yet, unmeasured compounds. In the case of $(EtMeP)_2$ a difference Δ^1J(PP) of 15 Hz is suggested whereas no such difference could be observed in earlier work,[10] although this is probably due to errors inherent in the type of spectral analysis involved. A difference of 19 Hz has been reported [21] for $(PhMeP)_2[|^1J(PP)| = 215 \pm 2$ and 234 ± 2 Hz]. The values were not assigned individually to the *racemic* and *meso* forms of this molecule. The diphosphane $(PhHP)_2$, on the other hand, does not show [22] any difference in ^1J(PP) between the two diastereoisomers. Recently, a ^1J(PP) difference of 48 Hz has been found [23] for the *racemic* and *meso* isomers of $[(CF_3)HP]_2$; the authors attributed this relatively large difference to a variation in the lone-pair orientation in the two forms. They proposed that the *racemic* isomer favours a *gauche* rotamer in which the two bulky electronegative groups are *gauche* to the lone pairs. This is the most stable form since the rotamer fulfils the factors which are known to stabilize a conformer, such as a *gauche* relationship of the lone pairs, a *trans* relationship of the bulky electronegative group (CF_3), and the maximum number of *gauche* interactions between the lone pairs and the polar bonds. At high temperatures, where the population of the *gauche* rotamer is expected to decrease, the value of ^1J(PP) becomes more negative On the other hand, the magnitude of ^1J(PP) for the *meso* form decreases (becomes less negative), which was explained on the basis of the preference of the electronegative group (CF_3) to adopt the *trans* disposition. This leads to the conclusion that the *meso* isomer favours the *trans* conformation in contrast to the *racemic* isomers. Accordingly it seems that the electronegativity of the substituents is the predominant factor.

In the case of tetra-alkyldiphosphanes, the electronegativity of the substituents varies very little. Presumably the factors that would affect the stability of the conformers are the orientation of the lone pairs and the bulk of the substituents. In our case, decreasing the temperature does not have a consistent effect. It results in an increase in the magnitude of ^1J(PP) for both isomers of $Bu^tEtPPMeEt$ but a decrease for the two isomers of $Bu^tPr^iPPMeEt$. This may indicate that both isomers of each compound favour a similar conformation and most likely exist in the *gauche* form. The magnitudes of ^1J(PP) for P_2Me_4 and $P_2Bu^t_4$ are found to decrease [11] at low temperature, which is in the same direction of change observed for $Bu^tPr^iPPMeEt$ but opposite to that observed for $Bu^tEtPPMeEt$ (Table). The magnitudes of ^1J(PP) for $Me_2PPBu^t_2$ and Et_2PPPh_2 are reported [2] to increase at low temperature. Low-temperature ^{13}C and ^1H n.m.r. studies [12,13] on $P_2Bu^t_4$ showed that it exists entirely in the *gauche* form. It may be expected, therefore, that the population of the *gauche* conformer will increase at low temperature. However, Raman studies [24] on P_2Me_4 showed that it exists in both *gauche* and *trans* forms in a ratio *ca.* 3 : 2 in the liquid state but entirely in the *trans* form in the solid state. Theoretical work on P_2H_4 carried out by Cowley *et al.*[25] and Albrand *et al.*[26] implied a more negative ^1J(PP) for the *gauche* form. Similar calculations [27] performed on P_2Me_4 also showed a more negative ^1J(PP) for the *gauche* form of this molecule. It should be noted, however, that McFarlane and McFarlane [4] proposed the more negative value of ^1J(PP) for the *trans* conformer, which agrees with the Raman studies but is opposite to the theoretical calculation. It is clear from the low-temperature work on $Bu^tPr^iPPMeEt$ and $Bu^tEtPPMeEt$ that there must be influences other than simple changes in rotamer population dominating the variation of ^1J(PP) with temperature. The temperature may, for instance, cause changes in the geometrical parameters and/or in solvent effects.

The SCF molecular orbital calculations [25-27] of J(PP) show a very strong dependence on dihedral angle, with large negative values for *gauche* conformers and moderate positive values for *trans* forms. The semi-eclipsed form is suggested to have near-zero J(PP). We believe these calculations can be reconciled with our results, although at first sight this is difficult since our discussion above implies the more stable diastereoisomers should have conformations nearer to the eclipsed form than the less stable ones [and hence *lower* values of $|J(PP)|$]. However, steric interactions in *trans* conformations can be seen to be invariably less for the diastereoisomer judged to be less stable overall. We propose, therefore, that the less stable diastereoisomers have significantly larger populations in the *trans* form than their more stable counterparts. This is, in effect, an extension of the principle of Albrand *et al.*[23] to situations with no electronegative substituents, and the dependence of J(PP) on dihedral angle then suffices to explain the differences in J(PP) between diastereoisomers. The marked increase of $|J(PP)|$ with substituent bulk may also reflect decreases in the amount of *trans* conformers (as suggested by comparisons [12,24] between P_2Me_4 and $P_2Bu^t_4$). However, expected changes in dihedral angle towards the semi-eclipsed form would act in the opposite direction, so presumably changes in CPC are also important and result in increases in $|J(PP)|$ with substituent bulk. This last mentioned conclusion is, perhaps reinforced by the anomalously high values of $|J(PP)|$, referred to above, when the most bulky substituents are involved.

For $Pr^i_2PPMeEt$, the value of J(PP) lies close to the line shown in Figure 3 for the more stable forms of $R^1R^2PPMeEt$. This also appears to be true for $Et_2PPMeEt$, although the situation is less clear in this case. These facts suggest that compounds of the type $R_2PPMeEt$ may have approximately the same proportion of *gauche* (or semi-eclipsed) rotamers as those of the more stable diastereoisomers $R^1R^2PPMeEt$, and that there is only a tendency to adopt *trans* conformations when this gives a significant easing of alkyl–alkyl repulsions compared to the adoption of the optimum dihedral angle (towards semi-eclipsing) in the '*gauche*' form. When only small alkyl groups are involved, as for P_2Me_4, the conformational balance is presumably more delicately maintained, resulting in the existence [24] of a mixture of *gauche* and *trans* forms.

Stereoisomer Populations.—As is shown in the Table, the populations of the stereoisomers are comparable in all cases. This is in marked contrast [11] to the case for compounds of type $(Bu^tRP)_2$, for which only the *racemic* forms can be observed. It appears, then, that steric effects do not lead to marked destabilisation unless there is at least one Bu^t group on each phosphorus. Since $P_2Bu^t_4$ itself has been prepared, the isomeric imbalance for $(Bu^tRP)_2$ is clearly a result of lability such as is present in the CH_2Cl_2 solutions of mixed diphosphanes, which allows thermodynamic control to be established between the diastereoisomers. The lack of population imbalance in the compounds studied here throws into doubt any explanations of variations in chemical shifts or coupling constants which rely on the existence of severe strain in the molecules.

Experimental

All samples were prepared in 12-mm o.d. n.m.r. tubes in a dry-box under nitrogen gas, then degassed by the freeze-pump-thaw technique and sealed. The solvent CH_2Cl_2 used was kept over molecular sieve for a long period (at least three months) before use. Perdeuteriobenzene was used to provide a ^2H field-frequency lock. The total concentration of tetra-alkyldiphosphanes was very roughly 40% by volume, with the two components in approximately equal amounts.

In the case of the two diphosphanes $P_2Pr^i_4$ and $(Bu^tMeP)_2$, each was first mixed with $(EtMeP)_2$ in a 12-mm n.m.r. tube, together with a small amount of C_6D_6 at ambient temperature. This mixture was frozen using liquid nitrogen, after which CH_2Cl_2 was transferred to the sample under vacuum and the tube was sealed. For these mixtures, the temperature of the sample was not allowed to rise substantially above that where total melting occurred. The sample tube in question was then placed as soon as possible in the probe, which was preset at low temperature. The ^{31}P-{^1H} spectra were recorded first at low temperature and then, for the $P_2Pr^i_4$–$(EtMeP)_2$ sample only, at ambient probe temperature.

The procedure for the other tetra-alkyldiphosphanes $(Pr^iEtP)_2$, $(Bu^tEtP)_2$, and $(Bu^tPr^iP)_2$, however, was as follows. The mixing with $(EtMeP)_2$ and C_6D_6 was carried out as above and then the CH_2Cl_2 was added (in the dry-box) at ambient temperature, after which the samples were degassed and sealed. The ^{31}P-{^1H} n.m.r. spectra were recorded at 36 °C as soon as possible after mixing and then at lower temperature subsequently.

The spectra was obtained at 40.5 MHz using a Varian XL100 spectrometer in the Fourier-transform mode, with spectral widths of 10 kHz and acquisition times of 0.4 s (or 5 kHz and 0.8 s respectively). The pulse duration corresponded to a flip angle of *ca.* 90°. Reasonable spectra were obtained with about 1 000 transients, although low-temperature spectra with good signal-to-noise ratios were achieved with only *ca.* 100 pulses. The sample temperatures were estimated using a thermometer inserted in an n.m.r. tube containing methanol, and are accurate to *ca.* ± 2 °C. The chemical shifts were measured by the method of Harris and Kimber,[28] using Ξ $(H_3PO_4) = 40\,480\,720$ Hz for consistency.[11]

The solutions in CH_2Cl_2 are not stable but decompose over a period of days. Moreover, in the preparation stages, certain impurities are formed, for example the peak denoted by an asterisk in Figure 1. The proton-coupled ^{31}P spectrum shows that this peak is due to a monophosphane and we believe [27] it arises from the more reactive of the two symmetric diphosphanes used, *i.e.* it is PMeEtH. Use of CD_2Cl_2 suggests the additional hydrogen does *not* come from the solvent. An impurity that appears later is identified [27] as a chlorophosphane arising from the other component diphosphane, *i.e.* PBu^tPr^iCl in the case of Figure 1.

Conclusions

Phosphorus-31 n.m.r. has provided unequivocal evidence for the existence in solution in CH_2Cl_2 of a number of new unsymmetrical tetra-alkyldiphosphanes as a result of scrambling reactions between symmetrical species. Several of the new species exhibit diastereoisomerism, and tentative assignments of configuration are given. The ^{31}P chemical shifts and J(PP) coupling constants show clear trends with the nature of the substituents, and the influence of β- and γ-methyl groups on δ(P) have been separated. The role of conformation is, however, difficult to evaluate for δ(P), but the data on J(PP) have been rationalised on the basis that the less stable diastereoisomers have a higher tendency partially to adopt the *trans* rotameric form than their more stable counterparts.

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