The Reaction of Diols with Triphenylphosphine and Di-isopropyl Azodicarboxylate. Part 2.[1] Formation of Cyclic Phosphoranes from 1,5—1,12-Diols

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Triphenylphosphine and di-isopropyl azodicarboxylate react with pentane-1,5-diol, hexane-1,6-diol, heptane-1,7-diol, octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol in tetrahydrofuran at 0 °C to give large-ring cyclic dioxytriphenylphosphoranes that appear to be oligomeric. Such phosphoranes undergo exchange reactions with each other to give mixed species. A conformationally restricted diol derived from sucrose affords an eight-membered cyclic dioxytriphenylphosphorane. ^{31}P And ^{13}C n.m.r. data for these phosphoranes are reported.

We recently described[1] a simple, mild procedure for the preparation of six- and seven-membered cyclic dioxytriphenyl-phosphoranes from triphenylphosphine (TPP) and 1,3- or 1,4-diols respectively. Cyclic phosphoranes containing four- and five-membered rings are well known,[2–4] however very little work has been done on the synthesis of larger ring cyclic phosphoranes, especially those containing more than one phenyl group attached to phosphorus. This paper describes our attempts to prepare larger (> seven-membered) cyclic dioxy-triphenylphosphoranes.

Results and Discussion

Treatment of TPP (1 mmol) in tetrahydrofuran (THF; 2 ml) at 0 °C with di-isopropyl azodicarboxylate (DIAD) (1 mmol) under nitrogen, followed by addition of pentane-1,5-diol (0.5 mmol) resulted in the immediate appearance of a single sharp peak (δ_P −55.9 p.p.m.) in the phosphorane region of the ^{31}P n.m.r. spectrum (there was also a minor peak at *ca.* δ_P +25 p.p.m. corresponding to triphenylphosphine oxide as described previously[1]). Examination of the ^{13}C n.m.r. spectrum of the same sample revealed a sharp doublet (δ_C 138.9, J 175 Hz) well downfield of the normal aromatic region of the spectrum. This doublet corresponds[1] to the one-bond coupling from phosphorus to the quaternary carbon atoms of the directly bonded phenyl groups.

Analogous ^{31}P and ^{13}C n.m.r. data were obtained with α,ω-diols up to dodecane-1,12-diol and these results are summarised in Table 1. The data for propane-1,3-diol and butane-1,4-diol[1] are included for comparison. It can be seen that the ^{31}P n.m.r. chemical shifts approach a limiting value of δ_P −55.6 p.p.m. for octane-1,8- and larger diols. This is consistent with values obtained[5] for dialkoxytriphenylphosphoranes of the type $Ph_3P(OR)_2$ (*e.g.* for R = pentyl,[6] hexyl and octyl, δ_P = −55.6 p.p.m.).

We have shown previously[1] that dialkoxytriphenylphosphoranes bearing an equatorial phenyl group [*i.e.* phosphoranes of the type (1)] exhibit much smaller one-bond coupling constants −($^1J_{P-C}$ *ca.* 120 Hz) than those [such as (2)] containing only equatorial groups ($^1J_{P-C}$ > 170 Hz). From Table 1, it is clear that all of the phosphoranes formed from α,ω-diols exhibit $^1J_{P-C}$ values typical of phosphoranes in which all three phenyl groups are equatorial, *i.e.* phosphoranes of the type (2) where the apical positions are occupied by oxygen atoms. It was also shown previously[1] that such phosphoranes could not be of the type (3).†

From a study of molecular models, it is impossible for a 1,3- or 1,4-diol to span both apical positions. For a 1,5-diol, a phosphorane of the type (2) is possible but it would involve

Table 1. ^{31}P And ^{13}C n.m.r. data (THF; 10 °C) for phosphoranes (5) formed from α,ω-diols

n	δ_P	$\delta_C{}^a$	$^1J_{P-C}$ (Hz)^a
3	−55.6	139.6	174
4	−56.0	139.6	173
5	−55.9	138.9	175
6	−55.8	139.9	175
7	−55.7	139.9	175
8	−55.6	139.9	175
10	−55.6	139.9	174
12	−55.6	139.9	174

^{a} For carbon bonded to phosphorus.

(1) (2) (3)
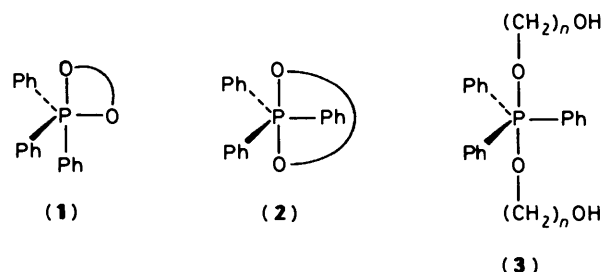
considerable ring strain, and more importantly extreme steric congestion of the methylene chain between two of the phenyl rings. The latter feature would almost certainly result in non-equivalent phenyl groups and no evidence (^{13}C or ^{1}H n.m.r.) was obtained for this. With pentane-1,5-diol, even a dimeric structure (4) is very congested. Similar steric congestion is

(4)
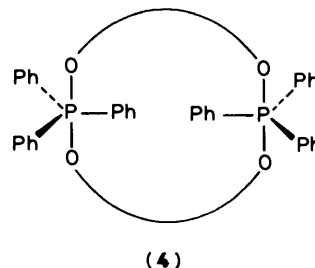
† Acyclic phosphoranes of this type can be prepared, however, using an excess of the diol.[1] In the case of propane-1,3- and butane-1,4-diols, these phosphoranes (3, n = 3,4 respectively) exhibit ^{31}P and ^{13}C n.m.r. chemical shifts that are different from those shown in Table 1.
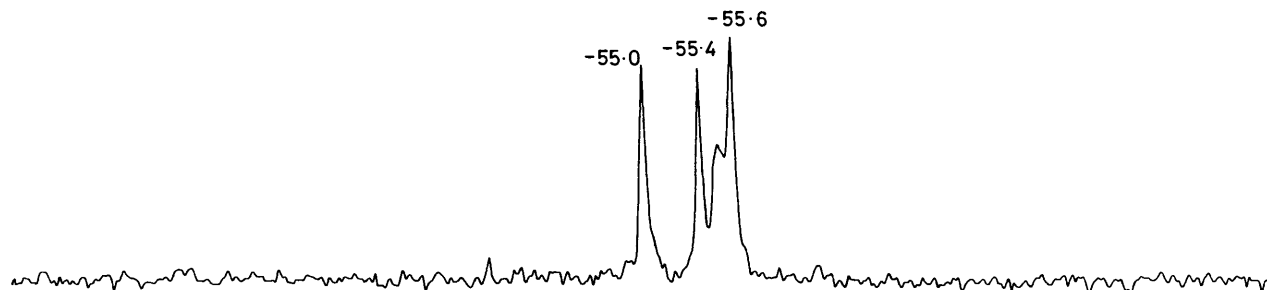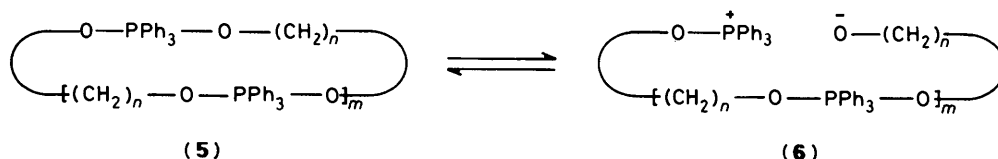
Figure 1. ^{31}P N.m.r. spectrum of phosphoranes formed from the slow addition of decane-1,10-diol (2 mg in 0.5 ml THF) to TPP (13 mg) and DIAD (10 μl) in THF (1.5 ml) at 0 °C

(5)   **(6)**

evident for all phosphoranes of the type (2) that could be formed from α,ω-diols up to at least dodecane-1,12-diol. We suggest therefore, that the phosphoranes formed from pentane-1,5-diol through to dodecane-1,12-diol, are oligomeric (5, $m \geqslant 2$) by analogy with the phosphoranes formed from propane-1,3- and butane-1,4-diols.[1] Evidence in support of an oligomeric (or polymeric) structure was obtained from studies employing high-dilution techniques. Thus, the slow addition of a dilute solution of pentane-1,5-diol (2 μl, 0.02 mmol) in THF (1.0 ml) to a solution of TPP (0.05 mmol) and DIAD (0.05 mmol) in THF (1.0 ml) at 0 °C under nitrogen, resulted in a slight broadening of the δ_P −55.9 p.p.m. peak and the appearance of two new phosphorane peaks (δ_P −55.6, −55.8 p.p.m.) which together accounted for ca. 30% of the phosphoranes formed. Similar results were obtained with the other α,ω-diols and these results are summarised in Table 2. It can be seen that in all cases, the use of high-dilution techniques results in the appearance of new phosphorane peaks. A typical spectrum is shown in Figure 1. The formation of multiple phosphorane peaks is difficult to explain if the original phosphoranes (Table 1) are monomeric or even dimeric. We conclude therefore, that the phosphoranes formed under 'normal' conditions from TPP, DIAD and α,ω-diols, are probably mixtures of large-ring cyclic oligomers (5), in which the apical positions are all occupied by oxygen atoms. The use of high-dilution conditions however, would be expected to lead to the formation of at least some monomeric phosphoranes of the type (1) as shown previously[1] for propane-1,3- and butane-1,4-diols. Dimers, trimers, etc. could also be formed. We have attempted to obtain ^{13}C n.m.r. evidence for the formation of monomeric phosphoranes of type (1) from some of the higher α,ω-diols (in particular decane-1,10-diol) but unfortunately the high-dilution conditions necessary for their formation resulted in solutions that were too dilute to give any detectable ^{13}C n.m.r. signals for the ipso carbon atoms (the instability of these phosphoranes also restricted data collection to a period of about 2 h). Although we have no firm evidence for the formation of monomeric species (1) except in the case of 1,3- and 1,4-diols,[1] it seems very reasonable that if high-dilution conditions result in exclusive (cyclic) monomer formation with propane-1,3-diol and predominant (70%) monomer formation with butane-1,4-diol, then the higher α,ω-diols should also result in the formation of some cyclic phosphoranes of type (1), though possibly in somewhat lesser amount than that observed for butane-1,4-diol.

An interesting feature of the results shown in Table 2 is that

Table 2. ^{31}P N.m.r. data (THF; 10 °C) for dioxytriphenylphosphoranes formed from diols HO(CH$_2$)$_n$OH under conditions of high-dilution

n	δ_P	Relative amounts (ca. %)
3	−54.9	100
4	−46.9	70
	−55.55	4
	−55.6	4
	−55.8	7
	−56.0	15
5	−55.6	15
	−55.8	15
	−56.9	70
6	−55.7	25
	−55.8	65
	−56.1	10
7	−55.3	20
	−55.5	20
	−55.7	60
8	−55.3	15
	−55.5	15
	−55.6	70
10[a]	−55.0	30
	−55.4	30
	−55.5	(Broad hump)
	−55.6	40
12	−55.0	30
	−55.5	25
	−55.55	(Shoulder)
	−55.6	45

[a] See Figure 1.

most of the diols studied give rise to two smaller phosphorane peaks of roughly equal intensity. It is tempting to speculate that both of these peaks are due to a monomeric phosphorane of type (1) which might exist in two conformations that interconvert only slowly on the n.m.r. time scale. An analogous effect has already been described.[7] Thus, one interpretation of Figure 1 is that the peaks at δ_P −55.0 and −55.4 p.p.m. are due to two conformational isomers of a (monomeric) cyclic phosphorane of type (1), the broad hump is due to dimers, trimers etc, and the peak at δ_P −55.6 p.p.m. is due to a mixture of cyclic oligomers.

Further evidence in support of an oligomeric structure for the phosphoranes in Table 1 is obtained by using a mixture of diols.
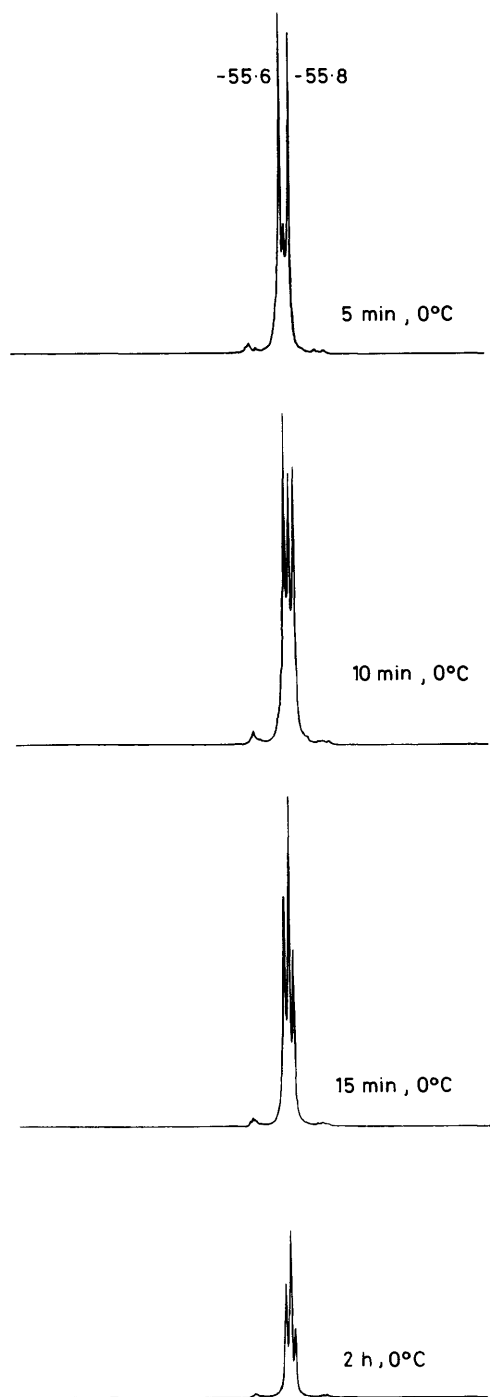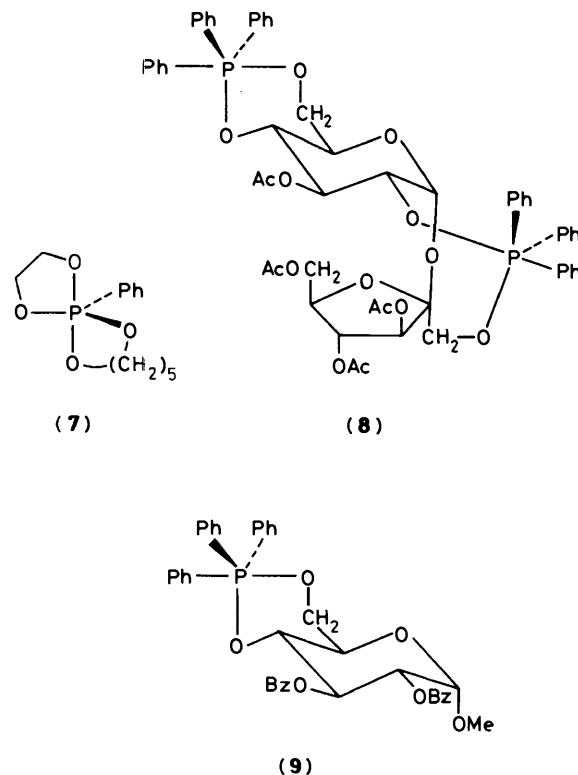
Figure 2. Result of mixing the dioxytriphenylphosphoranes derived from hexane-1,6-diol (δ_P -55.8 p.p.m.) and dodecane-1,12-diol (δ_P -55.6 p.p.m.)

Clearly, these (oligomeric) phosphoranes (5) formed from α,ω-diols are equilibrium mixtures with equilibration occurring presumably *via* the ring-opened oxyphosphonium species (6). We have no way of knowing just how large these oligomeric (or polymeric) species (5) are at the present time, but in view of the equilibration observed above, it seems reasonable to assume that they are mixtures where *m* has a range of values. Isolation of the phosphoranes (5) was not attempted due to their extreme sensitivity to moisture and to their rapid thermal decomposition at room temperature. Even at 0 °C there is substantial decomposition after 2 h as illustrated in Figure 2 (a corresponding increase in the triphenylphosphine oxide peak was observed as the phosphorane peaks decreased).

It is clear that the formation of large ($\geqslant$ seven-membered) cyclic dioxytriphenylphosphoranes of the type (1) from simple α,ω-diols is quite difficult, even under high-dilution conditions where the formation of such species should be kinetically favoured. The preferential formation of oligomeric species (5) is possibly a consequence of the desire to have both oxygen atoms in apical positions.[8] An example of the formation of an eight-membered-ring phosphorane (7) from pentane-1,5-diol has been reported,[7] but in this particular case, the diol must span an apical and an equatorial position and the formation of a phosphorane analogous to (5) is not possible. It is interesting to note that (7) exhibited two [31]P n.m.r. resonances which were attributed to two equilibrating conformers.

(7)

(8)

(9)

If the phosphoranes are monomeric, then using a mixture of two diols should give rise to only two phosphorane peaks in the [31]P n.m.r. spectrum. Conversely, if they are oligomeric ($m \geqslant 2$), then three peaks should be observed. Use of an equimolar mixture of hexane-1,6- and dodecane-1,12-diols gave rise to *three* phosphorane peaks (δ_P -55.6, -55.7, -55.8 p.p.m.) in the approximate ratio 1:2:1 respectively. Interestingly, if the phosphoranes from the two diols were prepared separately and then mixed, the peak corresponding to the 'mixed' phosphorane (δ_P -55.7) slowly appeared and gradually increased to a maximum over a period of about 15 min at 0 °C (Figure 2).

We have shown previously[1] that more highly substituted and conformationally restricted diols favour the formation of phosphoranes of type (1). The bis-diol derivative 3,3',4',6'-tetra-*O*-acetylsucrose provides an example of a conformationally restricted 1,5-diol (*cf.* the 2- and 1'-hydroxy groups) as well as a 1,3-diol. Treatment of TPP, (1 mmol) and DIAD (1 mmol) with this bis-diol derivative (0.5 mmol) in THF (2 ml) at 0 °C under nitrogen resulted in the formation of two sharp peaks (δ_P -50.4, -51.7 p.p.m.) in the [31]P n.m.r. spectrum. Examination of the [13]C n.m.r. spectrum revealed two sharp doublets (δ_C 146.3, *J* 122 Hz and 146.9, *J* 123 Hz) corresponding to the *ipso* carbon

atoms of the respective phosphoranes. The high-field [31]P n.m.r. signal has been assigned to the six-membered cyclic phosphorane in (8) by analogy with the phosphorane (9) (δ_P −51.7 p.p.m.; δ_C 145.7, J 123 Hz) described previously[1] while the low-field peak (δ_P −50.4 p.p.m.) has been assigned to the eight-membered-ring phosphorane in (8). The constraints imposed by the sucrose molecule preclude a diapical arrangement and the small $^1J_{P-C}$ values confirm an apical-equatorial disposition of oxygen atoms for both phosphoranes in (8). To our knowledge, this is the first reported example of a dioxytriphenylphosphorane containing an eight-membered ring. There has been one report[9] of the preparation of larger (i.e. > eight-membered) ring pentaoxyphosphoranes, but as in the case of (7), a bridging ligand was employed so that formation of phosphoranes analogous to (5) was not possible.

Conclusions

The simple, mild procedure developed for the preparation of dialkoxytriphenylphosphoranes[5] and of six- and seven-membered cyclic dioxytriphenylphosphoranes[1] leads mainly to the formation of large, cyclic oligomeric species with the larger (1,5- to 1,12-) α,ω-diols. Such species contain oxygen atoms in both apical positions. They undergo equilibration (i.e diol exchange) when mixed with like phosphoranes. This equilibration can be readily followed by [31]P n.m.r. spectroscopy. A conformationally restricted 1,5-diol resulted in the formation of an eight-membered cyclic (monomeric) dioxytriphenylphosphorane. We are currently investigating the use of such large-ring cyclic phosphoranes in synthesis.[10,11]

Experimental

[31]P And [13]C n.m.r. spectra were recorded as described previously.[1] The general procedure for the preparation of phosphoranes and the 'high-dilution' technique were also described previously.[1] The α,ω-diols used were commercial samples and were not further purified.

3,3′,4′,6′-Tetra-O-acetylsucrose.—This compound was prepared according to the literature procedure,[12] m.p. 121—122 °C (lit.,[12] 121—123 °C).

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