The Reaction of Diols with Triphenylphosphine and Di-isopropyl Azodicarboxylate. Part 1. Formation of Cyclic Phosphoranes from 1,3- and 1,4-Diols

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Triphenylphosphine and di-isopropyl azodicarboxylate react with propane-1,3-diol and butane-1,4-diol in tetrahydrofuran at 0 °C to give cyclic dioxytriphenylphosphoranes that appear to be oligomeric. Under conditions of high-dilution, however, the expected six- and seven-membered-ring phosphoranes are formed. Contrary to a previous report, propane-1,3-diol does not undergo cyclodehydration to give oxetane, but gives instead a pyrazolidine derivative. Substituted, and conformationally restricted, 1,3- and 1,4-diols form the expected six- and seven-membered-ring cyclic phosphoranes without recourse to high-dilution techniques. A ^{13}C n.m.r. method for distinguishing apical from equatorial phenyl groups in phosphoranes is reported: dialkoxytriphenylphosphoranes bearing an apical phenyl group exhibit much smaller one-bond coupling constants ($^1J_{P-C} \sim 120$ Hz) than those containing only equatorial phenyl groups ($^1J_{P-C} > 170$ Hz).

The chemistry of pentaco-ordinate phosphorus compounds has received an increasing amount of attention in recent years and much of the impetus has come from the realisation that a thorough understanding of the factors affecting the stability and chemistry of phosphoranes is vital to an understanding of displacement reactions at tetraco-ordinate phosphorus.[1] Phosphoranes have been implicated as transition states in numerous reactions,[2] including biological processes such as the action of ribonuclease on its substrate.[3] The number of methods available for the synthesis of phosphoranes is, however, quite limited.[1]

Recent work from this laboratory[4,5] and others[6] has shown that dialkoxytriphenylphosphoranes and diaryloxytriphenyl-phosphoranes can be readily prepared from triphenylphosphine (TPP), dialkyl azodicarboxylates,† and alcohols or phenols respectively. The method is convenient, mild, and appears to be general for primary and secondary alcohols, but fails with tertiary alcohols.[4a] We thought it would be of interest to explore this reaction with a range of diols, for although cyclic phosphoranes containing four- and five-membered rings are well known[1,7,8] almost no work has been done on larger-ring cyclic phosphoranes, especially those containing more than one phenyl group attached to phosphorus. A cyclic phosphorane, Ph_3PO_2, containing a three-membered ring was reported recently[9] as a likely intermediate in a novel phosphorus $\longrightarrow$ oxygen phenyl-migration reaction.

Results and Discussion
The method was tried out initially with ethylene glycol, as the expected phosphorane (11) is a known compound, having been prepared previously[10] by an exchange reaction between diethoxytriphenylphosphorane and ethylene glycol.

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 ethylene glycol (1

mmol), resulted in the immediate appearance of a single sharp peak (δ_P −36.2 p.p.m.) in the phosphorane region of the ^{31}P n.m.r. spectrum (there was also a minor peak at approximately δ_P +25 p.p.m. corresponding to triphenylphosphine oxide as described previously[4a]). Identical results were obtained by treatment of diethoxytriphenylphosphorane[4a] with ethylene glycol. The reported chemical shift (−35 p.p.m. in dichloromethane)[10] for (11) is consistent with an expected small solvent effect.[4a]

Treatment of TPP and DIAD with propane-1,3-diol under the same conditions resulted in the immediate appearance of *three* sharp peaks (δ_P −54.9, −55.2, and −55.6 p.p.m., relative proportions ∼ 5:6:15 respectively) in the phosphorane region of the ^{31}P n.m.r. spectrum. Analogous results were obtained in benzene, dichloromethane, and chloroform. Use of di-t-butyl azodicarboxylate instead of the di-isopropyl ester resulted in identical ^{31}P n.m.r. chemical shifts though a small change in the proportions (to 6:6:15 respectively) of the three peaks was noted. None of the three phosphoranes was particularly stable, but the highest-field (δ_P −55.6 p.p.m.) phosphorane was the least stable of the three. For example, on warming the sample to 40 °C for 15 min, the proportions of the three respective signals (relative to an internal standard of TPP) changed to 3:3:3 while the triphenylphosphine oxide peak increased in intensity correspondingly. At lower temperatures there was no evidence for any net interconversion between the three phosphoranes. Thus, after 3 h at 10 °C, the highest-field absorption had decreased considerably and was accompanied by the expected increase in the triphenylphosphine oxide peak, but the two lower-field peaks were virtually unchanged. The rate of decomposition of the three phosphoranes was solvent dependent, being much faster in chloroform than in THF. For example, after 1 h at room temperature in chloroform, the three phosphorane peaks had virtually disappeared while the triphenylphosphine oxide peak had increased correspondingly. Solvent-dependent stability of phosphoranes has been noted previously.[4a]

The proportions of the three phosphorane peaks changed substantially if the order of mixing was reversed. Thus, addition of DIAD to a mixture of propane-1,3-diol and TPP in THF

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† The use of diethyl azodicarboxylate in the synthesis of spiro-phosphoranes from cyclic phosphites has also been reported: J. P. Majoral, F. Kramer, T. N'gando M'pondo, and J. Navech, *Tetrahedron Lett.*, 1980, **21**, 1307; H. Goncalves, J. R. Dormoy, Y. Chapleur, B. Castro, H. Fauduet, and R. Burgada, *Phosphorus Sulfur*, 1980, **8**, 147; J. Navech, R. Kramer, and J. Majoral, *Tetrahedron Lett.*, 1980, **21**, 1449; S. A. Bone and S. Trippett, *J. Chem. Soc., Perkin Trans. 1*, 1976, 156.

‡ Diethyl azodicarboxylate can also be used[4a] in these reactions; however, the results may be complicated by exchange reactions between the diol and the ethyl ester, resulting in additional signals in the ^{31}P n.m.r. spectrum.

resulted in the same three phosphorane peaks but in the proportions 11:6:10 respectively.

Use of a slight (20%) excess of TPP and DIAD resulted in the formation of only *two* of the three peaks in the phosphorane region of the spectrum, the intermediate phosphorane peak (δ_P -55.2 p.p.m.) being absent. As expected, small peaks due to the betaine (1) and triphenylphosphine oxide were also present (δ_P $+44.1$ and $+25$ p.p.m. respectively). The relative ratio of the two phosphorane species formed was dependent on the concentration of reactants: addition of propane-1,3-diol (2 mmol) to a solution of the betaine (1) (2.2 mmol) in THF (2 ml) resulted in an increase in the proportion of the high-field phosphorane signal (ratio δ_P -54.9:δ_P -55.6 p.p.m. $= 1:7$), while lowering the concentrations of the three reagents resulted in an increase in the proportion of the low-field phosphorane signal [for example, 0.1 mmol of propane-1,3-diol resulted in a single phosphorane peak (δ_P -54.9 p.p.m.)].

Use of an excess (2-fold) of propane-1,3-diol resulted once again in the appearance of the three phosphorane signals, but the relative intensities of the two low-field signals increased relative to that of the high-field signal (δ_P -54.9:δ_P -55.2:δ_P -55.6 p.p.m. $= 3:5:2$). When a large (10-fold) excess of propane-1,3-diol was used, the only signal observed was at δ_P -54.9 p.p.m. It will be shown later that this phosphorane is different to that formed under the low-concentration conditions employed above, but fortuitously it has the same ^{31}P n.m.r. chemical shift.

The generation of these propane-1,3-diol phosphorane species was also attempted using the exchange procedure.[10] For example, treatment of dimethoxytriphenylphosphorane[4a] [1 mmol in THF (2 ml)] with propane-1,3-diol (1 mmol) resulted in the formation of five sharp peaks in the phosphorane region of the ^{31}P n.m.r. spectrum (δ_P -52.2, -53.6, -53.9, -54.9, and -55.2 p.p.m., relative proportions 14:8:3:2:1). After the mixture had been kept at room temperature for 2 h, these proportions had changed very little except that the δ_P -55.2 peak had disappeared. Thus, there was no formation of the high-field absorption (-55.6 p.p.m.) and very little formation of the two low-field absorptions (-54.9 and -55.2 p.p.m.) under these conditions. Conversely, when an equimolar mixture of methanol and propane-1,3-diol was treated with a slight excess of the betaine (1), four sharp signals were observed (δ_P -52.2, -53.9, -54.9, and -55.6 p.p.m., relative proportions $\sim 7:15:13:10$ respectively).

Isolation of these various phosphoranes was not attempted due to their extreme sensitivity to moisture and to their rapid thermal decomposition at room temperature. The propane-1,3-diol phosphoranes were much less stable than phosphorane (11): addition of a slight excess of ethylene glycol at 0 °C to any of the previous mixtures of phosphoranes resulted in the immediate formation of compound (11) (δ_P -36.2 p.p.m.) as the only phosphorane observed.

By comparison with propane-1,3-diol, other 1,3-diols used gave straightforward results with usually only a single phosphorane signal being observed even at low concentrations of reagents. Thus, addition of butane-1,3-diol to a slight excess of the betaine (1) in THF gave a product with a single sharp phosphorane peak (δ_P -55.1 p.p.m.). Use of a slight excess of diol, however, resulted in an additional phosphorane signal (δ_P -54.1 p.p.m.) being observed. The conformationally restricted 1,3-diols methyl 2,3-di-*O*(benzoyl-α-D-glucopyranoside and methyl 2,3-di-*O*(p-tolylsulphonyl)-α-D-galactopyranoside gave rise to single sharp phosphorane peaks in their products' ^{31}P n.m.r. spectra (δ_P -51.7 and δ -52.9 p.p.m. respectively). Glycerol also gave a single sharp peak, but it was clear from the ^{31}P chemical shift obtained (δ_P -35.9 p.p.m.) that this triol was behaving as a 1,2-diol, not a 1,3-diol.
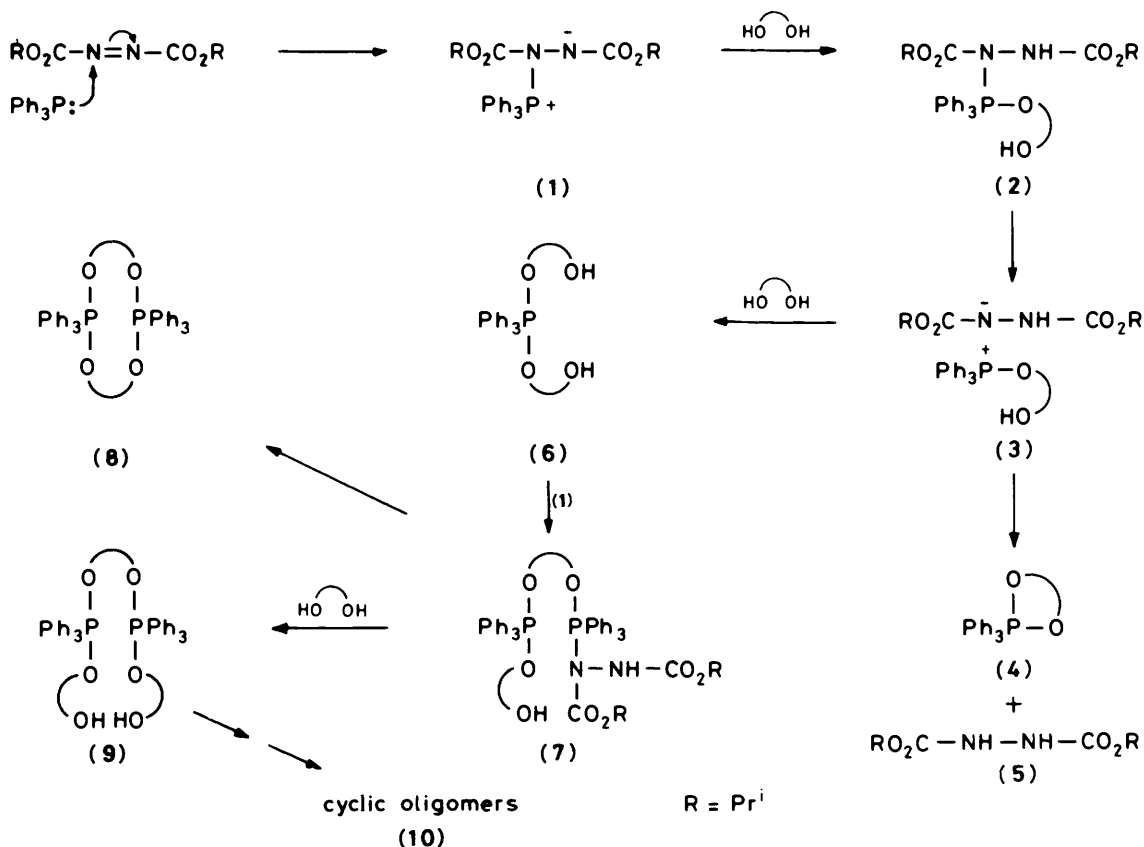
The results obtained with the simplest 1,4-diol were almost as complex as those obtained with propane-1,3-diol. Thus,

addition of butane-1,4-diol (1 mmol) to a solution of the betaine (1) (1.2 mmol) in THF (2 ml) at 0 °C resulted in a single sharp peak (δ_P -56.0 p.p.m.) in the phosphorane region of the ^{31}P n.m.r. spectrum. The same result was obtained at both high (1M) and low (0.1M) concentrations of reagents [a slight (20%) excess of betaine (1) was used in each case]. However, if instead of adding the neat diol dropwise to the betaine a *dilute solution* of butane-1,4-diol (0.02 mmol) in THF (1 ml) was added dropwise to a solution of the betaine (1) (0.05 mmol) in THF (1 ml) at 0 °C, there was a dramatic change in the phosphorane species formed: five sharp peaks were observed in the phosphorane region of the ^{31}P n.m.r. spectrum. The major ($\sim 70\%$) peak (δ_P -46.9 p.p.m.) was well downfield of the other four minor (total 30%) peaks (δ_P -55.55, -55.6, -55.8, and -56.0 p.p.m.; proportions $\sim 1:1:2:4$). Use of this high-dilution technique with propane-1,3-diol gave identical results to those obtained by addition of the neat diol (0.1 mmol) to the betaine in THF (*i.e.*, a single phosphorane peak, δ_P -54.9 p.p.m., was observed).

Treatment of an equimolar mixture of methanol and butane-1,4-diol with a slight excess of the betaine (1) resulted in three sharp peaks in the ^{31}P n.m.r. spectrum (δ_P -52.2, -54.1, and -56.0 p.p.m.; relative proportions $\sim 3:8:9$ respectively).

Other 1,4-diols examined included (*Z*)-but-2-ene-1,4-diol, but-2-yne-1,4-diol, pentane-1,4-diol, and hexane-2,5-diol. The first of these behaved similarly to butane-1,4-diol. Thus, addition of the but-2-ene-1,4-diol (1 mmol) to a solution of the betaine (1) (1.2 mmol) in THF (2 ml) at 0 °C resulted in a major (90%) phosphorane peak (δ_P -55.0 p.p.m.) and two minor (5% each) peaks (δ_P -54.8 and -45.4 p.p.m.), while dropwise addition of a dilute solution of the diol (0.02 mmol) in THF (1 ml) to the betaine (1) (0.05 mmol) in THF (1 ml) at 0 °C resulted in the low-field signal (δ_P -45.4 p.p.m.) becoming the major (95%) peak [there was also a minor peak (5%) present at δ_P -54.8 p.p.m.]. By contrast, but-2-yne-1,4-diol gave essentially a single peak (δ_P -53.1 p.p.m.) under both 'normal' and high-dilution conditions. Addition of pentane-1,4-diol to a slight excess of the betaine (1) (1.2 mmol) gave rise to two phosphorane signals (δ_P -48.4 and -52.5 p.p.m.; ratio $\sim 5:1$ respectively). At higher concentrations of reagents (~ 1.5M) the minor peak increased in intensity (to $\sim 30\%$) while at lower concentrations (~ 0.2M) it was not observed. Use of an excess (2-fold) of pentane-1,4-diol resulted in the appearance of a third phosphorane signal (δ_P -55.5 p.p.m.). This was the major peak (75%) observed under these conditions. Similar results were obtained with hexane-2,5-diol which also resulted in the formation of a major phosphorane (δ_P -49.6 p.p.m.; 93%) and a minor phosphorane (δ_P -51.4 p.p.m.; 7%). Once again, these phosphoranes were quite unstable. For example, the major phosphorane formed from hexane-2,5-diol was 80% decomposed after warming to 40 °C for 5 min (there was a corresponding increase in the triphenylphosphine oxide peak). Similarly, the major phosphorane (δ_P -48.4 p.p.m.) formed from pentane-1,4-diol had completely decomposed after 1.5 h at room temperature.

The foregoing ^{31}P n.m.r. results for the reaction of 1,3- and 1,4-diols with TPP and DIAD can be readily interpreted in terms of the formation of four different types of phosphorane [(4), (6), (9), and (10) respectively] as shown in the Scheme. In the normal course of events, the betaine (1), formed from TPP and DIAD, would be expected[4a] to react with diol to give an intermediate *O*,*N*-phosphorane (2) which would be in equilibrium with (3). The oxyphosphonium species (3) could then readily cyclise to give the cyclic phosphorane (4). This is clearly the case with 1,2-diols where, for example, the phosphorane (11) is formed from ethylene glycol. If, however, the cyclisation step (3) $\longrightarrow$ (4) is slow (on account of an unfavourable entropy term or angle strain or steric interactions in the transition state for ring closure) then reaction of salt (3)

$RO_2C-N=N-CO_2R$ $\longrightarrow$ $RO_2C-N-\bar{N}-CO_2R$ $\xrightarrow{HO\ OH}$ $RO_2C-N-NH-CO_2R$

$Ph_3P:$ Ph_3P+ Ph_3P-O HO

(1) (2)

O O Ph_3P PPh_3 O O

(8)

O OH Ph_3P O OH

(6)

$\xleftarrow{HO\ OH}$

$RO_2C-\bar{N}-NH-CO_2R$ Ph_3P-O HO

(3)

O O Ph_3P PPh_3 O O OH HO

(9)

$\xleftarrow{HO\ OH}$

O O Ph_3P PPh_3 O N-NH-CO_2R OH CO_2R

(7)

$\downarrow$ (1)

O Ph_3P-O

(4)

+

$RO_2C-NH-NH-CO_2R$

(5)

cyclic oligomers (10)

R = Pr^i

Scheme.

with a second molecule of diol to form the acyclic phosphorane (6) may be kinetically favoured [depending on the relative concentrations of (3) and the diol]. Phosphorane (6) would be expected to predominate when the diol is present in large excess. When the diol is present in only modest excess [say 20% over the betaine (1)] then compound (6) would react further with betaine to give compound (7) which could then cyclise to give a dimer (8) or react further with diol to give an acyclic phosphorane (9). In the presence of excess of betaine (1), acyclic phosphorane species such as (6) and (9) would react further to give cyclic dimers (8), trimers, and higher oligomers (10). Thus, in the presence of a slight excess of the betaine (1), two types of cyclic phosphorane species could be formed: the monomer (4) and (a mixture of) cyclic oligomers (10),* the ratio of which would depend on the diol and the reaction conditions employed. Clearly, the monomer (4) would be favoured under conditions of high dilution while cyclic oligomers (10) would be favoured by more concentrated solutions. In the presence of excess of diol, acyclic phosphoranes such as (6) or (9) could also be present.

It is now possible to make reasonable assignments to the three phosphorane signals observed in the case of propane-1,3-diol. The lowest-field signal (δ_P −54.9 p.p.m.) formed exclusively under high-dilution conditions in the presence of a slight excess of the betaine (1) has been assigned to 2,2,2-triphenyl-1,3,2-dioxaphosphinane (12). The highest-field signal (δ_P −55.6 p.p.m.), the major peak at high concentrations of reagents, has been assigned to a mixture of large-ring cyclic

phosphorane oligomers (14). The intermediate signal (δ_P −55.2 p.p.m.) has been assigned to the mixed phosphorane (13).† This phosphorane would be expected to have a chemical shift intermediate between that of (14) and the acyclic phosphorane (15) by analogy with previous work.[4a]

Of the other 1,3-diols examined, butane-1,3-diol presumably gives rise to the cyclic phosphorane (16) unless excess of diol is present, when the acyclic phosphorane (17) would be expected [primary alcohols react very much faster than secondary alcohols with the betaine (1)].[4a] The phosphoranes obtained from the two carbohydrate diols have been assigned the structures (18) and (19) respectively, while that from glycerol has been assigned the five-membered-ring structure (20). Five-membered-ring phosphoranes are well known[11] to have [31]P n.m.r. chemical shifts some 20 p.p.m. downfield of six-membered ring and acyclic phosphoranes.

Similar assignments have been made with the 1,4-diols. Thus, the single sharp absorption (δ_P −56.0 p.p.m.) observed with butane-1,4-diol under normal mixing conditions has been assigned to a mixture of large-ring cyclic phosphorane oligomers (21). The major peak (δ_P −46.9 p.p.m.) observed

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* Including dimers, etc.

† The fact that the phosphorane (13) accounts for some 20% of the total phosphorane phosphorus when only 'one equivalent' of propanediol was used is readily explained by the fact that preparation of the betaine (1) under the conditions used in making up the n.m.r. samples was always accompanied by the formation of a small amount (~10%) of triphenylphosphine oxide. Thus, the propanediol was effectively present in slight excess. Moreover, as the phosphorane (13) contains two phosphorus atoms, its molar percentage yield is of course half that indicated by the ratio of peaks in the [31]P n.m.r. spectrum.
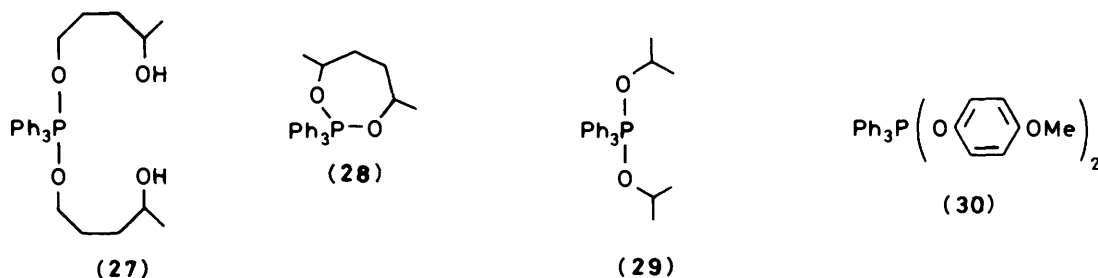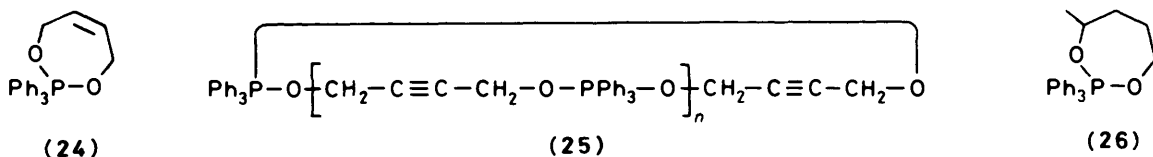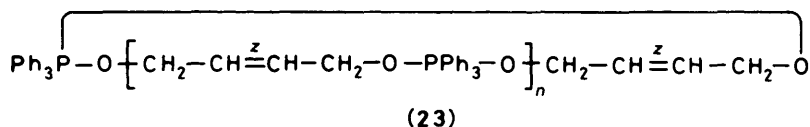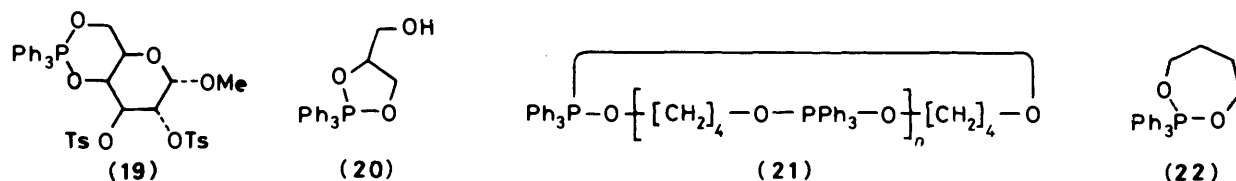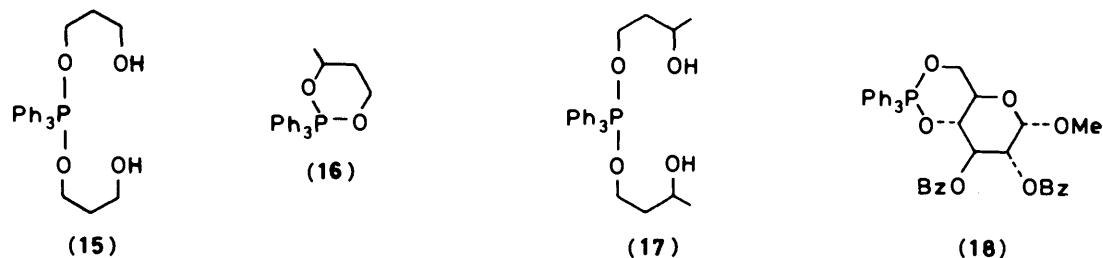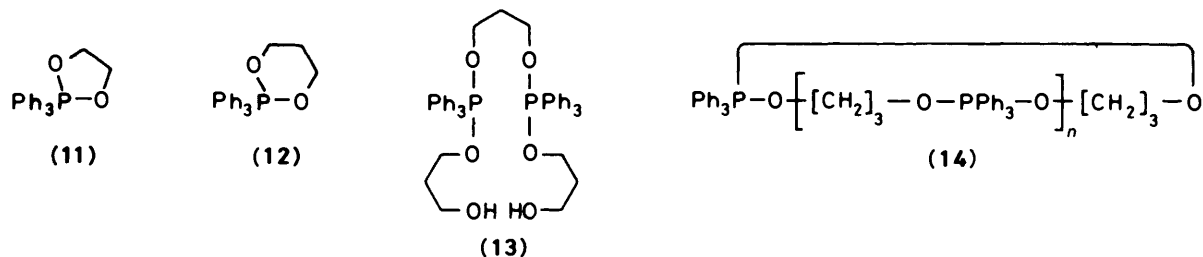
under conditions of high-dilution mixing has been assigned to the seven-membered ring 2,2,2-triphenyl-1,3,2-dioxaphosphepane (22) while the minor peaks (δ_P −55.55, −55.6, −55.8, and −56.0 p.p.m.) have been tentatively assigned to cyclic dimers, trimers, tetramers, and oligomers (21) respectively. With (Z)-but-2-ene-1,4-diol, the absorption (δ_P −55.0 p.p.m.) has been similarly assigned to a mixture of large-ring cyclic phosphorane oligomers (23), while the downfield absorption (δ_P −45.4 p.p.m.) has been assigned to the seven-membered-ring phosphorane (24). The minor phosphorane (δ_P −54.8 p.p.m.) is

due to a little (E)-diol impurity. The single phosphorane species observed in the case of but-2-yne-1,4-diol has been assigned to an oligomeric cyclic phosphorane (25). Formation of a seven-membered-ring phosphorane analogous to (24) is clearly not possible in this case because of the angle constraints imposed by the acetylenic linkage. The major peak observed in the case of pentane-1,4-diol has been assigned to the seven-membered-ring phosphorane (26), while the minor peak (δ_P −52.5 p.p.m.) is presumably due to an oligomeric species by analogy with the previous 1,4-diols. The phosphorane formed when pentane-1,4-

diol is in excess is clearly the acyclic species (27). The major phosphorane formed from hexane-2,5-diol has been similarly assigned to the seven-membered-ring species (28). The reason for the much more ready ring-closure to form six- and seven-membered-ring phosphoranes in the case of the substituted 1,3- and 1,4-diols respectively will be discussed later.

Although the above phosphorane structures are consistent with all of the ^{31}P n.m.r. data obtained, we sought further confirmation for these assignments. Isolation of pure phosphorane species did not appear to be possible on account of their high thermal and hydrolytic instability. Previous attempts to isolate similar phosphoranes have also been unsuccessful[10] as have attempts to observe parent ions by mass spectrometry.[6] These features appeared to preclude meaningful molecular-weight determinations. Examination of the three classes of dioxyphosphorane shown in the Scheme, viz. cyclic (4), acyclic (6) and (9), and cyclic oligomeric (10), and using the general rule[12] that the more electronegative atoms tend to occupy the apical positions of trigonal bipyramidal phosphoranes, it can be seen that cyclic phosphoranes (4) differ from acyclic phosphoranes [such as (6)] in that it is impossible for a 1,2-, 1,3-, or a 1,4-diol to span both apical positions. This means that cyclic phosphoranes (4) must possess at least one apical phenyl group, whereas acyclic phosphoranes would have all three phenyl groups in equatorial positions. Since one-bond phosphorus–carbon (and phosphorus–fluorine) coupling constants are much larger for equatorial groups than for apical groups[12-15] (consistent with the expected[7] shorter bond lengths and greater s-character of the former), then phosphoranes bearing an apical phenyl group should be distinguishable from phosphoranes bearing only equatorial phenyl groups by ^{13}C n.m.r. spectrometry. This was found to be the case.

Examination of the ^{13}C n.m.r. spectra of acyclic dialkoxy-triphenylphosphoranes such as (29) and diaryloxytriphenyl-phosphoranes such as (30), revealed in each case a sharp doublet (δ_C ca. 140 p.p.m., $J \sim 175$ Hz) well downfield of the normal aromatic region of the spectrum. Cyclic dioxytriphenyl-phosphoranes such as (11) also showed a downfield doublet (δ_C ca. 145 p.p.m.) but with a very much smaller coupling constant ($J \sim 120$ Hz). There were no signals present in this region of the spectrum for non-phosphorane compounds such as triphenyl-phosphine, triphenylphosphine oxide, or the betaine (1).* These doublets (a typical example is shown in the Figure) are due to the one-bond couplings from phosphorus to the quaternary carbon atoms of the directly bonded phenyl groups. Analogous assignments have been reported previously with both acyclic[6] and cyclic[16,17] phosphoranes, but no attempt appears to have been made to correlate the magnitude of the ^{13}C n.m.r. chemical shift or of the $^1J_{P-C}$ coupling constant with the chemical environment of the phenyl group(s) in the respective phosphoranes.

We have determined the ^{13}C n.m.r. chemical shifts and the $^1J_{P-C}$ values for the ipso carbon atoms for most of the major phosphoranes studied. These values, as well as the corresponding ^{31}P n.m.r. chemical shifts, are shown in the Table. It can be seen from the Table and from the small amount of data in the literature[6,16,17] that there are two discrete types of phenylphosphorane: those in which the phenyl groups are all equatorial and those in which a phenyl group must occupy an apical site. The former always exhibit large (>170 Hz) $^1J_{P-C}$ values whereas the latter exhibit much smaller (<130 Hz) $^1J_{P-C}$ values. The smaller coupling constants observed for cyclic
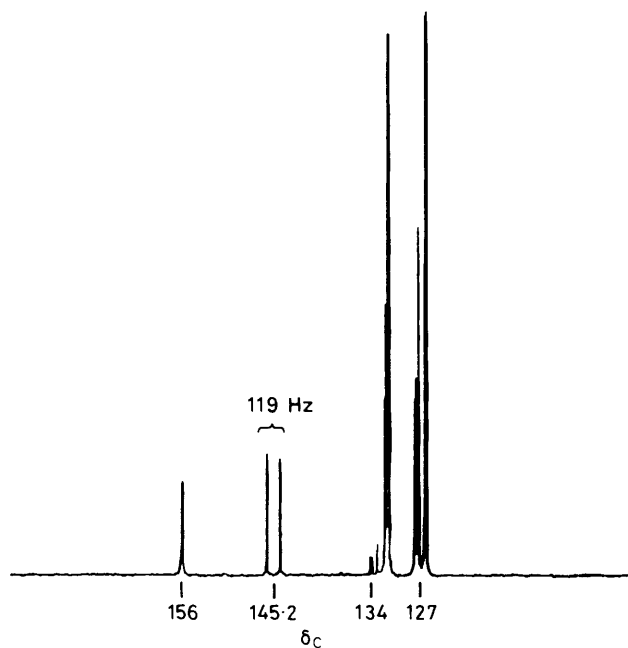

Figure. ^{13}C N.m.r. spectrum of phosphorane (11) — aromatic region

Table. ^{31}P and ^{13}C n.m.r. data (THF; 10 °C) for dioxytriphenyl-phosphoranes

Phosphorane	δ_P	$\delta_C{}^a$	$^1J_{P-C}$ (Hz)^a
(11)	−36.2	145.2	119
(12)	−54.9	148.2	123
(13)	−55.2	139.4	174
(14)	−55.6	139.6	174
(15)	−54.9	139.2	174
(16)	−55.1	148.3	123
(17)	−54.1	138.8	174
(18)	−51.7	145.7	123
(19)	−52.9	145.6	123
(20)	−35.9		
(21)	−56.0	139.6	173
(22)	−46.9	149.0	122
(23)	−55.0	139.3	173
(24)	−45.4	147.5	122
(25)	−53.1	138.1	173
(26)	−48.4	149.7	123
(27)	−55.5	139.5	174
(28)	−49.6	149.6	123
(29)	−49.6	140.9	176
(30)	−65.5	139.4	175
(31)	−53.6		
(32)	−53.9		
(33)	−54.1		

^{a} For carbon bonded to phosphorus.

phosphoranes (4) are clearly time-averaged values as only one downfield doublet was observed for each phosphorane, despite the fact that two of the phenyl groups occupy equatorial positions. A time-averaged value is not unexpected however in view of the ready pseudorotation that these phosphoranes are known[11,18] to undergo at ambient temperatures. By extrapolation, the $^1J_{P-C}$ value for a 'pure' apical phenyl substituent would be expected to be quite small (ca. 20 Hz).

The two types of phenylphosphoranes also exhibit characteristic shifts for the ipso carbons, but the difference is not as distinctive as for the $^1J_{P-C}$ values. Thus, phosphoranes bearing
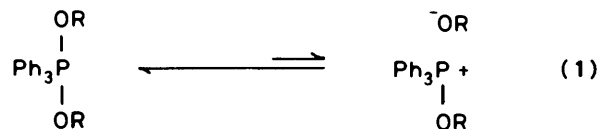
* These phosphorus compounds do show analogous doublets for the ipso carbon atoms, but these doublets are well upfield of those observed in the case of phosphoranes. For example, for the betaine (1), δ_C 123.5 p.p.m., $^1J_{P-C}$ 104 Hz.

only equatorial phenyl groups generally exhibit chemical shifts to slightly higher field ($\delta_C < 141$ p.p.m.) whereas those with an apical phenyl group usually exhibit slightly lower field values ($\delta_C > 141$ p.p.m.).

It is clear from the preceding discussion that the ^{13}C n.m.r. results provide substantial support for the assignments made on the basis of ^{31}P n.m.r. results alone. In particular, they provide very strong evidence for the formation of six- and seven-membered-ring cyclic phosphoranes from the various diols studied, even though high-dilution techniques were required in a number of cases. ^{13}C N.m.r. spectrometry also provided the means of distinguishing the cyclic phosphorane (12) from the acyclic phosphorane (15), both of which were obtained from propane-1,3-diol. It will be recalled that these two phosphoranes exhibited identical ^{31}P n.m.r. chemical shifts ($\delta_P - 54.9$ p.p.m.). However, they were clearly and unambiguously assigned on the basis of ^{13}C n.m.r. coupling constant and chemical-shift data (Table). In all cases, the ^{13}C n.m.r. results exactly paralleled the ^{31}P n.m.r. results. For example, the three peaks ($\delta_P - 54.9$, -55.2, and -55.6 p.p.m.; proportions 5:6:15) observed initially with propane-1,3-diol by ^{31}P n.m.r. spectrometry correlated with three doublets (δ_C 148.2, 139.4, and 139.6 p.p.m.; proportions 5:6:15) observed by ^{13}C n.m.r. spectrometry for the same sample. When the betaine (1) was present in slight excess, only two doublets (δ_C 148.2 and 139.6 p.p.m.) were observed in the ^{13}C n.m.r. spectrum, corresponding to the ^{31}P n.m.r. results. Similarly, at high (~ 1.5M) concentrations of reagents, only one doublet (δ_C 139.6 p.p.m.), corresponding to (14), was observed, while at low (~ 0.1M) concentrations, only the downfield doublet (δ_C 148.2 p.p.m.), corresponding to phosphorane (12), was observed in the ^{13}C n.m.r. spectrum. When propane-1,3-diol was present in excess (10-fold), however, a new doublet (δ_C 139.2 p.p.m.) was observed, corresponding to compound (15). None of the other phosphorane species were observed. Although the ^{13}C n.m.r. chemical shifts of the three phosphoranes (13), (14), and (15) are very close to each other, the three sets of doublets could be clearly seen with samples containing a modest excess of diol. For example, treatment of the betaine (1) (1 mmol) with propane-1,3-diol (2 mmol) in THF (2 ml) resulted in three sets of doublets in the ^{13}C n.m.r. spectrum (δ_C 139.2, 139.4, and 139.6 p.p.m.; relative proportions $\sim 3:5:2$ respectively, all with $^1J_{P-C}$ coupling constants of 174 Hz). The ^{31}P n.m.r. spectrum showed three corresponding peaks ($\delta_P - 54.9$, -55.2, and -55.6 p.p.m.; relative proportions $\sim 3:5:2$ respectively). The ^{13}C n.m.r. result shows clearly that the cyclic phosphorane (12) is not formed under these conditions, a result that is not obvious from the ^{31}P n.m.r. data alone.

It can be seen from the Table that all of the cyclic phosphoranes [of the type (4)] show small values (~ 120 Hz) for $^1J_{P-C}$, consistent with the ring spanning an apical and an equatorial position (i.e., one phenyl group in the remaining apical position). The ^{13}C n.m.r. coupling constants also tell us something about the cyclic oligomeric phosphoranes (10). Thus, from the ^{31}P n.m.r. data alone, it is not possible to distinguish dimeric phosphoranes (8) from higher oligomeric species (10). The large values (~ 174 Hz) observed for $^1J_{P-C}$ in phosphoranes such as (14) and (21), however, indicate that all three phenyl groups are equatorial, i.e., the bridging dioxy ligands occupy the apical positions in these phosphoranes. From a study of molecular models, it is virtually impossible for either propane-1,3-diol or butane-1,4-diol to form dimeric species (8) in which the oxygen atoms occupy the apical positions of trigonal bipyramidal phosphorus atoms, as the resulting structures are just too sterically congested. With propane-1,3-diol, even a trimeric species (14; $n = 2$) is extremely crowded and most unlikely. It is for this reason that we suggest an oligomeric structure (14; $n > 3$) for the major phosphorane formed from the

betaine (1) and propane-1,3-diol under 'normal' conditions of mixing (i.e., for concentrations greater than about 0.5M). Similarly, with butane-1,4-diol, it seems likely that the major phosphorane formed under all but high-dilution conditions is at least tetrameric (21; $n > 3$). The range of minor phosphorane species formed under high-dilution conditions and observed by ^{31}P n.m.r. spectrometry also supports an oligomeric structure. Unfortunately, these phosphorane solutions were too dilute and the species too minor to be detected in the ^{13}C n.m.r. spectrum. We have no way of knowing just how large these oligomeric (or polymeric) species are at the present time but it seems reasonable to assume that they are mixtures where n has a range of values. Certainly they are cyclic as they are formed under conditions of excess of betaine (1) so that there can be no free hydroxyl groups present. The sharp ^{31}P and ^{13}C n.m.r. signals observed for these cyclic oligomeric mixtures might suggest low-molecular-weight species rather than high-molecular-weight (cyclic) polymers. However, the latter cannot be excluded as there could easily be high (internal) molecular mobility even in high-molecular-weight species, possibly as a consequence of rapid equilibria of the type shown in equation (1). Such an

$$\begin{array}{ccc}
\overset{\displaystyle OR}{\underset{\displaystyle OR}{\overset{|}{\underset{|}{Ph_3P}}}} & \rightleftharpoons & \overset{\displaystyle ^-OR}{\underset{\displaystyle OR}{\overset{|}{\underset{|}{Ph_3P\,+}}}} \qquad (1)
\end{array}$$

equilibrium is necessary to explain the various exchange reactions of oxyphosphoranes [including, for example, the rapid reaction of compounds (12)—(15) with ethylene glycol to give product (11)]. The rate of the association process in equation (1) is known to be extremely fast (at the diffusion limit) in related aryloxyphosphoranes.[19] Interestingly, the cyclic oligomer (14) was not formed by an exchange reaction between dimethoxy-triphenylphosphorane and propane-1,3-diol. The main species formed under these conditions were the mixed phosphoranes (31) ($\delta_P - 53.6$ p.p.m.) and (32) ($\delta_P - 53.9$ p.p.m.). The phosphorane (32) was the major species formed when a mixture of methanol and propane-1,3-diol was treated with a slight excess of the betaine (1). Under these conditions the cyclic monomer (12) and oligomer (14) were also formed but, as expected, the phosphorane (31) was not present. These assignments are based on the observation[4a] that mixed phosphoranes generally have ^{31}P chemical shifts that are approximately half way between the two parent phosphoranes. For example, phosphorane (31) has a chemical shift approximately half way between that of dimethoxytriphenyl-phosphorane ($\delta_P - 52.2$ p.p.m.) and compound (15) ($\delta_P - 54.9$ p.p.m.). Analogous results were obtained in the case of methanol–butane-1,4-diol to give the mixed phosphorane (33) ($\delta_P - 54.1$ p.p.m.).

(31)   (32)   (33)
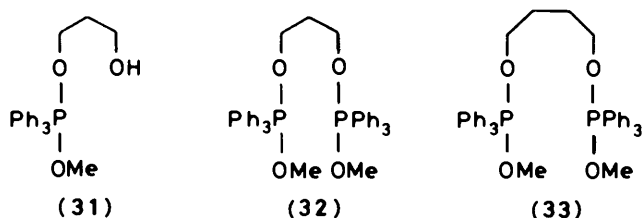
Possibly the most important result to come out of this work is the apparent instability of six- and seven-membered-ring phosphoranes such as (12) and (22). This contrasts with five-membered rings which are well known to result in enhanced phosphorane stability.[7,8] The difference between five- and six-membered rings is clearly illustrated in the case of glycerol,

where reaction with the betaine (1) resulted only in the formation of a five-membered-ring phosphorane. There was no sign of formation of a six-membered-ring phosphorane, even though reaction at the two primary positions of glycerol might have been expected to be particularly easy. Thus, the chelate effect [20] appears to be very strong in the case of five-membered-ring phosphoranes but quite weak when it comes to ring-closure to form a six(or seven)-membered-ring phosphorane. The effect is so weak that at relatively low ($\sim$0.5M) concentrations of reagents [betaine (1) and propane-1,3-diol or butane-1,4-diol] an intermolecular reaction to form an oligomeric phosphorane species (10) competes very favourably with intramolecular cyclisation to give the six-(12)- or seven-(22)-membered-ring phosphoranes respectively. Clearly, there is some factor which is destabilising the transition state for ring-closure. This is probably ring strain. In the case of six-membered ring phosphoranes such as (12), p_π–d_π back-bonding from the oxygens to phosphorus forces the ring to adopt a boat conformation. Such a conformation has been found [21,22] in related six-membered-ring phosphoranes. From a study of models, and assuming π back-bonding from sp^2-hybridised oxygen atoms to phosphorus d-orbitals of suitable symmetry (e.g., $3d_{x^2-y^2}$ for equatorial oxygen and $3d_{yz}$ for apical oxygen), phosphorane (12) exhibits a strong flagpole-like van der Waals interaction between the apical oxygen p-orbital and a hydrogen atom on position 3 of the ring [see structure (34)]. There is also torsional strain owing


(34)
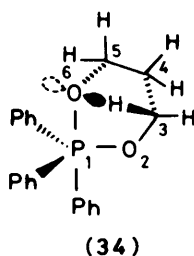
to the eclipsed hydrogen atoms on positions 4 and 5. Little or no relief of strain is achieved by use of an sp^3-hybridised apical oxygen atom, in contrast to five-membered-ring phosphoranes such as (11) where there is considerable relief of torsional strain. Use of an sp^3-hybridised apical oxygen means that back-bonding from oxygen to phosphorus can only occur from the equatorial oxygen atom, and in the case of five-membered ring phosphoranes there is very good evidence for this. First, ^{31}P n.m.r. chemical shifts of these phosphoranes are usually about 20 p.p.m. downfield from those of their acyclic counterparts,[11] indicating considerably less shielding of the phosphorus atom. Secondly, apical oxygen P–O bond lengths are usually much longer in five-membered-ring phosphoranes than in six-membered-ring or acyclic phosphoranes.[21-23] It would appear, then, that unlike five-membered-ring phosphoranes which are particularly stable,[8,11,24] six-membered-ring phosphoranes such as (12) suffer from van der Waals and torsional strain, rendering them less stable than might otherwise have been expected. Presumably the resulting increased energy of the system is reflected in the transition state for formation of phosphoranes such as (12).

The flagpole-like van der Waals repulsion that is apparent for the six-membered-ring phosphorane (12) is even more pronounced in the case of the seven-membered-ring phosphorane (22). Presumably this feature is at least partly responsible for the greater difficulty in forming compound (22). Even high-dilution techniques did not result in the exclusive formation of (22) and, in contrast to the propane-1,3-diol case, the phosphepane (22) was not formed at all under conditions where neat butane-1,4-diol was added to a solution of the betaine (1).

Interestingly, the more 'chelate-like' diol (Z)-but-2-ene-1,4-diol did facilitate cyclisation to form a seven-membered-ring phosphorane, though the same type of 'flagpole' interaction was still apparent from a molecular model. Even here, however, high-dilution techniques were required for exclusive formation of compound (24). Examination of molecular models suggests that an sp^3-hybridised apical oxygen results in reduced van der Waals ('flagpole') repulsion and it is conceivable that the ^{31}P n.m.r. downfield shift [ca. 9 p.p.m.] observed for these seven-membered-ring phosphoranes may reflect a more sp^3-like apical oxygen in phosphepane (22) [and (24)] than in the corresponding six-membered-ring phosphorane (12).

The difficulty of formation of seven-membered-ring phosphoranes from butane-1,4-diol and (Z)-but-2-ene-1,4-diol contrasts with the apparent ease of formation of such phosphoranes from the substituted diols pentane-1,4-diol and hexane-2,5-diol. The easier cyclisation in the latter two cases is presumably due in part to the operation of the Thorpe–Ingold or gem-dialkyl[25] effect. In addition, the cyclisation step [(3) $\longrightarrow$ (4), Scheme] should be favoured kinetically as the betaine (1) reacts very much more slowly with secondary alcohols than with primary alcohols.[4a] This would slow down the oligomerisation process dramatically [for example, steps (6) $\longrightarrow$ (7) and (9) $\longrightarrow$ (10), Scheme]. Similar arguments apply to the formation of the six-membered ring phosphoranes (16), (18), and (19) although in the latter two cases the chelate effect would be expected to be more important on account of the conformational restrictions imposed by the pyranose rings.

There are few literature reports[16,26-28] of seven-membered-ring phosphoranes and only one of these[16] is of the type (4). In general, seven-membered-ring phosphoranes of this type are unstable, and break down rapidly to give tetrahydrofurans.[10,29] The corresponding six-membered-ring phosphoranes might be expected, by analogy, to break down to oxetanes and indeed there is a literature report[30] that oxetane itself is formed in high yield by treatment of propane-1,3-diol with TPP and diethyl azodicarboxylate in chloroform. We examined this reaction (using both diethyl and di-isopropyl azodicarboxylate) by ^{13}C n.m.r. spectrometry and were surprised to find that after 1 h at room temperature, although the phosphorane signals had disappeared, there was no sign of any oxetane* present. The only unusual signals observed were at δ_C 46.4 and 25.5 p.p.m., which correspond to the pyrazolidine derivative (35). This was subsequently isolated by chromatography and the structure confirmed in the usual way. The formation of the pyrazolidine derivative rather than oxetane is consistent with the results of Evans et al.[31] who isolated 3-ethoxypropan-1-ol from the reaction of diethoxytriphenylphosphorane and propane-1,3-diol.

(35)
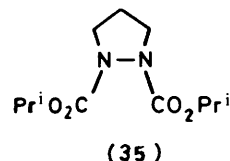
Conclusions

A simple procedure for the preparation of six- and seven-membered-ring cyclic dioxytriphenylphosphoranes from triphenylphosphine and 1,3- or 1,4-diols respectively, is reported. Although high-dilution techniques are required in some cases, the method appears to be general, and being a very mild

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* Apparently oxetane can be formed under different conditions — J. T. Carlock, personal communication.

procedure it is superior in many cases to the older methods of synthesis of this type of compound such as exchange of diethoxytriphenylphosphorane with diols[10] or reaction of peroxides with triphenylphosphine.[27] The ease of formation of cyclic dioxytriphenylphosphoranes appears to be five-membered > six-membered > seven-membered. There is some instability associated with six- and seven-membered ring phosphoranes, presumably as a result of ring-strain and the desire to have both oxygen atoms in apical positions. Dioxy-triphenylphosphoranes with both oxygen atoms apical are readily distinguished from phosphoranes in which one oxygen is apical and the other equatorial by ^{13}C n.m.r. $^1J_{P-C}$ coupling constants.

Experimental

^1H, ^{31}P, and ^{13}C N.m.r. spectra were recorded at 10 °C with a Bruker CXP-300 spectrometer. ^{31}P and ^{13}C Spectra were acquired by using a 45° flip angle, a 2s recycle delay, and 0.4s acquisition time with gated proton decoupling. Negative ^{31}P chemical shifts are upfield of external phosphoric acid (85%). ^1H and ^{13}C Chemical shifts are reported in p.p.m. relative to internal tetramethylsilane. Mass spectra were obtained using a Kratos MS-25 instrument. Microanalyses were performed by the Chemistry Department, University of Queensland. M.p.s were determined with a Tottoli apparatus and are uncorrected. Column chromatography was performed on Kieselgel-60 (Merck; 70—230 or 230—400). All solvents were redistilled. THF was dried by refluxing over sodium sand followed by distillation. All of the simple diols used were commercial samples and were not further purified with the exception of propane-1,3-diol which, because of the additional peaks observed in the ^{31}P n.m.r. spectrum of some of its reaction products (see text), was purified by chromatography and distillation under reduced pressure.

Methyl 2,3-Di-O-benzoyl-α-D-glucopyranoside.—This compound, obtained as a syrup, $[\alpha]_D$ 155° (c 1 in ethanol) {lit.,[32] $[\alpha]_D$ 155° (c 1) in ethanol)} was prepared from methyl 2,3-di-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside[33] by removal of the benzylidene group with aqueous acetic acid (1:2; 100 °C; 30 min) using the standard procedure.[34]

Methyl 2,3-Di-O-(p-tolylsulphonyl)-α-D-galactopyranoside.—Similar removal[34] of the benzylidene group from the corresponding 4,6-O-benzylidene derivative[35] gave the title compound, m.p. 82—83 °C; δ_H(CDCl$_3$) 2.27 (1 H, br s, OH), 2.43 (3 H, s, ArMe), 2.47 (3 H, s, ArMe), 3.12 (1 H, br s, OH), 3.31 (3 H, s, OMe), 3.8—4.0 (3 H, m, 5-H and 6-H$_2$), 4.39 (1 H, br s, 4-H), 4.73 (1 H, dd, $J_{2,1}$ 3.5, $J_{2,3}$ 10.0 Hz, 2-H), 4.83 (1 H, dd, $J_{3,4}$ 3.2 Hz, 3-H), 4.84 (1 H, d, 1-H), 7.23 and 7.33 (2 × 2 H, 2 d, J_{ortho} 8.6 Hz, ArH), and 7.60 and 7.72 (2 × 2 H, 2 d, J_{ortho} 8.4 Hz, ArH); δ_C(CDCl$_3$) 21.7 (ArMe), 55.7 (OMe), 62.6 (C-6), 68.7* (C-4), 70.4* (C-3), 73.7* (C-2 and -5), 97.8 (C-1), and 128.0, 129.7, 129.9, 133.0, and 145.1 (ArC) [* assignments tentative] (Found: C, 48.5; H, 5.5. C$_{21}$H$_{26}$O$_{10}$S$_2$·H$_2$O requires C, 48.45; H, 5.42%).

Preparation of Phosphoranes (11)—(33). *General Procedure.*—TPP (262 mg, 1 mmol) was dissolved in THF (2 ml) under nitrogen in a 10 mm n.m.r. tube containing a small sealed capillary of phosphoric acid (85%). The solution was cooled to 0 °C and DIAD (200 μl, 1 mmol) was added to the swirled and cooled mixture, followed by the necessary diol (1 mmol). The tube was stoppered, sealed with Parafilm, and shaken vigorously for several minutes before the ^{31}P (or ^{13}C) n.m.r. spectrum was recorded. Usually the betaine (1) crystallised from

the THF upon addition of the DIAD and cooling for several min, but it redissolved as soon as the diol was added. In those experiments where an excess of the betaine (1) was required, either the amount of diol was kept constant and the amounts of TPP and DIAD were increased (to 1.2 mmol each), or the amount of diol was reduced (to 0.8 mmol). The 'high-dilution' technique involved addition of a solution of the diol (ca. 2 μl) in THF (1 ml) dropwise from a Pasteur pipette (allowing the solution to run slowly down the inside wall of the n.m.r. tube) to a slight excess of the betaine (1), (ca. 0.05 mmol) in THF (1 ml) under nitrogen. The tube was shaken vigorously and cooled in ice–water during the addition (during 3—5 min) then stoppered and the n.m.r. spectrum was recorded immediately. This technique gave better results than those obtained by dropwise addition of the diol solution from a small dropping funnel to a magnetically stirred solution of the betaine (1) in a small flask, followed by transfer to the n.m.r. tube. A probe temperature of 10 °C was used as these phosphoranes are thermally unstable, often decomposing quite rapidly at or above room temperature. There was a small temperature effect on the ^{31}P n.m.r. chemical shift in some cases; for example the phosphorane derived from hexane-1,6-diol[36] had a chemical shift of δ_P −55.8 p.p.m. at 10 °C and −55.6 p.p.m. at 20 °C. In general, the chemical shifts of the phosphoranes were insensitive to concentration changes, were unaffected by various concentrations of triphenylphosphine oxide (the chemical shift of the latter varied between +24.0 and +26.0 p.p.m.; it was therefore useless as an internal standard for comparison of chemical shifts), but were dependent on the solvent to some extent. For example, the three phosphoranes (12), (13), and (14) had ^{31}P n.m.r. chemical shifts (in benzene) of −54.2, −54.5, and −55.2 p.p.m., and values of −54.7, −53.3, and −53.7 p.p.m. respectively in dichloromethane. The ^{31}P n.m.r. chemical shifts were reproducible to within ±0.1 p.p.m. using the internal capillary of 85% phosphoric acid. Even better reproducibility (±0.05 p.p.m. or better) was obtained if TPP was used as internal reference. In practice a slight excess (1—5%) of TPP (over DIAD) was employed and the phosphorane chemical shifts were referenced to the TPP (set at δ_P −5.20 p.p.m.) signal.

Reaction of TPP, DIAD, and Propane-1,3-diol.—TPP (262 mg, 1 mmol) was dissolved in dry chloroform (2 ml) and the solution was stirred at 0 °C under nitrogen. DIAD (200 μl, 1 mmol) was added slowly to the stirred solution during ca. 3 min, followed by the propane-1,3-diol (72 μl, 1 mmol). The reaction mixture was stirred for 1 h at 0 °C and then at room temperature for 48 h. Evaporation under reduced pressure followed by column chromatography on silica gel [ethyl acetate–hexane (1:2)] afforded 1,2-bis(isopropoxycarbonyl)pyrazolidine (35), (72 mg, 20%, or 60% based on recovered diol), m.p. 32—34 °C; $\nu_{max.}$(neat) 1 700 cm^{-1} (C=O); m/z (70 eV) 244 (M^+), 158 (M^+ − propene − CO$_2$), 143 (M^+ − propene − OCHMe$_2$), 116 (M^+ − 2 × propene − CO$_2$), and 71 (158 − OCHMe$_2$ − CO$_2$); δ_H(CDCl$_3$) 1.27 (12 H, d, J 6.3 Hz, 4 × Me), 2.05 (dt, 2 H, J 7.2 Hz, CH$_2$CH$_2$CH$_2$), 3.25 (m, 2 H, 2 × CHN), 3.93 (m, 2 H, 2 × CHN), and 4.95 (septet, 2 H, J 6.3 Hz) [the two multiplets at δ_H 3.25 and 3.93 coalesced to give a broad hump upon heating the product in (CD$_3$)$_2$SO at 70 °C]; δ_C(CDCl$_3$) 22.1 (CH$_3$), 25.6 (CH$_2$CH$_2$CH$_2$), 46.4 (CH$_2$N), 69.9 (CHO), and 156.9 (C=O) (Found: C, 53.9; H, 8.2; N, 11.3. C$_{11}$H$_{20}$N$_2$O$_4$ requires C, 54.08; H, 8.25; N, 11.47%).

In addition, di-isopropyl hydrazine-1,2-dicarboxylate (5; R = Pr^i) (140 mg, 70%), triphenylphosphine oxide (280 mg, 98%), and propane-1,3-diol (50 mg, 68%) were isolated and characterised by i.r. and t.l.c. comparison with authentic samples.

Virtually identical results were obtained if THF was used as solvent.

Acknowledgements

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