Organophosphorus Intermediates. IX* The Cleavage of α, ω -Bisdiphenylphosphinoalkanes with Lithium. A ³¹P N.M.R. Study

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Abstract

The title phosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 2-5), react with lithium in tetrahydrofuran to give the corresponding 1, *n*-dilithio-1, *n*-di(phenylphosphines) directly with little or no intermediacy of the 1-lithio-1-phenyl-*n*-diphenylphosphinoalkanes which can, however, be obtained by arylation of the diphosphides. Methylenebisdiphenylphosphine and 1,4-diphenyl-1,4-diphosphinane undergo exclusive phosphorus-alkyl carbon cleavage. The chemistry and ³¹P n.m.r. spectroscopy of the diphosphides are described and the mechanism of the cleavage reaction is discussed. Some cleavage reactions in liquid ammonia are described.

Introduction

Organophosphides—organic phosphorus compounds with a phosphorus-metal bond—are a very reactive class of substances widely useful in forming phosphoruscarbon bonds. Their chemistry was studied in considerable detail by Issleib and his coworkers¹ in the early sixties and they have since found extensive use in preparative work. They act as powerful, soft nucleophiles and are easily alkylated and arylated. Methods for their preparation usually involve cleavage of P-H, P-halogen of P-P bonds with metals or organometallic reagents either in tetrahydrofuran or liquid ammonia. Less commonly a P-C bond may be cleaved with a metal, though in this case two organometallics are formed, equation (1):

$$\mathbf{R}_{2}\mathbf{P}\mathbf{R}' + \mathbf{M} \to \mathbf{R}_{2}\mathbf{P}\mathbf{M} + \mathbf{R}'\mathbf{M} \tag{1}$$

Aguiar¹ neatly resolved this latter complication in the case of the cleavage of triphenylphosphine with lithium in tetrahydrofuran by the addition of t-butyl chloride which destroyed the phenyllithium but which did not react with lithium diphenylphosphide, thus providing a simple route to the reactive diphenylphosphide starting from readily available and easy to handle materials.

* Part VIII, Aust. J. Chem., 1982, 35, 363.

¹ Maier, L., and Kosolapoff, G. M., (Eds) 'Organic Phosphorus Compounds' Vol. 1 (a) Ch. 2; (b) Ch. 1 (Wiley-Interscience: New York 1972).

Our interest in these substances stemmed initially from our long standing interest in diphosphorus compounds in general^{2,3} particularly diphosphorus heterocycles,⁴ and also since in recent years there has been intense interest in the properties of diphosphines as ligands particularly as they relate to homogeneous catalysis.⁵ As a range of alkane-1, *n*-diylbisdiphenylphosphines is now commercially available, it seemed to us that these could serve as convenient, easily purifiable, air-stable precursors of the diphosphides (2) which should in turn be readily alkylated with appropriate dihalides or diesters to afford a range of heterocycles (3; Scheme 1).



We were very interested to examine (3) to determine their stereochemical, spectroscopic and coordination properties and to explore their utility in the synthesis of heterocycles containing bridgehead phosphorus atoms. We further hoped that the monophosphides (4) could, by a sequence of alkylation, cleavage and further alkylation, lead to macrocyclic polyphosphines. Finally, we wished to accumulate data on ${}^{2}J_{\rm PP}$ and ${}^{3}J_{\rm PP}$ to provide a convenient basis for conformational analysis of di- and poly-phosphorus heterocycles.

Cleavage of phosphorus-carbon bonds has been achieved using alkali metals in tetrahydrofuran or dioxan¹ and has also been reported in liquid ammonia, though very few examples of the latter reaction are described in the literature.^{1,6} The group lost is normally the most electronegative one, e.g., aryl before alkyl, though this order breaks down for aryldialkylphosphines and trialkylphosphines do not cleave at all.⁷ The diphosphides (2; n = 2-6) are known^{8,9} having been obtained by Issleib's group by treatment of the corresponding disecondary phosphines with phenyllithium, the requisite diphosphines being prepared by reaction of monometallated phenylphosphine with the appropriate 1, *n*-dichloroalkane. The diphosphides (2) could be isolated as yellow crystalline solids, solvated with dioxan. The only polyphosphide obtained by phosphorus-carbon bond cleavage appears to be the tetraphosphide C[CH₂P(Na)Ph]₄, prepared in high yield from the corresponding tetrakisdiphenylphosphine by reaction

- ⁸ Issleib, K., and Krech, F., Chem. Ber., 1961, 94, 2656.
- ⁹ Issleib, K., and Standtke, K., Chem. Ber., 1963, 96, 279.

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² Brophy, J. J., and Gallagher, M. J., Aust. J. Chem., 1967, 20, 503.

³ Brophy, J. J., and Gallagher, M. J., Aust. J. Chem., 1969, 22, 1385, 1399, 1405.

⁴ Driver, G. E., and Gallagher, M. J., J. Chem. Soc., Chem. Commun., 1970, 150.

⁵ Pignolet, L. H., (Ed.) 'Homogeneous Catalysis with Metal Phosphine Complexes' (Plenum Press: New York 1983).

⁶ Ellerman, J. E., and Poersch, F., Angew. Chem., Int. Ed. Engl., 1967, 6, 355.

⁷ Issleib, K., and Volker, R., Chem. Ber., 1961, 94, 392.

with sodium in liquid ammonia.^o Experimentally, we considered that room temperature reactions would be more convenient and set out to determine whether cleavage of phosphorus-carbon bonds with lithium in tetrahydrofuran would provide a useful and convenient route to the phosphides (2) and (4).

Results

Though all the diphosphines (1; n = 1-5) react when stirred under argon in tetrahydrofuran with lithium ribbon, wire or powder, the reaction is erratic, sometimes having a long (24 h) induction period and generally ceasing before complete dissolution of the metal and with unchanged starting phosphine still present. These features were particularly serious when the reactions were carried out on a small scale. Careful exclusion of oxygen and deoxygenation of solvents by saturation with argon gave more reliable initiation and better yields. Somewhat surprisingly the presence of small amounts of water (c. 0.1-0.5%) does not inhibit the reaction and phosphide formation in unpurified commercial tetrahydrofuran proceeded with at least the same ease as with the same solvent freshly distilled from lithium aluminium hydride or potassium-benzophenoneketyl. Indeed, reactions in rigorously dried solvent often had very long induction times which could be shortened by the addition of traces of water or of undried solvent or by addition of amines in general but particularly tetramethylethylenediamine, though potential electron-transfer agents, e.g. naphthalene, had no appreciable effect. All these problems could be substantially overcome by sonication which gave rapid initiation and virtually complete solution of the metal in a short period. A similar acceleration was reported by Chou and his collaborators^{10,11} while this work was in progress. Reaction mixtures prepared from phosphines and lithium are invariably dark red to reddish-brown in colour but the



¹⁰ Chou, T.-S., Yuan, J.-J., and Tsao, C.-H., J. Chem. Res. (S), 1985, 18.
¹¹ Chou, T.-S., Tsao, C.-H., and Hung, S. C., J. Org. Chem., 1985, 50, 4329.

phosphides themselves when isolated are much paler coloured, usually yellow, and when redissolved give yellow solutions so that the origin of the characteristic dark red colour is unknown though it may be due to radical-anion formation.^{12,13}

Cleavage of Individual Phosphines: (a) Methylenebis(diphenylphosphine)

This diphosphine was unique in showing no evidence for phenyl group cleavage; the sequence of reactions observed instead is shown in Scheme 2.

The variation in behaviour is presumably because the weakly electronegative diphenylphosphino group makes the diphenylphosphinomethyl moiety more stable as a leaving group than phenyl. The lithiomethyldiphenylphosphine (7), previously obtained by Peterson and Hays¹⁴ by metallation of methyldiphenylphosphine, was not observed in the reaction mixture. The same electronegativity effect of the diphenylphosphino group would acidify the aliphatic protons of (1; n = 1) and cause it to be rapidly converted into the organolithium compound (8), the major product. Our chemical shift value for this species (-0.8 ppm);¹⁵ however, we confirmed our assignment by protonation of the reaction mixtures which regenerates the diphosphine (1; n = 1) together with the secondary phosphines (5) and (11).



(b) Ethane-1,2-diylbis(diphenylphosphine) (1; n = 2)

Cleavage of this compound affords predominantly the diphosphide (2; n = 2) and lithium diphenylphosphide (6), independently of the molar ratios of the starting materials. Occasionally, a very low yield (<5%) of the monophosphide (4; n = 2) is seen and is readily recognizable from its ³¹P n.m.r. spectrum ($\delta -14 \cdot 6, -40 \cdot 75$; $J \, 17 \cdot 5$). The percentage of the reaction proceeding via cleavage of the P-CH₂ bond varied widely and erratically (0-30%) but we were unable to trace this variation to any specific cause though oxygen or oxidation products seemed to favour the side reaction. Addition of bromobenzene portionwise to the reaction mixture resulted in substantial (c. 80%) conversion into the monophosphide (4; n = 2) before reformation of the starting material was observed; an excess of bromobenzene regenerates (1; n = 2) in high yield. Treatment of the diphosphide (2; n = 2) with an excess of methyl iodide or t-butyl chloride resulted in essentially complete conversion into the corresponding

¹² Britt, A. D., and Kaiser, E. T., J. Phys. Chem., 1965, 69, 2775.

¹³ Britt, A. D., and Kaiser, E. T., J. Org. Chem., 1966, 31, 112.

¹⁴ Peterson, D. J., and Hays, H. R., J. Org. Chem., 1965, 30, 1939.

¹⁵ Coloquhoun, I. J., McFarlane, H. C. E., and McFarlane, W., J. Chem. Soc., Chem. Commun., 1982, 220.

ditertiary phosphines (12; n = 2; $R = CH_3$ or Bu^t). We see no spectroscopic evidence for the presumed intermediate (14) or for ethyldiphenylphosphine which would be formed from it by proton abstraction from the solvent and we assume that it decomposes to give ethylene and lithium diphenylphosphide since ethylene may be detected in the effluent gases (Scheme 3).

When we examined the cleavage reaction of propane-1,2-diylbis(diphenylphosphine) with lithium in tetrahydrofuran we observed only lithium diphenylphosphide as the product. Cleavage of the heterocycle (3; m = n = 2) was sluggish and proceeded with ring-opening to give (15) in addition to the diphosphide (2; n = 2).



Phosphines (1; n = 3, 4, 5)

Essentially only the diphosphides were observed regardless of the ratio of metal to phosphine or the stage of the reaction at which the measurement was made. Only two peaks are seen in the spectrum corresponding to the diphosphide and starting diphosphine. That the high-field peak is indeed the diphosphide is confirmed by stepwise arylation with bromobenzene. In each instance when the halide is first added a new peak appears to low field of the diphosphide resonance and further additions of halide steadily increase the intensity of this new peak whilst the diphosphide resonance diminishes. With an excess of bromobenzene the new peak also disappears and the starting diphosphine is reformed in high yield. The Ph₂P absorption in the monophosphides (4; n = 2-4) is close to that for the starting material but (4; n = 5) showed a Ph₂P absorption appreciably upfield ($\Delta\delta - 8\cdot 8$) of its parent diphosphine.

We also briefly examined homogeneous reactions and found that addition of a solution of lithium in liquid ammonia to the diphosphines (1; n = 2,3) in liquid ammonia-tetrahydrofuran results in immediate discharge of the colour but no formation of the diphosphides (2; n = 2,3). The dominant reaction for (1; n = 2) appears to be cleavage of the P–CH₂ bond and though in the case of (1; n = 3) small amounts of the monoanion appear to be formed, large amounts of starting material were always recovered. These reactions are much less clean and much more difficult to carry out reproducibly than those in tetrahydrofuran as solvent and we did not examine them in detail. Reaction with sodium in liquid ammonia-tetrahydrofuran gave better yields, (1; n = 2) giving only P-CH₂ cleavage while (1; n = 3) gave useful amounts of monophosphide (4; n = 3) (50%). The latter reactions are of interest since no detectable (by ³¹P n.m.r.) amount of bond cleavage was observed with sodium in tetrahydrofuran alone even after prolonged sonication, though a pale red colour developed early on. Others^{10,11} have reported ready cleavage of P-C bonds by potassium in tetrahydrofuran but we have not examined this. No useful cleavage of the diphosphines occurred with lithium in hydrocarbon solvents, such as benzene, in the presence of N, N, N', N'-tetramethylethylenediamine (tmda) or hexamethylphosphoric triamide (hmpo) though triphenylphosphine was observed

to cleave readily under these conditions. ³¹P chemical shifts of the phosphide (6) were very different from those in tetrahydrofuran [δ (benzene/tmda) $-27\cdot4$; δ (benzene/hmpo) $-13\cdot65$; cf. δ (tetrahydrofuran) $-20\cdot8$]. It is interesting, however, that addition of tmda to tetrahydrofuran solutions of the diphosphide (2; n = 2) did not produce any substantial change in chemical shift though crystalline diphosphides (2), if present, rapidly dissolved upon addition of tmda or other tertiary amine.

Not unexpectedly, the reactivity of the diphosphides is very high and they oxidize and protonate very rapidly. When we attempted to remove the phenyllithium formed in the cleavage step by adding t-butyl chloride we observed that the corresponding diastereoisomeric di-t-butylphosphines (12; $\mathbf{R} = \mathbf{Bu}^t$, n = 2, 3) were rapidly formed indicating that alkylation was competitive with deprotonation of the halide by phenyllithium. This easy alkylation was unexpected and we re-examined the reaction of lithium diphenylphosphide and t-butyl chloride but observed no reaction, thus confirming Aguiar's original observations.¹⁶ Chou and his collaborators also noted this alkylation¹¹ and suggested that it could be minimized by carrying out the reaction at 0°. We found that treating the phosphides with an excess of t-butyl chloride at -10° resulted in no detectable (³¹P n.m.r.) alkylation. The Chinese workers reported, using mass spectral evidence, that only monoalkylation occurred with t-butyl chloride but this is a consequence of the ease with which the t-butyl groups are lost in the mass spectrometer and the parent diphosphine (12; n = 2, $\mathbf{R} = \mathbf{Bu}^t$) may be seen by chemical ionization mass spectrometry and isolated after conversion into the dioxide.



We briefly examined also the cleavage of some monophosphines in the hope of gaining more information on the limiting factors of the cleavage reaction. Benzyldiphenylphosphine (16) (Scheme 4) and dibenzylphenylphosphine (17) reacted readily with Li/tetrahydrofuran. Whereas the cleavage of (16) was very clean and product assignment unambiguous, the dibenzylphenylphosphine showed many puzzling features which we hope to report on in detail later. However, we found no evidence for loss of phenyl. Tribenzyl-, tris-2-cyanoethyl- and tris-dimethylaminophosphines all failed to react with lithium in tetrahydrofuran even on prolonged sonication.

³¹P n.m.r. data for the diphosphines and their derivatives are given in Table 1.

Discussion

The unexpected formation of the diphosphides in these reactions seemed unusual, the more so as it was essentially independent of the chain length of the diphosphines. Since nothing is known of the structure of these phosphides in solution or the solid state we determined the crystal structure of (2; n = 2), described in detail elsewhere.¹⁷

¹⁶ Aguiar, A. M., Beisler, J., and Miller, A., J. Org. Chem., 1962, 27, 1001.

¹⁷ Brooks, P., Craig, D. C., Gallagher, M. J., Rae, A. D., and Sarroff, A., *J. Organomet. Chem.*, 1987, **323**, C1.

n	\mathbf{R}^1	R ²	δ ^A	J^{B}
1	Ph	Ph	-23.3 ^C	
2	Ph	Ph	$-14 \cdot 2^{\mathbf{D}}$	
	Ph	Li	-14.6, -41.9	$^{3}J_{\rm PP}$ 17.5
	Ph	Н	-15.45, -49.8	${}^{3}J_{\rm PP}$ 21.0
				${}^{1}J_{\rm PH}$ 203.8
	Li	Li	-61.9	•••
	Н	н	-48.9, -48.7	¹ Ј _{РН} 204.7
	CH ₃	CH ₃	-32.3, -32.4	
	Bu ^t	Bu ^t	8.2, 7.6	
	Ph	Et	-14.6, -22.8	${}^{3}J_{\rm PP} 27.5$
	Н	Et	-24.0, -45.2	$^{3}J_{\rm PP}$ 20.6
3	Ph	Ph	-18.5	
	Ph	Li	-16.9, -54.6	
	Ph	Н	-18.7, -55.7	$^{1}J_{\rm PH}$ 204.7
	Li	Li	-63.0	
	Н	н	- 55 • 4	$^{1}J_{\rm PH}$ 204.7
3	Bu ^t	\mathbf{Bu}^{t}	1.1, 7.5	
4	Ph	Ph	$-18 \cdot 1$	
	Ph	Li	-17.8, -53.1	
	Ph	Н	-16.3, -52.8	$^{1}J_{\rm PH}$ 205.0
	Li	Li	- 54·85	
	Н	Н	- 52.8	$^{1}J_{\rm PH}$ 205.0
5	Ph	Ph	-17.6	
	Ph	Li	-26.4, -55.7	
	Ph	Н	-26.4, -54.8	¹ J _{PH} 205∙6
	Li	Li	- 55.6	
	Н	Н	- 54.8	

Table 1. ³¹P n.m.r. data for diphosphines and derivatives PhPR¹(CH₂)_nR²PPh

^A In ppm from external $(DO)_4P^+$ (Glonek, T., and Van Wazer, J. R., J. Magn. Reson., 1974, 13, 390) in tetrahydrofuran; positive shifts are downfield. ^B In Hz. ^C Lit.^{1b} -23.6. ^D Lit.^{1b} -13.2.



A drawing of the result (with the tetrahydrofuran molecules omitted for clarity) is shown in Fig. 1. Though the solid-state structure is interesting it reveals no features which might explain its preferred formation even if this structure persisted in solution and we now believe that this behaviour is due to the phosphine initially binding strongly to the metal surface followed by a slow step (or steps) leading to bond cleavage. If the last process were sufficiently slow it would allow bonding of both ends of the molecule essentially independently of the chain length. This sequence may break down for very long chains but we have not examined this. In his original work on the cleavage reaction⁷ Issleib suggested that the capacity of the phenyl group to delocalize part of the negative charge on the phosphorus was the factor necessary for the reaction to proceed and certainly subsequent spectroscopic^{18,19} and X-ray^{17,20} studies are consistent with contributions of the type (17) to the resonance hybrids of



the phosphides. However, aryldialkylphosphines may lose either an aryl or an alkyl group, usually the former,²¹ so that electron delocalization in the product phosphide can hardly be the driving force. More probable in our opinion is that the ArP grouping is necessary either for the initial absorption or subsequent decomposition of the metal-phosphine complex. It would be surprising if trialkylphosphines did not absorb on the metal surface yet there is no evidence for any decomposition even when a good leaving group such as benzyl is available, though phosphinous halides, R_2PCl , in general react readily.²² We had been particularly hopeful for tris-2-cyanoethylphosphine on the grounds that any 2-cyanoethyl anion formed would be expected to decompose irreversibly, equation (2):

$(NCCH_2CH_2)_3P \xrightarrow{Li} (NCCH_2CH)_2PLi + NCCH_2CH_2Li \rightarrow LiCN + C_2H_4$ (2)

This phosphine should also be less electron-rich than other trialkylphosphines and hence similar in electron density to triphenylphosphine. Its failure to react supports the notion that the ArP grouping is essential in the initial stages of the reaction. Another likely candidate which failed to react was tris-dimethylaminophosphine though here steric factors might intrude. Triethyl and triphenyl phosphites both showed no signs of reaction after many hours sonication.

Nothing is known of the actual mechanism though Kaiser has reported that in the reaction of triphenylphosphine with sodium, potassium or lithium, an initial radical ion formed by electron transfer from metal to phosphine cannot be detected by e.s.r.¹² The spin-active species formed in these and in lithium cleavage reactions²¹ of a range of dialkylaryl- and diarylalkyl-phosphines is the radical-ion formed by electron addition to the phosphide. These deeply coloured species appear to be present from the very first stages of the reaction and though their actual concentration has never been determined they produce no effect on the ³¹P n.m.r. chemical shifts of

¹⁸ Batchelor, R., and Birchall, T., J. Am. Chem. Soc., 1982, 104, 674.

¹⁹ Zschunke, A., Riemer, M., Schmidt, H., and Issleib, K., Phosphorus Sulfur, 1983, 17, 237.

²⁰ Hope, H., Olmstead, M. O., Power, P. P., and Xu, X., J. Am. Chem. Soc., 1984, 106, 819.

²¹ Grim, S. O., and Molenda, R. P., Phosphorus, 1974, 4, 189.

²² Mallion, K. B., and Mann, F. G., J. Chem. Soc., Suppl. 2, 1964, 6121.

the phosphides²¹ and it is reasonable to assume that they are not present in large amount. Their ubiquity and low concentration may have no significance or they may be important intermediates, possibly functioning as electron-transfer species. It seems strange if they have no mechanistic function that their concentration does not build up as the reaction proceeds. It must be noted, however, that radical-anion formation does not accompany cleavage for dilute solutions of triphenylphosphine.¹²

The apparently absolute requirement for the presence of an Ar-P grouping before reaction will occur with lithium in tetrahydrofuran suggests to us that an important step in the cleavage process, possibly even the limiting step, may be electron transfer from the metal to the aryl group, this process being facilitated by the lowering of the energy of the lowest unoccupied molecular orbital by substitution of ring hydrogen by phosphorus. Such a lowering has been observed²³ for substitution by Si, Ge and Sn and the ability of phosphorus(III) to function as an electron-withdrawing agent has long been known.²⁴ Subsequent decomposition of this radical anion to give a radical and an anion could occur followed by electron uptake by the radical, equation (3):

$$\mathbf{R}_{3}\mathbf{P} + \mathbf{L}\mathbf{i} \to \mathbf{R}_{3}\mathbf{P}^{-\bullet}\mathbf{L}\mathbf{i}^{+} \to \mathbf{R}_{2}\mathbf{P}^{-}\mathbf{L}\mathbf{i}^{+} + \mathbf{R}^{\bullet} \stackrel{\mathsf{L}\mathbf{i}}{\to} \mathbf{R}^{-}\mathbf{L}\mathbf{i}^{+} \tag{3}$$

If this were the case, however, it would be expected that the group expelled would be that giving rise to the most stable radical and this makes it difficult to account for the loss of alkyl groups in the cleavage reactions of aryldialkylphosphines. On the other hand, if the organic group were expelled as an anion it would be equally difficult to justify the observed leaving group preference.

³¹ P N.M.R. Spectra

These data are summarized in Table 1. The spectra of the diphosphides (2) show in general a rather small effect due to the phenyl groups. Whereas dialkyl phosphides²¹ show chemical shifts substantially upfield ($\Delta\delta$ -10 to -40) of the corresponding dialkylphosphines, aryl and arylalkyl phosphides are normally found downfield of the parent phosphines,^{18,19,21} a factor generally attributed to electron delocalization from phosphorus to the aromatic ring. This effect reaches an extreme with phosphole anions^{25,26} which absorb far downfield ($\Delta\delta$ 100–140) of the corresponding secondary In contrast, the diphosphides (2; n = 2-5) absorb upfield of the phosphines. corresponding discondary phosphines (13; n = 2-5) though the effect diminishes sharply as the chain length increases ($\Delta\delta$ -13.1 to 0.8). On the other hand the secondary-tertiary phosphines (4; X = H) show the reverse effect ($\Delta\delta$ 7.9 to 0.9) on deprotonation which again decreases rapidly with chain length. These effects are interesting and probably reflect differing solution structures particularly as they seem to be at a maximum for both (2) and (4) when n = 2, 3 but our efforts to obtain more information on this, specifically by low temperature lithium spectra, have been frustrated by instrumental difficulties. Too much should not be made of these relatively small effects, however, as results on monophosphides show considerable variation of chemical shift as a result of structural changes in solution.¹⁹

²⁴ Chatt, J., and Williams, A. A., J. Chem. Soc., 1954, 4403.

²³ Giordan, J. C., and Moore, J. H., J. Am. Chem. Soc., 1983, 105, 6541.

²⁵ Quin, L. D., and Orton, W. J., J. Chem. Soc., Chem. Commun., 1979, 401.

²⁶ Lauzon, G. de, Charrier, C., Bonnard, H., and Mathey, F., Tetrahedron Lett., 1982, 23, 511.

¹ H Spectra

Given the nature of the reaction mixtures interpretation of these was not generally practical, however samples of the phosphides (6) and (2; n = 2) were prepared in perdeuterotetrahydrofuran and, after comparison with the spectrum of starting materials and using spectral subtraction techniques, a clean spectrum of the diphosphide (2; n = 2) was obtained. It showed no very unusual features; the alkyl protons appeared as a pseudo 1:1:1 triplet ($\delta 2.34$, J 7.2 Hz) downfield of the parent diphosphine (c. 1:2:1, t $\delta 2.8$, J 4.2 Hz), no doubt as a consequence of second-order effects associated with these symmetrical diphosphorus compounds.² The aromatic protons of (2; n = 2) are well separated and show less pronounced second-order effects. Their chemical shift values are close to those previously reported for (6).^{18,19} These protons are upfield of those in the parent (1; n = 2; $\Delta\delta 0.5-1.0$), whose aromatic spectrum is, in fact, considerably more complex.

Experimental

General

All manipulations were carried out in an atmosphere of dry argon by using dry solvents deoxygenated by saturating them with argon. All ³¹P n.m.r. measurements were carried out in tetrahydrofuran solvent on a Bruker WP-60 pulsed n.m.r. machine operating at 24.28 MHz with a digital resolution of ± 0.5 Hz. Chemical shift values are the average of a number of different runs and were reproducible to ± 0.5 ppm. Part of this variation may be due to concentration effects since this varied widely (0.1-0.5 M) in different runs. Substantial concentration dependent variations have been observed for phenyl phosphide and diphenyl phosphide.¹⁷ Occasionally (D_6) benzene was added to reaction mixtures to provide a lock signal and this resulted in downfield shifts of c. 1 ppm. Spectroscopic results are summarized in Table 1. The structures of the phosphides are confirmed in two ways: (A) arylation with an excess of bromobenzene to reform starting material which may be identified by direct comparison; and (B) protonation, followed by measurement of the undecoupled spectra to identify the secondary phosphines which appear as broadened doublets as a consequence of the large ${}^{1}J_{\rm PH}$ (≈ 200 Hz). Propane-1,2-diylbisdiphenylphosphine was prepared by the literature method²⁷ but was not obtained crystalline though its ³¹P n.m.r. ($\delta_A - 20.7$; $\delta_B 1.36$; $J_{AB} 20.5$) agreed with literature values.²⁸ Treatment with an excess of sulfur gave colourless crystals of propane-1,2-diylbis(diphenylphosphine sulfide), m.p. 168–169° (CH₃OH) (Found: C, 67.9; H, 5.3; S, 13.4%; m/z, 476 (8%). $C_{27}H_{26}P_2S_2$ requires C, 68.1; H, 5.5; S, 13.4%; mol. wt, 476). ³¹P n.m.r. (C₆H₆) δ_A 54.1; δ_B 41.5; J_{AB} 57.8. All reactions involving phosphides were carried out at room temperature or below to avoid possible complications arising from ether cleavage.^{21,22,29}

Except where noted, all phosphines were commercially available materials (Aldrich, Strem) and their purity was checked by m.p. and ³¹P n.m.r. Ethylene, formed in the cleavage of (1; n = 2), was detected by passing argon through the reaction mixture, then through a cold trap and into a solution of Br₂ in CCl₄. The product, BrCH₂CH₂Br, was identified by ¹H n.m.r. and g.l.c. Sonication of phosphide preparations was carried out by immersing the reaction flask in water in a commercial ultrasonic cleaning bath. Dissolution of the metal was complete in 0.5-1 h.

Ethane-1,2-diylbis(t-butylphenylphosphine) (12; $R = Bu^{t}$)

A solution of the diphosphide (2; n = 2) prepared from the diphosphine (1; n = 2) (9.5 g) and lithium (0.9 g, 4 mol) in tetrahydrofuran was allowed to react with t-butyl chloride (6.1 g, 2 mol) at room temperature (2 h). The solution was diluted with water (300 ml) and extracted

²⁷ Fryzuk, M. D., and Besnich, B., J. Am. Chem. Soc., 1978, 100, 5491.

²⁸ Payne, N. C., and Stephan, D. W., J. Organomet. Chem., 1981, 221, 203.

²⁹ Issleib, K., and Roloff, H.-R., Chem. Ber., 1965, 98, 2091.

three times with toluene (400 ml) which was dried and evaporated to afford the crude *meso*- and DL-*phosphines* as a waxy solid. ³¹P n.m.r. δ 8.2, 7.6. The electron impact mass spectrum of the mixture did not show a parent ion but the base peak was at m/z 302 (M – 56). The chemical ionization technique (isobutane as ionizing gas) showed a strong peak m/z 359 (M + 1). Oxidation of the mixture (1 g) with H₂O₂ in acetone gave a mixture of the corresponding dioxides which after chromatography on silica gel and elution with toluene/ethanol (3:1) afforded the oxides as a white crystalline solid, m.p. 150–185°. ³¹P n.m.r.: δ 52.4, 50.9. Repeated recrystallization (EtOAc) gave a single pure isomer of *ethane-1,2-diylbis(phenyl-t-butylphosphine) dioxide* as colourless needles, m.p. 209–212° (Found: C, 62.0; H, 8.6. C₂₂H₃₂O₂P₂.2H₂O requires C, 62.0; H, 8.5%). ¹H n.m.r. δ 1.0, 18H, ψ t,² t-Bu; 2.26, 5.3H, bs, CH₂CH₂; 7.53, 10H, bm, ArH. ³¹P n.m.r. δ 52.65 (CHCl₃). m/z 391 (M+1, 2%); 333 (M – C₄H₉, 100%); 277 (M – C₈H₁₇, 100%). v_{max} 3500 (OH); 1190 (P=O) cm⁻¹.

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