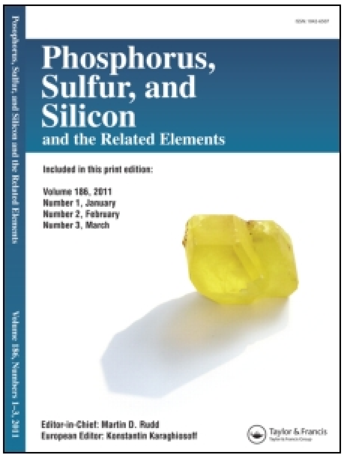

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Preparation & Stereochemistry of some Diphosphorus Heterocycles

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PREPARATION & STEREOCHEMISTRY OF SOME DIPHOSPHORUS HETEROCYCLES

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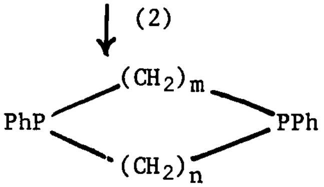
Abstract Cleavage of $Ph_2P(CH_2)_nPPh_2$(n=2-5) with Li in THF provides a convenient source of the corresponding dianions which may be alkylated with $X(CH_2)_nX$ (X=Cl,Br,n=1-3) to give diphosphorus heterocycles with a ring size 5-7. These are separated into their stereoisomers and stereochemical assignments made. An alternative route to an eight-membered ring is described.

We have long had an interest in diphosphorus heterocycles and wished to obtain stereochemically pure samples of some simple examples for three reasons: (i) Their coordination chemistry should prove interesting particularly in relation to homogeneous catalysis; (ii) The spectral and stereochemical properties of the simpler members needed to be determined to provide a basis for structural and stereochemical assignments in more complex molecules; and (iii) We hoped to utilise them in the synthesis of phosphorus heterocycles containing one or more bridgehead phosphorus atoms since the chemistry of these systems is virtually unknown. In the main we utilised the alkylation of diphosphides, a preparative route developed by Issleib and his collaborators.[1] To prepare the diphosphides we used the cleavage of phenyl groups from 1,n-bisdiphenylphosphinoalkanes with lithium. Attempts to remove the PhLi with *t*-BuCl were complicated by alkylation at phosphorus.[2]

$$Ph_2P(CH_2)_nPPh_2 \longrightarrow PhP(Li)(CH_2)_nP(Li)Ph + 2PhLi$$

(1)



These reactions were more complex than expected but were relatively easy to follow by ^{31}P n.m.r. In the case of (1,n=1) exclusive cleavage of the alkyl group was observed and also to a lesser extent in (1;n=2). Most surprising was the exclusive formation of the diphosphides (2) regardless of the ratio of diphosphine to lithium. The expected intermediate monophosphides could only be observed by arylation of (2). An x-ray structure of the diphosphide (2;n=2) (Fig. 1) revealed no structural features to account for this unexpected behaviour. We now believe that this is simply a consequence of a rapid initial binding of the molecule to the metal surface followed by a much slower cleavage step. Such a process should allow both ends of the diphosphine to bind to the metal before further reaction occurs.

Alkylation of the diphosphides proceeded as expected and afforded the heterocycles 3-6 which were separated into their stereoisomers. The eight-membered ring(7)was prepared from 1 (n=4) by quaternisation, saponification, and reduction with $HSiCl_3$. Only one of the diastereoisomeric dioxides of(7)reduced in this way.

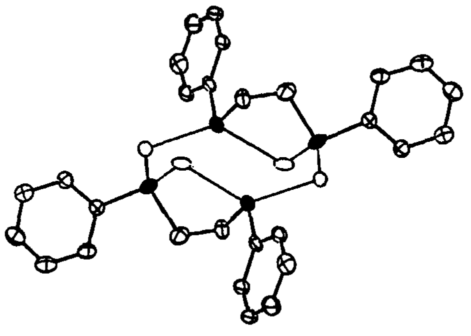


Fig. 1
X-ray structure of 2(n=2)

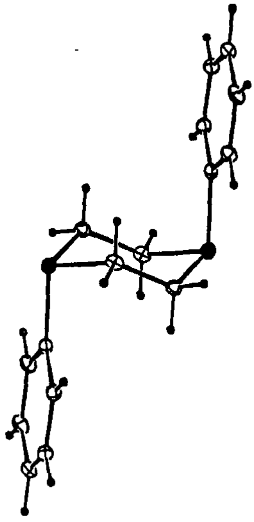
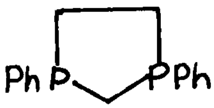
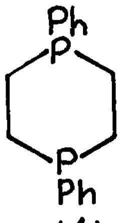


Fig. 2
X-ray structure of *trans*-4

Stereochemistry was assigned on the basis of mass and infra-red spectra and in the *trans*-1,4-diphosphinane by x-ray (Fig. 2). *Trans* isomers in general show greater phenyl transfer from one phosphorus to the other than in the *cis* isomers as reflected in the relative abundance of the ion (9) in the EI mass spectrum. The i.r. spectra show a striking difference in the 750-800cm^{-1} region with one of the isomers showing two strong peaks and the other four which we attribute to phenyl group absorptions either in identical or slightly different environments.


(3)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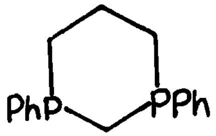
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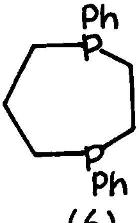
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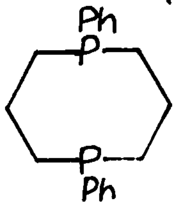
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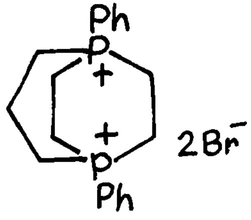
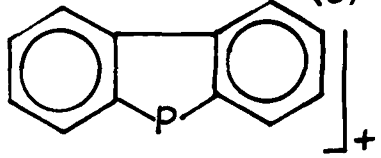

(8)


(9)

We also examined the action of acetylene on the diphosphides (2;n=2,3) since Aguiar had shown that lithium diphenylphosphide reacted readily to give (1;n=2)[3] but the dominant reaction for the diphosphides (2;n=2-5) was deprotonation to give the corresponding disecondary phosphines, presumably due to the enhanced basicity of aralkyl versus diaryl phosphides. In the presence of a strongly basic amine (DBU), a low yield of the heterocycles (4) and (6) was obtained.

Contrary to a previous report, attempts to further cyclise (4) by bis quaternisation with ethylene dibromide failed, but did succeed with (6) giving (8). In heterocycles where two or fewer methylenes separate the two phosphorus atoms, quaternisation at one site de-activates the other and makes the intermolecular reaction with another molecule of diphosphine more favourable.

A summary of some physical data for the stereoisomers is given below:

	M.p. (^{o}C)		δ^{31}P	
	c	t	c	t
3	51-52	76-77	-0.75	-1.5
4	98-101	168-170	-27.5	-28.0
5	53-54		-33.5	-34.1
6	72-73	73-74	-20.3	-25.9
7	74-76.5		-21.1	

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