

REACTIONS OF METAL PHOSPHIDES AND ARSENIDES. A RARE EXAMPLE OF DEBROMINATION

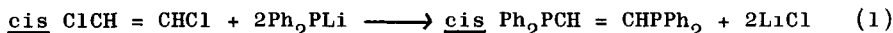
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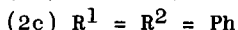
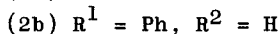
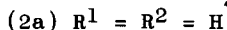
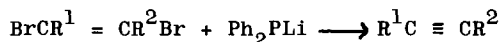
Attack on halogen by trivalent phosphorus has been commonly observed and these compounds have been widely used as debrominating agents.<sup>1</sup> Attack on halogen by phosphide anions is rare<sup>2</sup> and we are aware of only one example of debromination, that of 1,2-dibromoethane to give ethylene.<sup>3</sup> In view of this a similar debromination of vinyl dibromides seemed likely.

Aguiar has investigated the reactions of diphenylphosphide with 1,2-dichloroalkenes<sup>4</sup> and obtained the corresponding diphosphines (1). We have now shown that similar reactions with 1,2-dibromoalkenes follow a quite



different route involving initial attack on halogen, presumably due to the greater polarisability of bromine than chlorine.

The addition of 1,2-dibromoethylene (2a; 64% cis:36% trans by nmr) to a refluxing solution of an equimolar quantity of lithium diphenylphosphide in THF gave, after 2 hours, acetylene. A similar reaction with two mole equiva-



lents of phosphide gave acetylene and after oxidation with hydrogen peroxide and chromatography on silica gel, trans-1,2-vinylenebis(diphenylphosphine) dioxide (3)<sup>4</sup> in small yield.

Analogous reactions with 1,2-dibromostyrene (2b; 29% cis:71% trans by nmr)<sup>5</sup> and 1,2-dibromostilbene (2c) gave the corresponding acetylenes (see Table). Appreciable amounts of unreacted dibromides were recovered from reactions with one mole equivalent of phosphide; in the reaction with dibromostilbene, (1,2-diphenylvinyl)diphenylphosphine oxide (4) was also isolated after chromato-

graphy.

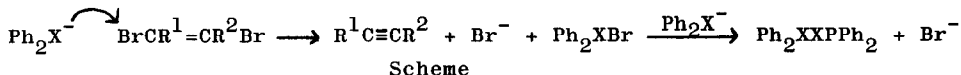


Reaction of dibromides (2a), (2b) and (2c) with one and two mole equivalents of lithium diphenylarsenide gave the corresponding acetylene (see Table)

**TABLE:** Percentage Yields of Acetylenes from Debromination Reactions

Dibromide	Lithium diphenylphosphide		Lithium diphenylarsenide	
	one mole	two mole	one mole	two mole
BrCH=CHBr	50	80	33	46
BrCPh=CHBr	7	37	2	53
BrCPh=CPhBr	19	33	32	54

The recovery of dibromide and the lower yields obtained from reactions with an equimolar quantity of phosphide or arsenide suggest a 1:2 stoichiometric requirement for the reaction and hence the mechanism shown in the scheme.



Attempts to gain information about the stereochemistry of the debromination were unsuccessful due to the rapid cis to trans isomerisation of the dibromides under the reaction conditions.<sup>6</sup>

The yields of phenyl acetylene and tolan are probably reduced by further reaction with phosphide<sup>7</sup> and arsenide<sup>8</sup>. This was confirmed in the case of 1,2-dibromostilbene by the isolation of (4). Volatility and a relative low reactivity towards nucleophiles presumably excludes this reaction for acetylene, although smaller steric effects apparently allow some substitution at carbon in this case.

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### References

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2. E.g. W. Hewertson and I.C. Taylor, Chem.Comm., 1970, 119.
3. K. Issleib and D.W. Muller, Chem.Ber., 1959, **72**, 3175.
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6. It has been suggested that phosphines, being 'soft' two electron nucleophiles, probably give only anti-elimination (I.J. Borowitz, D. Weiss, and R.K. Crouch, J.Org.Chem., 1971, **36**, 2377).
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