

REACTIONS OF METAL PHOSPHIDES AND ARSENIDES. EVIDENCE FOR DEHYDROBENZENE IN
PHOSPHORUS-INDUCED DEHALOGENATIONS

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The strongly basic properties of metal phosphides have been used to generate dehydrobenzene from fluorobenzenes via ortho fluoroanions.¹ However, the generation of dehydrobenzene through dehalogenation by phosphorus compounds has not been reported. Our unsuccessful attempts to dehalogenate 1,2-dihalo benzenes with tertiary phosphines were probably predictable since these phosphines will only dehalogenate relatively reactive dihalides.²

In view of our recently reported³ success in dehalogenating vinyl dibromides with metal phosphides and arsenides we have investigated the reaction of orthodihalobenzenes with these reagents.

1,2-Dibromobenzene was added to a refluxing solution of two molar equivalents of lithium diphenylphosphide and five molar equivalents of furan in THF and refluxing continued for 3 hours. After oxidation with aqueous hydrogen peroxide, glc (2% SGR at 150°) showed the presence of 1,2-dibromobenzene (29%) and chromatography on silica gel (ethyl acetate) gave triphenylphosphine oxide, m.p. 156-157°, and traces of 2-bromophenyldiphenylphosphine oxide, m.p. 136-7°; glc (2% SGR at 245°) gave yields of 55% and 1% respectively for these latter products and indicated the presence of a further product of shorter retention time. Glc under appropriate conditions confirmed the absence of >0.05% of the benzyne-furan adduct (1), biphenylene, naphthalene and naphthols.

Analogous reactions with 1,2-dichloro- and 1,2-diiodobenzene gave triphenylphosphine oxide and the corresponding 2-halophenyldiphenylphosphine oxide (Table), while 2-halodiazonium salts gave triphenylphosphine oxide as the

only isolated product. Reactions with three molar equivalents of metal phosphide or with two molar equivalents at 0° gave similar products but in reduced yields. In no case was the adduct (1) detected.

The reaction of 1,2-dihalobenzenes with lithium diphenylarsenide [containing $\langle 5\% (C_6H_5)_3As \rangle$] gave tarry products from which variable yields of triphenyl arsine could be isolated by chromatography on silica gel.

Table: Reaction of Phosphide with 1,2-Dihalobenzenes

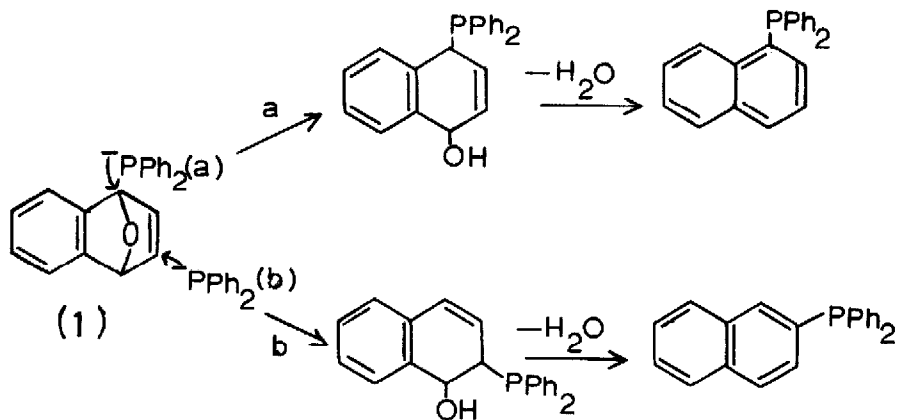
Halide	Percentage Yields		
	Dihalide	$(C_6H_5)_3PO$	$o-XC_6H_4(C_6H_5)_2PO$
Dichloro	14	20	0.35
Dibromo	29	55	1.0
Diiodo	49	20	0.3

In view of the recent report⁴ that the adduct (1) reacts with strong bases our failure to observe (1) could be explained by decomposition in the presence of excess phosphide. Indeed, refluxing the furan adduct with two molar equivalents of phosphide in THF for 3 hours and oxidative work-up followed by HPLC (spectrophysics 3500, 3 mm x 250 mm, 5 μ spherisorb silica, 1.2 ml/mm, 40% CHCl₃/pentane) gave 1- and 2-naphthyldiphenylphosphine oxides (2:3), authentic samples of which were prepared from the corresponding Grignard reagents. Reinvestigation of our original reactions showed the presence of small amounts of naphthyldiphenylphosphine oxides in the case of 1,2-dibromo- and 1,2-diiodo benzene, but not in the case of 1,2-dichlorobenzene.

In the presence of strong base diphenylisobenzofuran (DPB) appears to be a more satisfactory trapping agent than furan.⁴ The major product of phosphide induced dehalogenation in the presence of DPB, followed by peroxide work-up, was 1,2-dibenzoylbenzene⁵, m.p. 147-148°, but glc (2½% SGR, 240°) and mass spectrometry showed the presence of the benzyne adduct (2) and the derived products (3) and (4).

presently investigating the details of the mechanism.

The two alternative sites for nucleophilic attack on the adduct (1) followed by dehydration, provide routes to 1- and 2-naphthylphosphines (Scheme 2).



Scheme 2

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