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REACTIONS OF METAL PHOSPHIDES AND ARSENIDES. ADAMANTENE FROM 1,2-DIBROMO- AND 1,2-DIIODOADAMANTANE

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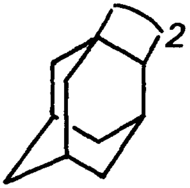
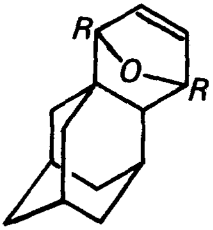
Under circumstances where nucleophilic attack on carbon is unfavourable, metal phosphides act as adequate dehalogenating agents to give acetylenes from vinyl halides[2] and dehydrobenzene from 1,2-dihalobenzenes[3]. In view of this the generation of anti-Bredt olefins by a similar reaction of the appropriate dihalide seemed likely. Adamantene has proved especially elusive since the generally used Hoffmann elimination route failed and in dehalogenation reactions only the iodides provided any evidence for an adamantene intermediate.[4,5]

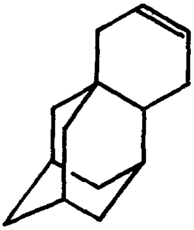
The addition of 1,2-diiodoadamantane to a refluxing solution of lithium diphenylphosphide in THF, followed by refluxing for two hours and oxidation with hydrogen peroxide gave adamantene dimer (1) (identified by glc comparison with an authentic sample[4] on 2-CEMS, SGR and Silicone grease columns), 1-adamantyldiphenylphosphine oxide, m.p. 219-222°, and 2-adamantyldiphenylphosphine oxide, m.p. 209-211°, which were spectroscopically identical with authentic samples prepared by the reaction of phosphide with 1- and 2-bromoadamantane followed by oxidation. Glc (2m silicon gum rubber column at 240°) also showed the presence



(1)



(2) R=H
(3) R=Me



(4)

of an as yet unidentified compound which combined glc/ms showed to be isomeric with the adamantylphosphine oxides. An analogous reaction with 1,2-dibromoadamantane gave similar results, but reaction with 1,2-dichloroadamantane gave trace amounts of 1- and 2-adamantyldiphenylphosphine oxides and 1-chloro adamantane as the only identified products. The results are summarised in the Table.

Similar reactions in the presence of furan or 2,5-dimethylfuran, gave the same products and no trace of the adducts (2) or (3)[6]; however, a reaction at 0° for 2 days in the presence of butadiene gave the adduct (4)[4] in low yield (glc at 215° on 2m SGR on chromosorb W).

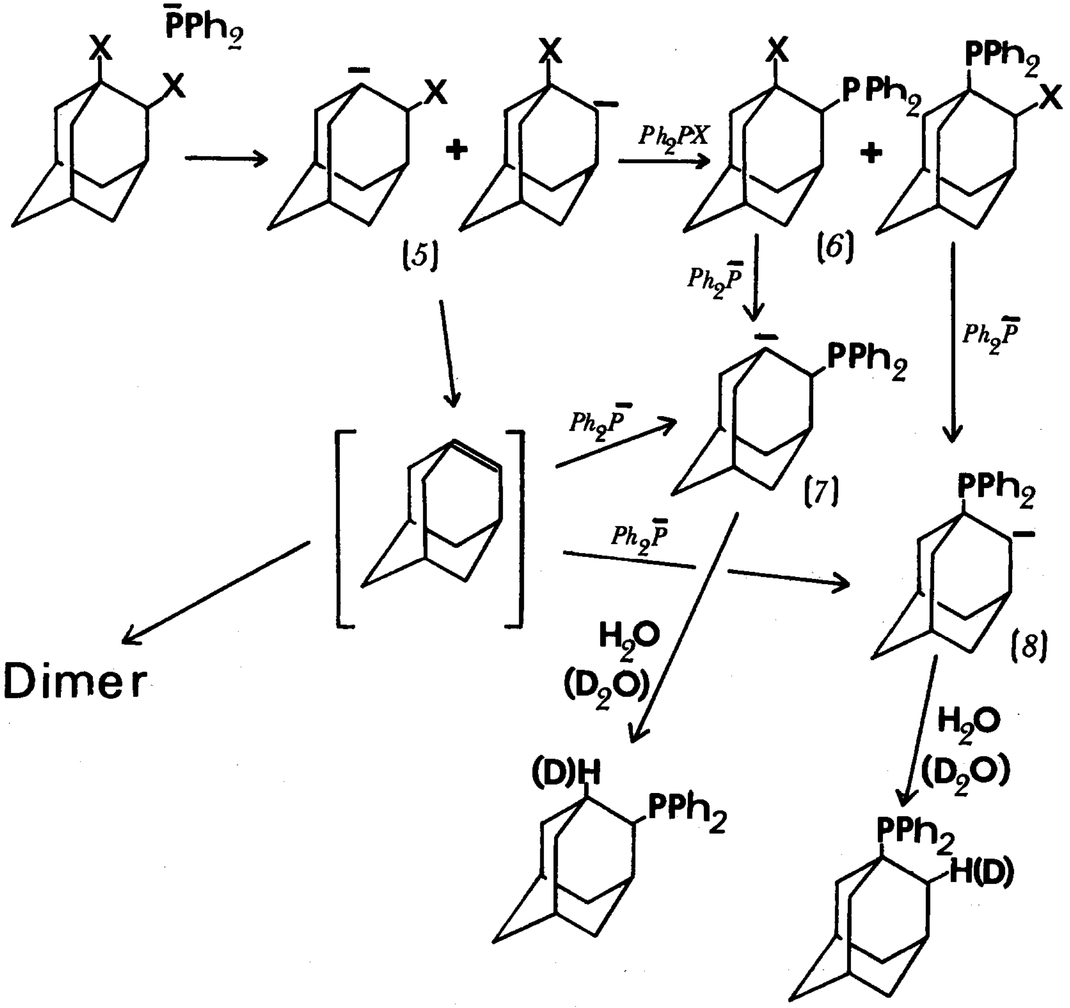
Table. Reaction of Phosphide with 1,2-Dihaloadamantanes

Halide	Percentage Yields			
	Dimer[a]	1-Adamantyl-phosphine oxide[a]	2-Adamantyl-phosphine oxide[a]	Unknown[b]
Dichloro	0	0.2	0.8	0
Dibromo	5	7.4	3.7	7.7
Diiodo	4	10.3	5	13.9

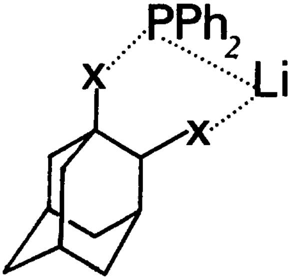
(a) estimated by glc (2m SGR at 240°) and by HPLC (Spectraphysics 3500, 3mm x 250mm, 5µ spheresorb silica, 1.8ml/min, 35% $CHCl_3$/pentane)

(b) estimated by glc as in (a) assuming a similar detector response to that of adamantyldiphenylphosphine oxides. Similar results were obtained from HPLC using an ultraviolet detector (column as in (a), 1.2ml/min, 5% $CHCl_3$/pentane).

Scheme 1 summarises possible mechanisms of formation for the observed products. The isolation of the dimer (1) and the adduct (4) from reactions with 1,2-dibromo- and 1,2-diiodoadamantane strongly supports the involvement of such an intermediate from the dibromo compound. That the formation of 1- and 2-adamantylphosphine oxides also involves adamantene in these cases is indicated by both the similar product ratio of 1- to 2-oxides in each case and by its absolute value, since on the basis of carbanion stability an adamantene route should give 1-adamantyldiphenylphosphine oxide as the major isomer (in spite of Hammond's postulate[7] all known nucleophilic additions to strained alkenes are regioselective in a Markovnikov manner). The opposite preference would be predicted for a route via the haloadamantyldiphenylphosphines (6) and this is observed in the reaction with 1,2-dichloroadamantane. Although deuteration studies do not distinguish between the alternative pathways they do implicate the anions (7) and (8) since both 1- and 2-adamantyldiphenylphosphine oxide obtained from experiments quenched with D_2O were $>$ 80% monodeuterated.



The detailed mechanism of adamantene formation from the adamantyl anion (5) is still obscure since this intermediate faces the problem of non-alignment of the lone-pair orbital and the bond to the leaving group. No explanation of this has been offered, although sp^3 hybridisation of the lone pair in (5) could provide some small overlap.[4] In view of the tendency for alkyl lithiums to exist as aggregates in solution[8] it is significant that adamantene does not appear to be an intermediate in experiments with sodium diphenylphosphide, and a species such as (9) would presumably assist the halide leaving group. The involvement of species related to (9) has been suggested[9] in the reactions of phosphides with halobenzenes.



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