

The Question of Acenaphthylene- and Benzyne-Participation in Novel Transformations of Some Phosphole Ylides

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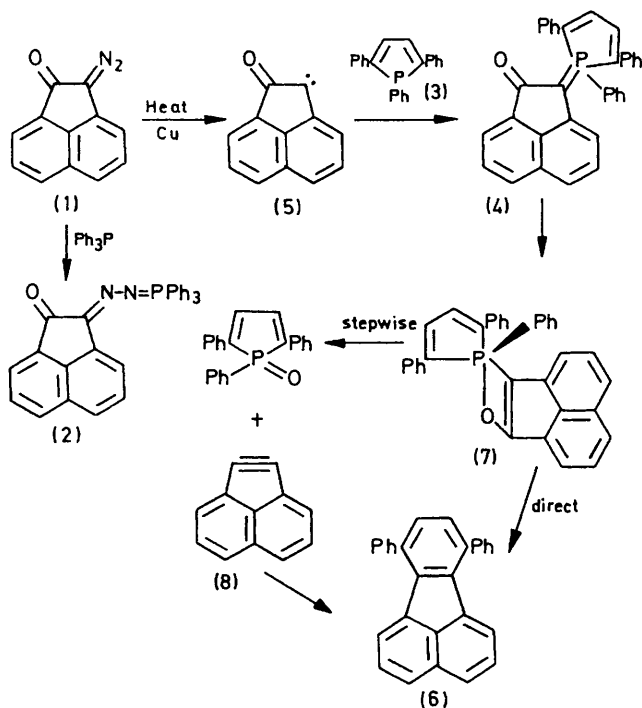
Summary 1,2,5-Triphenylphosphole reacts with 1-diazo-acenaphthen-2-one (1) to give the corresponding strained phosphole ylide (4), which, at 175° in diphenyl ether readily gives 7,10-diphenylfluoranthene (6) while the benzyne-type adduct, 1,4-diphenylnaphthalene, is obtained from (a) 1,2,5-triphenylphosphole and *o*-bromophenol and (b) 1,2,5-triphenylphosphole oxide and HBr.

WE report further examples¹ of the remarkable transformations which ylides based on the strained P^{IV} phosphole group undergo.

While triphenylphosphine reacts readily with 1-diazo-acenaphthen-2-one (1) to give the phospholazine (2), in the expected fashion, 1,2,5-triphenylphosphole (3), being less nucleophilic due to ring strain, reacts only above the

decomposition point (150°) in the presence of copper, to give the phosphole ylide (4), presumably *via* capture of the 1,2-ketocarbene (5). The latter ylide smoothly decomposes at 175° in diphenyl ether to give 7,10-diphenylfluoranthene (6) (64%), as shown by comparison with an authentic specimen.² An attractive explanation of this reaction is that it proceeds as a result of relief of ring strain in passing from the strained ylide (4) through the strain-free P^V intermediate (7) to 1,2,5-triphenylphosphole oxide and the hitherto undetected 1,2-acenaphthylene (8), which together then react *via* cycloaddition to give 7,10-diphenylfluoranthene, and the expectation of this was the rationale of our experiment (Scheme 1). This is not supported by successful trapping of the elusive aryne by tetraphenylcyclopentadiene, however, although it should be noted that alterna-

tive routes via intramolecular rearrangement or bimolecular reaction of the ylide (4) would require the ascent of very formidable steric barriers.

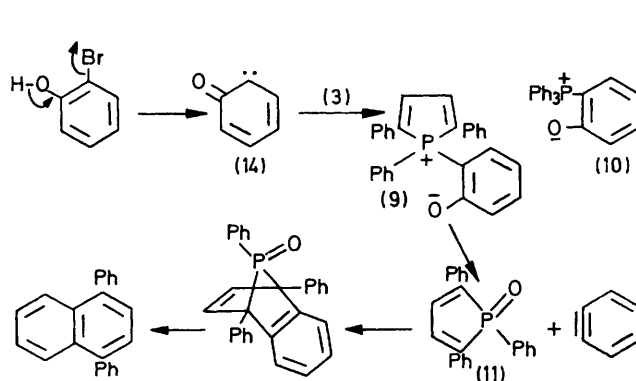


SCHEME 1

In a related case we attempted to prepare the ylide (9) in the expectation that it would decompose to give benzene, in contrast to the known failure of the non cyclic betaine (10) to do so.³ On attempting to prepare (9) by reaction at 250° of 1,2,5-triphenylphosphole (1 mol) with *o*-bromophenol (1 mol), following the preparation of *p*-hydroxyphenyl-triphenylphosphonium bromide from triphenylphosphine and *p*-bromophenol,⁴ we obtained instead 1,4-diphenyl-naphthalene (34%), thus suggesting reaction as in Scheme 2.

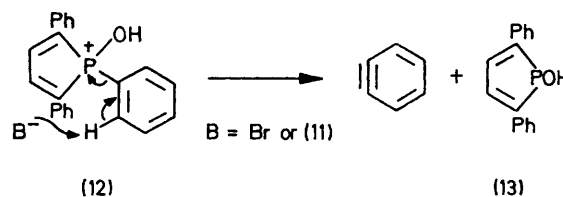
Since hydrobromic acid is evolved in this reaction we also tested the possibility that 1,4-diphenyl-naphthalene arose either entirely or partially from reaction of either triphenylphosphole or triphenylphosphole oxide (11) with HBr. Control experiments established that reaction of catalytic amounts of HBr with the phosphole oxide at 240° gave 1,4-diphenyl-naphthalene (23%). Since no reaction occurred in the absence of HBr, and none with the phosphole and HBr, then reaction at least in part, by Scheme 3 is suggested, *via*

protonation of the phosphole oxide to give a charged, strained quasiphosphonium intermediate (12) which in this case achieves release of strain by elimination of benzyne and presumably the phosphorus moiety (13) which, being trivalent as well as five membered, is unstrained.



SCHEME 2

We stress that we are unable, at this stage to comment on the relative or absolute importance of Schemes 2 and 3 and, although models show them to be very unlikely, we are unable to discount intramolecular routes, because attempts to trap benzyne by added anthracene failed.



SCHEME 3

Finally, we draw attention to the fact that the mechanism of the reaction of bromophenols with triphenylphosphine⁴ is unknown. Our demonstration⁵ of the participation of 1,2-ketocarbene (14) in thermolysis of sodium *o*-bromophenoxide suggests that serious consideration should be given to the possibility that the former reaction may also involve this intermediate (Scheme 2).

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² E. D. Bergmann, *Nature*, 1948, 161, 889.

³ H. J. Bestmann and G. Hofmann, *Annalen*, 1968, 716, 98.

⁴ R. N. McDonald and T. W. Campbell, *J. Amer. Chem. Soc.*, 1960, 82, 4669; L. Horner, H. Hoffmann, H. G. Wippel, and D. Michael, *Ber.*, 1962, 95, 523.

⁵ J. I. G. Cadogan, J. T. Sharp, and M. J. Trattles, *J.C.S. Chem. Comm.*, 1974, p. 900.