On the Mechanism of Reductive Cyclisation of Nitro-compounds by Tervalent Organophosphorus Compounds

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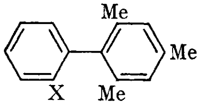
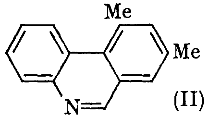
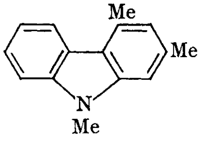
MANY extensions of the reductive cyclisation of nitro-compounds by tervalent organophosphorus compounds[1] have been described.[2] The main mechanistic interest in these cases centres on the possibility of the participation of nitrenes, evidence for which is generally taken to be the occurrence of abstraction and insertion reactions with C–H bonds. Thus, the formation of 8,10-dimethylphenanthridine (II), 2,4,9-trimethylcarbazole (III), and 2′-amino-2,4,6-trimethylbiphenyl (IV) has been attributed to the participation of a nitrene in the decomposition of 2′-azido-2,4,6-trimethylbiphenyl (I; X = N_3) in hexadecane at 230°.[3]



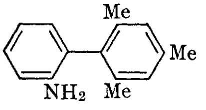
(I)



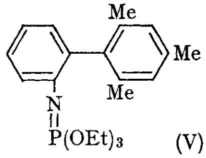
(II)



(III)



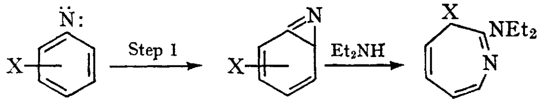
(IV)



(V)

Investigation of the reaction of 2′-nitro-2,4,6-trimethylbiphenyl (I; X = NO_2) with excess of triethyl phosphite has now led to the detection of (IV; 13%) and triethyl *N*-(2′,4′,6′-trimethylbiphenyl-2-yl)phosphorimidate (V; $\geqslant$ 15%, by comparison with an authentic specimen). Products of insertion, (II) and (III), were absent (undetectable by g.l.c.). These results are compatible with the intermediacy of a nitrene which abstracts hydrogen to give (IV) and couples with triethyl phosphite, present in excess, to give (V), rather than undergo the presumably less energetically favourable insertions to give (II) and (III). In accord with this, repetition of the experiment in an excess (*ca.* 50 mol.) of (A) isopropylbenzene and (B) t-butylbenzene, under which conditions the coupling reaction to give (V) would be expected to be reduced and the insertion reactions to be enhanced, gave, in addition to (IV) and (V), the insertion product (II) [(A), 14%; (B) 12%)]. Further, in (A) the amount of hydrogen abstraction increased [(IV); 32% *cf.*, 19% in (B)] with the concomitant formation of bi-α-cumyl (11%). This suggests abstraction by a triplet species to give an α-cumyl radical which subsequently dimerises. In these experiments the identification of (V) was confirmed by hydrolysis to, and comparison with, authentic diethyl *N*-(2′,4′,6′-trimethylbiphenyl-2-yl)phosphoramidate.

Related to this problem is the suggestion that phenylnitrene and 7-azabicyclo[4,1,0]hepta-2,4,6-triene (VI; X = H) are successive intermediates in the ring expansion which occurs on decomposition of phenyl azide in the presence of amines (Scheme 1).[4]



Scheme I (VI) (VII)

This ring expansion has been elegantly utilised[5] to support the suggestion[6] of nitrene participation in the triphenylphosphine-deoxygenation of nitrosobenzene (Scheme 1; X = H). Application of this test to the case of nitro-compounds was difficult in view of the more drastic conditions required. In this connection we have now shown that approximate half-lives for cyclisation of 2-nitrobiphenyl in excess (15–20 mol.) of various tervalent phosphorus compounds are as follows: $(EtO)_2PMe$, 160 min./61°; $(Et_2N)_3P$, 40 min./111°; $(EtO)P(NEt_2)_2$, *ca.* 5 min./121°; $(EtO)_3P$, 50 min./145°. Reaction of diethyl methylphosphonite, the most reactive reagent, with nitrobenzene and with 2-nitrobiphenyl in excess of diethylamine has now been shown to give 2-diethylamino-3-*H*-azepine (VII; X = H; 83%) and 2-diethylamino-3-phenylazepine (VII; X = Ph; 13%) respectively, thus indicating a strong similarity between these reactions and those of phenyl azide in diethylamine. In addition to the latter azepine, carbazole (67% compared with 86% in the absence of the amine) was also formed. This raises several possibilities, including (i) that both products are formed from the nitrene or some other electron-deficient species without the intermediacy of (VI), (ii) that both are formed from (VI), or (iii) that Step 1 is reversible and that carbazole is formed from the nitrene while the azepine is formed from (VI). Regardless of these possibilities it appears from the above experiments that the parallelism between decomposition of azides and tervalent organophosphorus-reduction of nitro-compounds is established in these cases, and that the evidence in favour of nitrene participation in the latter reaction is as acceptable as in the former.

[*Added in proof:* G. Smolinsky and B. I. Feuer (*J. Org. Chem.*, 1966, **31**, 3882) have now reported that (I; X = NO_2), in excess of triethyl phosphite, gives, after hydrolysis, a trace of (IV) and a compound (18%) tentatively identified by n.m.r. as diethyl *N*-(2′,4′,6′-trimethylbiphenyl-2-yl)phosphoramidate.]

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