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ON THE MECHANISM OF DEOXYGENATION OF AROMATIC NITRO AND NITROSO COMPOUNDS

P.K. Brooke, R.B. Herbert and F.G. Holliman

Department of Organic Chemistry, The University, Leeds LS2 9JT

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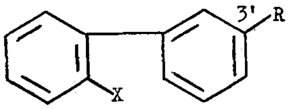
The nature of the products obtained in the deoxygenation of nitro and nitroso compounds by tervalent phosphorus compounds points to the involvement in some cases of nitrenes as intermediates particularly when the same products are obtained from the thermolysis of the corresponding azides.[1,2] A comparison of the ratios of products obtained has also been used as a test for common intermediates in the deoxygenative and thermolytic reactions.[3,4] The widely differing conditions employed in these reactions, however, makes close comparison of the nature of the products and their ratios unreliable. This objection has been removed by carrying out the two reactions in the same medium by novel application of a technique widely used in biosynthetic studies: if a pair of substrates, one isotopically labelled, are reacted in the same medium any common intermediate would be pooled and all products arising therefrom would carry the label in equal proportions.

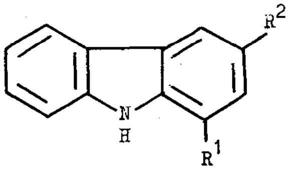
The thermal cyclisation of 3'-substituted 2-azidobiphenyls and deoxygenative cyclisation of the corresponding nitroso compounds were chosen for study. Accordingly the dideuterio nitroso compound was reacted with triethyl phosphite in the presence of undeuteriated azide; 1 molecular equivalent of triethyl phosphite was used as azide reacted rapidly with excess reagent affording the phosphorimidate by a non-nitrene mechanism.[5] Decalin, chlorobenzene and triethyl phosphate were used as solvents. The results (table 1) show that the pathways in chlorobenzene and decalin are different and thus the deoxygenation reaction proceeds largely by a non-nitrene mechanism whilst the reactions in triethyl phosphate proceed via a common intermediate. It follows from the differing results in the three solvents that this common intermediate in triethyl phosphate cannot be the nitrene and is most probably the bipolar species (2) formed directly from the nitroso compound by reaction with triethyl phosphite and from the azide by reaction of the intermediate nitrene, or perhaps the azide itself, with triethvl phosphate.



R = Me or OMe

1 $X = N_3$ or NO

2 $X = \overset{-}{N}\text{-O-}\overset{+}{P}(OEt)_3$



3 R^1 = Me or OMe, R^2 = H

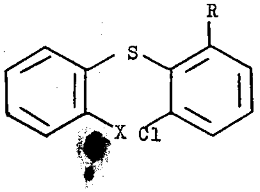
4 R^1 = H, R^2 = Me or OMe

Table 1. Cyclisation of 3,5-dideuterio-2-nitroso- and 2-azido-3'-substituted biphenyls (1) at 150-155° except in chlorobenzene when 132°.

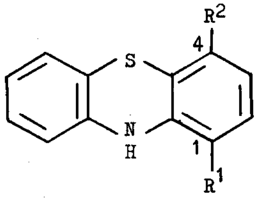
3'-Substituent	Solvent	Ratio (3) : (4)	d_2/d_0 ratio (3)	d_2/d_0 ratio (4)
Me	$(EtO)_3PO$	62.5 : 37.5	0.141	0.140
Me	$(EtO)_3PO$	62 : 38	0.137	0.137
OMe	$(EtO)_3PO$	43 : 57	0.802	0.803
Me	Decalin	65 : 35	0.259	0.211
OMe	Decalin	41.5 : 58.5	1.21	1.41
Me	Chlorobenzene	62 : 38	0.957	0.600
OMe	Chlorobenzene	42 : 58	3.16	3.44

This difference in reaction mechanism has been postulated in explanation of those cases where there are marked differences in the products of the two reactions.[2,4] We have confirmed the differences in the products from (5) and (8), and (6) and (9)[2] and have now shown that decomposition of the azide in triethyl phosphate changes the product composition in the direction of that observed with the nitro compound (Table 2) thus providing strong evidence for the participation of an intermediate such as (7).

Using the labelling technique, we have also been able to show that there is a common element in the cyclisation of nitro and nitroso biphenyls to carbazoles in triethyl phosphite. This is best accounted for by reaction of the nitro compound proceeding by way of the nitroso compound.



5 $R = Me, X = N_3$
6 $R = Cl, X = N_3$
7 $R = Me \text{ or } Cl, X = \bar{N}{-}O{-}\overset{+}{P}(OEt)_3$
8 $R = Me, X = NO_2$
9 $R = Cl, X = NO_2$
10 $R = Cl \text{ or } Me, X = NH_2$



11 $R^1 = Me \text{ or } Cl, R^2 = H$
12 $R^1 = H, R^2 = Me \text{ or } Cl$

Table 2. Cyclisation of the 2-azido- and 2-nitro-phenyl phenyl sulphides (5), (6), (8) and (9).

Sulphide	Solvent	Products (%)		
		(10)	(11)	(12)
(5)	Decalin	17.0	31.0	—
(5)	$(EtO)_3PO$	—	13.0	26.8
(8)	$(EtO)_3PO$	—	17.6	31.0
(6)	Decalin	9.7	51.0	4.7
(6)	$(EtO)_3PO$	3.9	44.0	22.5
(9)	$(EtO)_3PO$	—	34.0	43.7

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