

Unexpected Dipolarophilic Activity of Diphenylvinylphosphine towards Nitrones

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The reactivity of diphenylvinylphosphine towards nitrones is dominated by the dipolarophilic nature of its double bond rather than by the ability of the P^{III} to act as an oxygen acceptor.

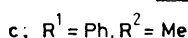
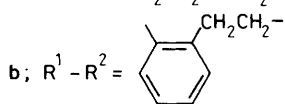
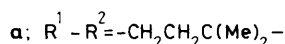
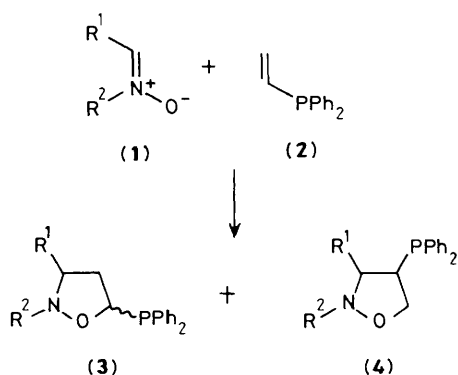
Phosphines were early found to act as efficient deoxygenating agents towards a variety of amine oxides including nitrones.¹⁻³ Both acyclic¹ and cyclic nitrones [5,5-dimethylpyrroline *N*-oxide (DMPO)⁴ (**1a**) and 3,4-dihydroisoquinoline *N*-oxide⁵ (**1b**)] were reported to undergo smooth deoxygenation to the parent imine upon treatment with triphenylphosphine under thermal conditions, the driving force for the process being the formation of a strong P=O bond. We now demonstrate that nitrones can undergo facile 1,3-dipolar cycloaddition to diphenylvinylphosphine (**2**) with almost complete exclusion of the oxygen transfer process (Scheme 1).

Thus, the reaction of 1.3 equiv. of DMPO (**1a**) with 1 equiv. of diphenylvinylphosphine (**2**) (benzene, room temperature, 6 days) led to the formation of the corresponding phosphinoisoxazolidines (**3a**) in 88% yield (³¹P n.m.r., entry 1, Table 1). Analogous reactions of two other nitrones (**1b**) and (**1c**) (entries 2 and 3) were similarly successful even though prolonged heating was applied in these cases in order to attain more practical conversion rates. Oxidation of the phosphine function in all these cases was practically negligible. The products were conveniently isolated by simple crystallisation of the crude reaction mixtures from ligroin or by a quick passage through a short pad of silica gel. All products were assigned the structures displayed on the basis of careful ¹H, ¹³C, and ³¹P n.m.r. analyses of the isolated materials as well as crude reaction mixtures. In all three cases a strong preference for the formation of the 5-substituted isoxazolidine was manifested, as expected on the basis of perturbation theory.⁶

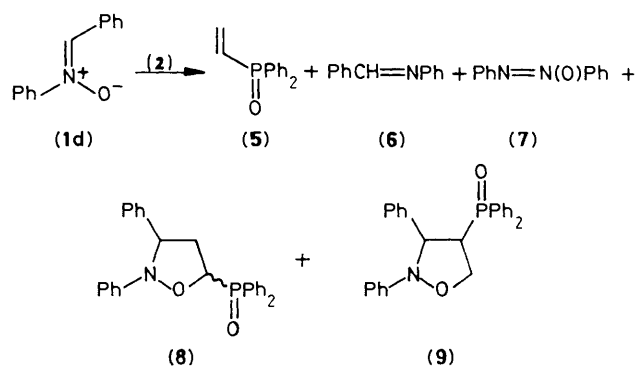
In the reaction of *C,N*-diphenyl nitron (**1d**) with (**2**) (1:1 stoichiometric ratio) in boiling benzene the deoxygenation of the nitron turned out to be the preferred reaction pathway as

evidenced by the isolation of diphenylvinylphosphine oxide (**5**) (32% yield) as well as by detection of benzylideneaniline (**6**) and azoxybenzene (**7**) in the crude reaction mixture (g.c.-m.s.) (Scheme 2). A mixture of isomeric 5- and 4-substituted phosphinylisoxazolidines, (**8**) and (**9**) respectively (Scheme 2), was also formed in 32% yield† with their ratio being exactly the same as found earlier in the reaction of the same nitron with diphenylvinylphosphine oxide (**5**).⁷ It can therefore be concluded that oxidation of phosphorus precedes the cycloaddition in the studied case since with the reversed sequence of events much more of the 5-substituted isomer would have been expected, due to the electron donating character of the phosphino group. With two equivalents of the nitron (**1d**) the adducts (**8**) and (**9**)⁷ can be isolated in 76% overall yield.

Whereas the absence of deoxygenation process, even in the presence of an excess of nitron, in entries 1 and 2 can be explained by the high dipole reactivity of the cyclic nitrones (even though both were reported to be deoxygenated by triphenylphosphine)^{4,5} the divergent behaviour of the two acyclic nitrones (**1c**) and (**1d**) is less apparent, since *C,N*-diphenyl nitron (**1d**) is known to be at least five times more reactive as a dipole than *C*-phenyl-*N*-methyl nitron (**1c**).⁸ The observed difference in reactivity is probably due to the higher polarity of the N–O bond in the *N*-phenyl nitron which makes the oxygen more readily accessible for phosphorus.‡



Scheme 1



Scheme 2

† Unreacted phosphine (**2**) (ca. 30% from ³¹P n.m.r.) was also detected.

‡ An experiment involving the nitrones (**1c**) and (**1d**) and the phosphine (**2**) in 1:1:1 ratio showed that the oxidation of phosphine (**2**) by (**1d**) was again the preferred process [the intermediate formation of diphenylvinylphosphine oxide (**5**) could be monitored by ³¹P n.m.r.]. Although compounds (**3c**) and (**4c**) could be detected, the major compounds of the complex mixture derived indeed from the addition of the two nitrones to the vinylphosphine oxide (**5**), with the previously observed isomeric ratio.⁷

Table 1. Reaction of nitrones with diphenylvinylphosphine (**2**).

Entry	Nitrone	Reaction conditions	Products (regioisomeric ratio)	% Yield ^a	³¹ P N.m.r. of adducts		
					5-Subst. (diast. ratio)		4-Subst.
1	(1a)	Room temp., 6 days	(3a)	62 (88)	-8.77	-7.76	—
					(6:1)		
2	(1b)	80 °C, 24 h	(3b)	45 (79)	-7.02	-3.02	—
					(2:1)		
3	(1c)	80 °C, 48 h	(3c) (4c) (87:13)	63 (75)	-6.36	-9.62	-7.13
					(2.3:1)		
4	(1d) ^b	80 °C, 48 h	(8) (9) (40:60)	76	28.09	27.76	27.27
					(1.7:1)		

^a Yields of isolated phosphorus containing products; in parentheses are ³¹P n.m.r. yields. ^b 2 equiv.

In summary, it has been demonstrated that 1,3-dipolar cycloaddition of nitrones to vinylphosphine is a viable process with the possible exclusion of *N*-aryl nitrones. Phosphinoisoxazolidines are of great potential utility as ligands.

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