[2 + 2] Cycloadducts from Isocyanates and Azaphospholes[1]

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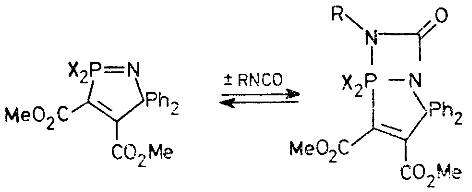
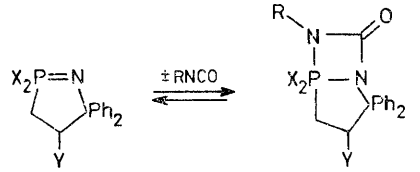
Summary Methyl isocyanate adds with its C=N group to the P=N group of 1,2λ^5-azaphospholes and -azaphospholines; depending on the nature of the ring and the phosphorus substituents the bicyclic adducts are stable or redissociate in solution or/and decompose in a Wittig-type reaction.

STAUDINGER[2] has shown that phosphinimines convert isocyanates into carbodiimides. The reaction is proposed to involve a zwitterionic intermediate and a four-membered ring transition state,[3,4] but an intermediate adduct has not yet been detected or isolated.

Incorporating the phosphinimine in a five-membered ring strongly enhances its addition ability[1,5] as it faciliates five-co-ordination of phosphorus. In fact cyclic phosphinimines such as the 1,2λ^5-azaphospholes (**1**) and -azaphospholines (**2**)[6] give adducts with methyl isocyanate which in part can be isolated in crystalline form.† They are found to be [2+2] cycloadducts with five-co-ordinate phosphorus as a bridgehead common to the four- and five-membered ring, as shown by the high-field ^{31}P chemical shift (see below). In contrast to the Wittig-type transition state suggested above and to the expected preference,[4] the isocyanate adds with its C=N, not its C=O, bond.‡ This is shown by the observed coupling of the phosphorus with the methyl protons of the added isocyanate [J_{PNCH} *ca.* 5 Hz (see Table], and also by the i.r. carbonyl frequency at *ca.* 1740 cm^{-1}.



(**1**) (**3**)



(**2**) (**4**), Y = CO_2Me
(**5**), Y = CN

Compared with the normal cases, the adducts (**3**)—(**5**) are stabilized with respect to both redissociation and Wittig-type decomposition. The degree of stabilization depends on the nature of the five-membered ring and on the substituents R at the phosphorus. With R = Me all the addition equilibria are completely on the side of the adducts, no dissociation being detected in solution. Crystals of the dimethylamino-derivative (**3c**) on the other hand lose methyl isocyanate on standing and turn yellow [the colour of (**1**)]. They become colourless again when exposed to methyl isocyanate vapour. In solution an equilibrium between (**3c**) and (**1**) is observable spectroscopically, the extent of dissociation (75% in 0·5 M $CDCl_3$ at 20 °C) increasing with temperature.

TABLE

			δ^{31}P, solvent			J_{PNCH}/
	R	X	C_6H_6	$CDCl_3$	Me_2SO	Hz
(**3a**)	Me	Me		−67·3	−66·3	4·6
(**3b**)	Me	Ph		−59·2	−58·8	4·9
(**3c**)	Me	Me_2N		−31·0		5·5
(**4a**)	Me	Me		−58·2		4·1
(**4b**)	Me	Ph		−53·1		5·2
(**5a**)	Me	Me		−64·2		5·2
(**6a**)	Ph	Me	−57·2	−55·4	−50·5	
(**6b**)	Ph	Ph		−49·0	−47·8	

The diphenyl adduct (**3b**) does not dissociate in solution, but the adduct (**4b**) dissociates completely, cannot be isolated, and can only be detected in excess of methyl isocyanate at <0 °C. The less saturated ring (**1**) thus gives adducts which are more stable with respect to redissociation than adducts of (**2**). The adducts (**4**) and especially (**5**) are also less stable with respect to Wittig-type decomposition producing phosphine oxides. Compound (**5a**), for example, decomposes completely in 16 h at room temperature yielding a single, isomeric product.

Phenyl isocyanate also forms stable adducts with (**1**). The phosphorus chemical shift of the adduct (**6a**) [but not that of (**6b**)] moves to low field with increasing solvent polarity, indicating some equilibrium participation of the zwitterionic form. Even for (**6a**) the contribution from this form is small, while with more electrophilic phosphorus as in (**6b**) or more nucleophilic nitrogen as in (**3a**) it is absent. The zwitterionic form is more important for the isothiocyanate adducts.[7]

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† One adduct of this type has been prepared by trapping a 1,3,4,2λ^5-oxadiazaphosphole *in situ* with methyl isocyanate (A. Schmidpeter, J. Luber, and Th. v. Criegern, *Z. Naturforsch.*, 1977, **32b**, 845).

‡ Compounds with a 1,3,2λ^5-diazaphosphetidinone ring have been prepared previously from chlorophosphoranes and urea derivatives by condensation (H. Ulrich and A. A. R. Sayigh, *Angew. Chem.*, 1964, **76**, 647; *Angew. Chem. Internat. Edn.*, 1964, **3**, 585; M. Becke-Goehring and H. Schmid, *Z. anorg. Chem.*, 1970, **372**, 285; A. Schmidpeter, J. Luber, D. Schomburg, and W. S. Sheldrick, *Chem. Ber.*, 1976, **109**, 3581).

[1] For Part 28 of the series on Four- and Five-membered Phosphorus Heterocycles see A. Schmidpeter and Th. v. Criegern, *Angew. Chem.*, 1978, **90**, 64; *Angew. Chem. Internat. Edn.*, 1978, **17**, 55.
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