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RING-CLEAVAGE BY METHANOL OF A DIAZAPHOSPHOLENE-CYCLOADDUCT. SEPARATION OF FOUR DIASTEREOMERIC β-PHENYLHYDRAZONE-PHOSPHINATES

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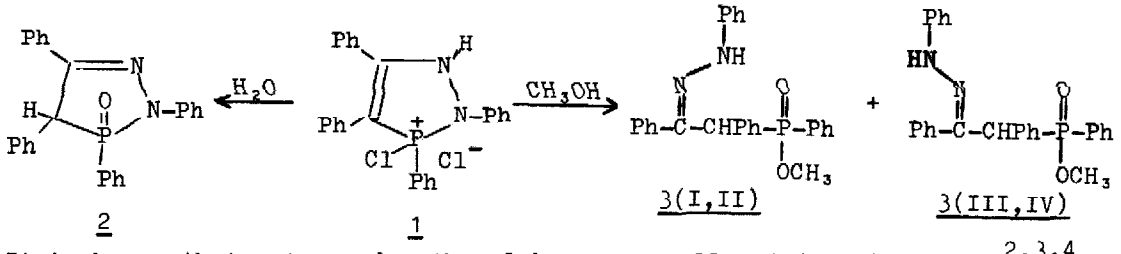
In previous work[1] we reported that phenylazostilbene forms cycloadduct 1 with phenyldichlorophosphine and that hydrolysis of 1 gives an isomeric mixture of the five-membered cyclic diazaphospholene oxides 2 without ring-opening.



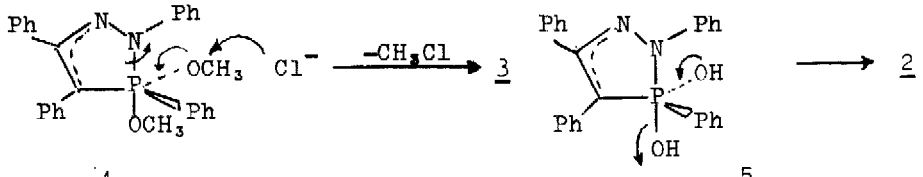
It is known that water and methanol have generally similar behaviour[2,3,4] in reacting with small cyclic phosphorus compounds and that methanolysis of related oxaphospholenes[5] occurs without ring-opening.

We have found that 1 undergoes exclusively ring-opening when treated with a slight excess of dry methanol at room temperature with formation of a mixture of the diastereomeric β-phenylhydrazone methylphosphinates 3 (65% yield). Evolution of CH_3Cl was observed. The four expected diastereomers 3 can be isolated in pure form by silica gel chromatography (elution with benzene-ether (4:1) mixture). Tentative configurational assignment about the C=N bond has been determined essentially[6] by proton NMR (see Table). The differences in the chemical shift of the NH proton and the methine proton resonance[7] suggest that isomers 3I and 3II have the cis configuration defined as that in which the anilino and benzylic groups are on the same side of the C=N bond. To our knowledge this is the first case of separation and characterization of pure isomers about the C=N bond of hydrazones of phosphorus compounds. A probable mechanism for this reaction involves the formation of the phosphorane such as 4; in the presence of HCl apical departure of the diaza group and nucleophilic attack of chloride on the activated carbon atom yields 3 with loss of CH_3Cl. In the case of hydrolysis of 1 the hypothetical intermediate is 5.

TABLE - NMR Spectra[a] of 3 in $CDCl_3$ Solution

Compound	δ_{POCH_3}	J_{POCH_3}	δ_{PCH}	J_{PCH}	$\delta_{Arom.}$	δ_{NH}
3I Rf= 0,55 pf= 126-128°	3,70(d)	10,5	5,03(d)	20,7	670-800(m)	11,05
3II Rf= 0,48 pf= 157-159°	3,75(d)	10,5	5,15(d)	22,2	650-780(m)	10,50
3III Rf= 0,16 pf= 154-156°	3,45(d)	10,5	4,25(d)	18,0	650-770(m)	---[b]
3IV Rf= 0,10 pf= 119-121	3,49(d)	10,5	4,32(d)	21,7	630-760(m)	---[b]

[a] Concentration of 3 to 5 mol % phenylhydrazone were used; Chemical shifts is parts per million from Me_4Si; J values in hertz; [b] Masked by aromatic protons



4 5

However a hydroxyl group is more apicophilic than methoxy group[2] and in our case it may be also more apicophilic than the diaza group. For this reason in our hydrolysis, ring-retention is favoured over ring-opening. In some reported[2,5] cases both the hydroxyl and methoxyl groups are more apicophilic than the ring ligands favouring the ring-retention. On the contrary in other cases[3,4] both the hydroxyl and methoxyl groups are less apicophilic than a ring ligand favouring the ring-opening.

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