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PHOTOCHEMICAL REACTIONS OF PHOSPHAALKENES

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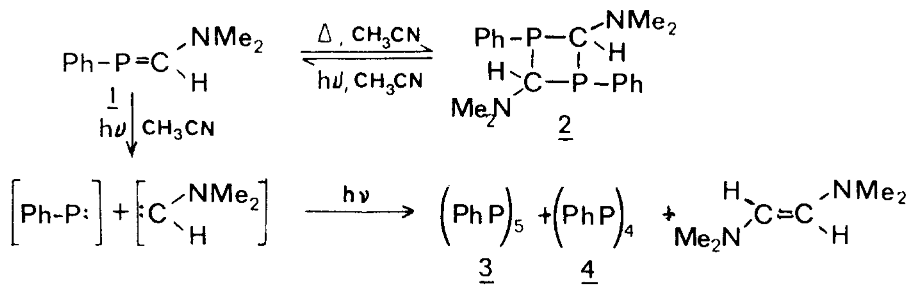
Summary : Photolysis of phosphaalkenes leads to an inversion of polarity of the phosphorus carbon double bond and to a cleavage into transient phosphinidene and carbene ; unexpected alcoholysis of a P$_{III}$-C bond and the [4+2] cycloaddition of a linear phosphaalkene on a diene are also reported.

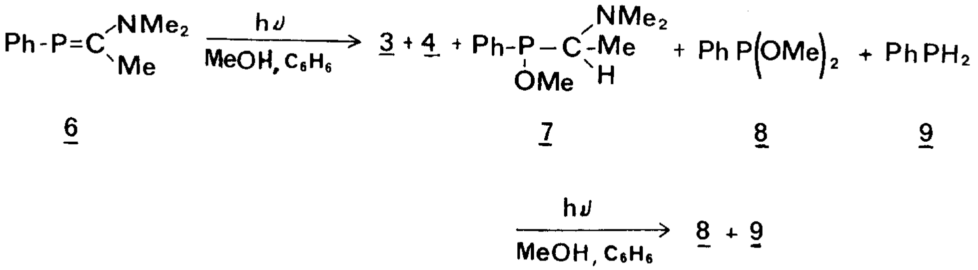
Very few papers have described the photochemical behavior of phosphorus derivatives with a phosphorus carbon double bond. Most of them are concerned with the irradiation of phosphorus ylide Ph$_3$P=CRR^1 [1].

Our interest both in photochemical reactions and in unusually hybridized phosphorus compounds led us to study the photolysis of dicoordinated phosphorus derivatives of general formula R-P=X (X = C< ; N- ; P-). We report here results concerning phosphaalkenes.

Compound 1 [2] slowly dimerizes into 2 at room temperature. However, photolysis of pure 2 at 254 nm leads quantitatively to monomer 1 which is transformed on prolonged irradiation (two days) into pentaphenylcyclopentaphosphane 3, tetraphenylcyclotetraphosphane 4 (in the ratio 4:1) and to bis 1,2-(dimethylamino)ethylene. These experimental facts allow us to postulate the transient formation of phenylphosphinidene and dimethylamino carbene. These results are corroborated by the photochemical reaction observed with derivative 6 (thermally more stable than 1). In this case, the transient dimethylaminomethyl carbene gives rise to bis 2,3-(dimethylamino)2-butene and to isopropylene methylamine resulting from migration of a methyl group from the nitrogen to carbon.



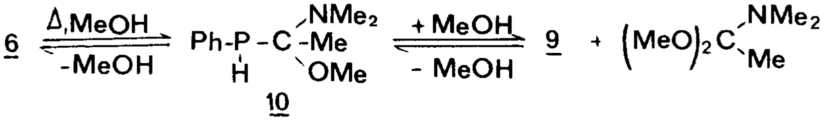
When the irradiation of 6 is performed in benzene solution in the presence of methanol, besides the cyclophosphanes 3 and 4, phenyldimethoxyphosphine 8, phenylphosphine 9 and the methanol adduct 7 (two diastereoisomers, δ^{31}P = + 117 and + 118 p.p.m) are obtained. Prolonged photolysis only affords a mixture of 8 and 9 (70/30). We showed that 8 and 9 came from subsequent irradiation of 3 with methanol [3,4].



6 7 8 9

Note that 7 undergoes an unusual alcoholysis of the P_{III}-C bond giving 8.

Surprisingly heating of 6 in acetonitrile methanol solution, in the presence (or not) of base, leads to the formation of the other [1-2] addition product 10 which is in equilibrium with the starting product 6 and with 9.



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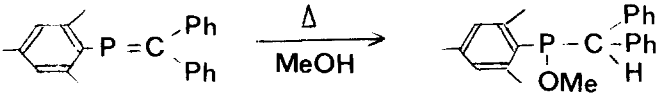
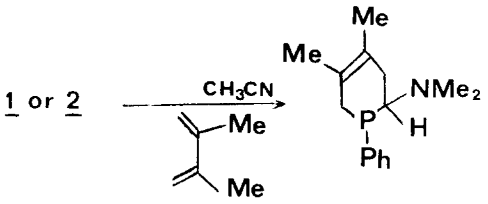
Thus it seems that the polarity of the phosphorus carbon double bond dramatically changes when 6 is thermally or photochemically excited.

Furthermore we observe an "umpolung" effect induced by the dimethylamino group during the thermal addition of methanol to 6. Indeed Bickelhaupt [5] described the reverse addition of methanol to 11 in the presence of sodium methoxide, yielding 12.



11 12

Only a few cycloaddition reactions of phosphaalkenes have been reported until now [6]. Most of them involve cycloaddition of cyclic monomers mainly obtained by heating the corresponding dimers or tervalent phospholes. Diels Alder reactions failed with 11 [7] certainly because of steric hindrance. Refluxing 1 in benzene in the presence of excess of 2,3-dimethyl butadiene affords, besides 2, two phosphorus compounds ($\delta^{31}P$ = -46, -41 p.p.m). The major one ($\delta^{31}P$ = -46 p.p.m, 40%, b.p. 60°/1 mm, mass fragmentation M^+ 247, 232, 217, 203, 190, 165 ...) has been characterized as 13. 13 is produced in better yield (80%) when 1 or 2 are irradiated in acetonitrile or benzene : in this case, all dimer 2 is transformed into 1 which gives 13 by a thermal cycloaddition [8].



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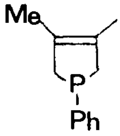
During the irradiation of 1 or 2 in the presence of 2,3-dimethylbutadiene, neither phospholene 14, resulting from a possible reaction of phenylphosphinidene with 2,3-dimethylbutadiene, nor 3 and 4, occuring from the initial formation of phenylphosphinidene or from a photochemical fragmentation of 14 [9] , were detected in the resulting mixture by ^{31}P n.m.r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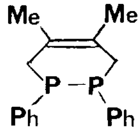
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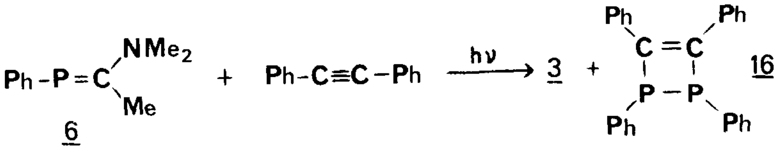
On the other hand photolysis of 6 in benzene solution and in presence of 2,3-dimethyl butadiene gives 14 ($\delta^{31}P$ = -33 ppm, yield 15%), 15 ($\delta^{31}P$ = -23 ppm, yield 75%). No direct [4+2] cycloaddition product can be detected in this case.

Moreover the irradiation of 6 with tolane leads to three phosphorus derivatives. Two of them were identified as pentaphenylcyclopentaphosphane 3 and 1,2,3,4-tetraphenyl 1,2-diphosphetene 16 ($\delta^{31}P$ = -37,5 ppm ; mp : 158-159° ; yield 20%). We do not succeed yet in the isolation of the third one ($\delta^{31}P$ = +3 ppm). Compound 16 was already obtained ([10,11]) by reacting 3 with tolane in forcing conditions (240 °C, 6 hrs, yield 15%) ([12]).



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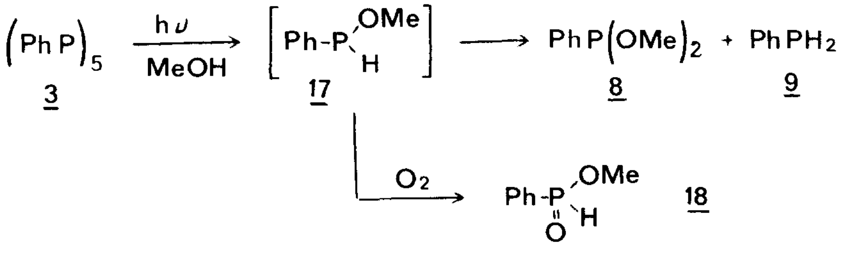
[3] Moreover the fact that photolysis of a non-deoxygenated solution of 3 gives 18 ($\delta^{31}P$ = + 25,2 p.p.m.J_{P-H} = 558 Hz) as well as 8 and 9, is in good agreement with the preliminary formation of 17 .



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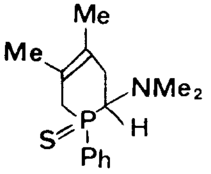
[8] Addition of sulphur to 13 in refluxing benzene affords 13' in quantitative yield. 13': $\delta^{31}P$ = + 31 ppm ; m.p. = 111-112 °C ; mass fragmentation = M+ 279, 223, 191, 159, 138 ; $\delta^{1}H$ = 3,12 , 3,17 (s, Me), 3,8 (s, NMe_2).



13'

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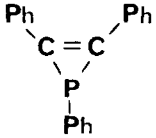
[12] It is interesting to note that in our reaction we never observed the formation of pentaphenyl-1,2,3 triphospholene as Ecker[10] or Charrier and al.[11] did during the reaction of $(Ph)_5P$ with tolane. This could imply either a [2+2] cycloaddition of an instable diphosphene Ph-P=P-Ph with tolane or a [1+2] cycloaddition of a phenylphosphinidene with tolane, formation of the three membered ring 19 then insertion of phenylphosphinidene into the cycle 19 with finally formation of 16.



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