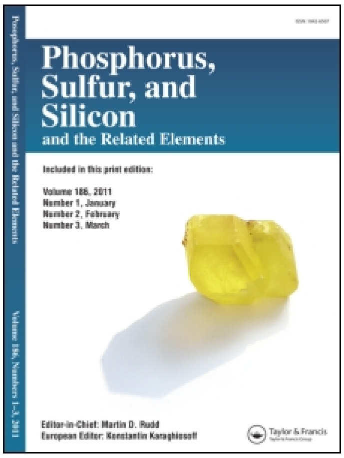

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Thermal and photochemical reactivity of phosphaalkenes

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THERMAL AND PHOTOCHEMICAL REACTIVITY OF PHOSPHAALKENES

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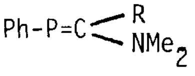
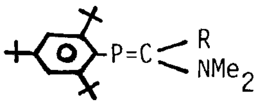
The reactivity of acyclic dicoordinated phosphorus derivatives has intensively been studied. Nevertheless, up to date, a very few examples of photochemical reactivity of these compounds have been described. We wish to report here some thermal and photochemical reactions of phosphaalkenes 1-4.[1]



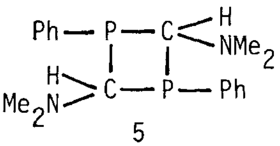
$Ph\text{-}P{=}C\begin{smallmatrix}R\\NMe_2\end{smallmatrix}$



1 R=H[2]
2 R=Me[2]

3 R=H (F=96-7°;NMR ^1H,^{13}C,^{31}P : $\delta=85$; $M^+=333$;analysis)
4 R=Me (oil; NMR ^{31}P : $\delta=96.3$)

The σ^2-phosphorus double bond systems possess two energetically closed spaced HOMOs, π and σ.[3] The amino group of 1 acts as a π-donor : the π-MO should be raised in energy. Thus phosphaalkene 1 slowly dimerizes at room temperature into 5 ; irradiation of 5 allows to recover the monomer 1. This compound 1 also reacts with 2,3-dimethyl butadiene affording the phosphorinne 6 by a [2+4] cycloaddition reaction.



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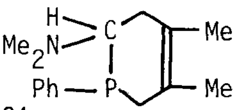
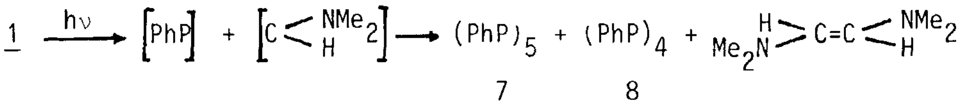


6 (NMR ^{31}P : $\delta=-46$;$M^+=247$;analysis)

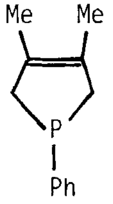
On the other hand, prolonged irradiation of 1 in acetonitrile and in absence of any trapping reagent gives rise to a mixture of pentaphenyl cyclopentaphosphane 7, tetraphenyl cyclotetraphosphane 8 (in the proportion of 4/1) and of 1,2-bis(dimethylamino) ethylene, certainly via the preliminary formation of phenylphosphinidene and dimethylaminocarbene. Thus the [2+4] cycloaddition reaction of 1 with dimethyl butadiene is faster than the phosphinidene generation.



$$\underline{1} \xrightarrow{h\nu} [PhP] + \left[C{<}\genfrac{}{}{0pt}{}{NMe_2}{H}\right] \longrightarrow (PhP)_5 + (PhP)_4 + \genfrac{}{}{0pt}{}{H}{Me_2N}{>}C{=}C{<}\genfrac{}{}{0pt}{}{NMe_2}{H}$$

7 8

Substitution of the hydrogen bonded to the sp^2 carbon of 1 by a methyl group (derivative 2) brings on a change of reactivity. Compound 2 does not dimerize.[2] Moreover, no [2+4] cycloaddition reaction was observed with 2,3-dimethyl butadiene. In this case, the phospholene 9 (15%) and the diphosphorinne 10 (75%) are obtained by irradiation. Similarly, photolysis of 2 in presence of tolane leads to the formation of the diphosphetene 11 and of the polyphosphane 7. Compounds 9, 10 and 11 were already obtained by reacting a polyphosphane respectively with 2,3-dimethyl butadiene or with tolane.[4-6]



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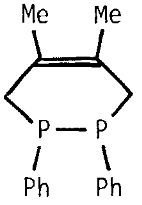

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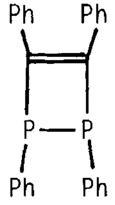

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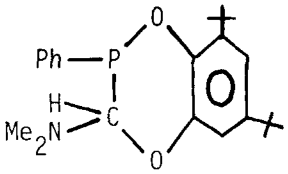
The transient formation of phenylphosphinidene can be postulated in all these reactions. Moreover, photolysis of 2 in acetonitrile leads to 7 and 8. The transient dimethylamino(methyl)carbene formed in this reaction gives 2,3-bis(dimethylamino) 2-butene by dimerization and isopropylene methylamine by migration of a methyl group from nitrogen to carbon.

The addition of 3,5-ditertiobutyl orthobenzoquinone to 1 - in order to trap the phenylphosphinidene - takes place at 0° without any radiation and affords 13 via 12 by a ring contraction reaction. 12 has been characterized at -40° by NMR ^1H, ^{13}C and ^{31}P (δ= 85.7 and 83.5). Similar results have been obtained with 2 and 3. It is of interest to note the high instability of 12 compared to those of analogous compound recently described in the litterature.[7]



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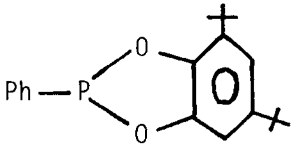

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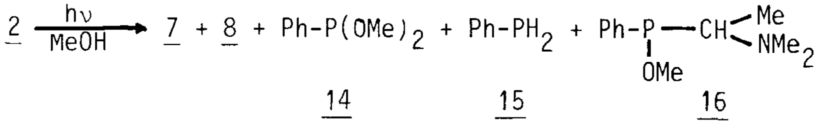
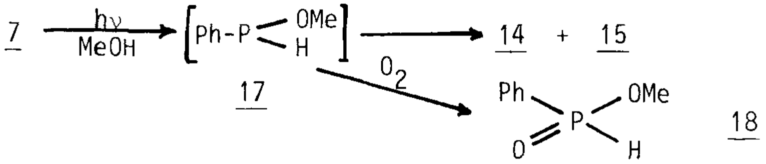
When the irradiation of 2 is performed in benzene solution in the presence of methanol, besides the cyclophosphanes 7 and 8, phenydimethoxyphosphine 14, phenylphosphine 15 and the methanol adduct 16 (two diastereoisomers, $\delta^{31}P$=117 and 118) are obtained.



$$\underline{2} \xrightarrow[\text{MeOH}]{h\nu} \underline{7} + \underline{8} + \underset{\underline{14}}{\text{Ph-P(OMe)}_2} + \underset{\underline{15}}{\text{Ph-PH}_2} + \underset{\underline{16}}{\text{Ph-}\underset{\text{OMe}}{\text{P}}\text{—CH}\left<\begin{matrix}\text{Me}\\ \text{NMe}_2\end{matrix}\right.}$$

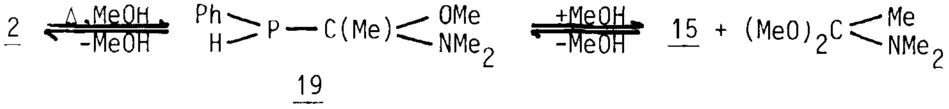
Prolonged photolysis only affords a mixture of 14 and 15 (70/30). We showed that 14 and 15 came from subsequent irradiation of 7 with methanol. Moreover the fact that photolysis of a non-desoxygenated solution of 7 gives 18 ($\delta^{31}P$=25.2 ; J_{PH}= 558 Hz) as well as 14 and 15 is in good agreement with the preliminary formation of 17.



$$\underline{7} \xrightarrow[\text{MeOH}]{h\nu} \underset{\underline{17}}{\left[\text{Ph-P}\left<\begin{matrix}\text{OMe}\\ \text{H}\end{matrix}\right.\right]} \longrightarrow \underline{14} + \underline{15}$$

$$\underline{17} \xrightarrow{O_2} \underline{18}$$

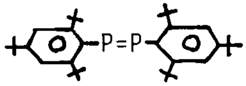
Note that 16 undergoes an unusual alcoholysis of the P(III)-C bond giving 14. Surprisingly, heating of 2 in acetonitrile methanol solution, in presence (or not) of base, leads to the formation of another 1,2-addition product 19 which is in equilibrium with the starting compound 2 and with 15. Thus it seems that the polarity of the phosphorus-carbon double bond dramatically changes when 2 is thermally or photochemically excited.



$$\underline{2} \underset{-\text{MeOH}}{\overset{\Delta,\text{MeOH}}{\rightleftharpoons}} \underset{\underline{19}}{\left.\begin{matrix}\text{Ph}\\ \text{H}\end{matrix}\right>\text{P—C(Me)}\left<\begin{matrix}\text{OMe}\\ \text{NMe}_2\end{matrix}\right.} \underset{-\text{MeOH}}{\overset{+\text{MeOH}}{\rightleftharpoons}} \underline{15} + (\text{MeO})_2\text{C}\left<\begin{matrix}\text{Me}\\ \text{NMe}_2\end{matrix}\right.$$

Furthermore we observed an "umpolung" effect induced by the dimethylamino group during the thermal addition of methanol to 2. Indeed Klebach and al.[8] described the reverse addition of methanol to 1-mesityl 2,2-diphenyl phosphaethylene in the presence of sodium methoxide.

Compounds 3 and 4 are stable and do not dimerize. Photolysis does not generate the corresponding phosphinidene or the diphosphene 20.



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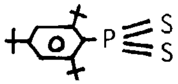

21

Addition of sulphur to 3 affords the first metadithiophosphonate 21 which has been characterized by NMR ^{1}H, ^{31}P (δ = 295.3), mass spectrometry (M^{+} = 340) and by its reactions with methanol and 2,3-dimethyl butadiene. This metadithiophosphonate 21 is also obtained by reacting sulphur with tritertiobutylphenylphosphine.

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