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PHOTOLYTIC REARRANGEMENT OF PHOSPHORUS AZIDE : EVIDENCE FOR A TRANSIENT METAPHOSPHONIMIDATE.

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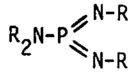
Photolysis of the oxide of diphenylphosphine azide gives rise to a transient metaphosphonimidate, a new tricoordinated pentavalent phosphorus compound. Evidence for this species was given by trapping reactions on a variety of substrates.

Although chemistry of unusually hybridized phosphorus compounds has been the subject of one of the most exciting areas in the last ten years, only few papers report investigations on tricoordinated pentavalent phosphorus derivatives (1-8) (1-15).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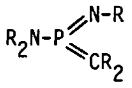
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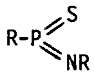
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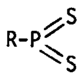
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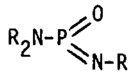
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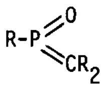
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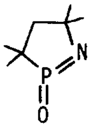
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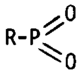
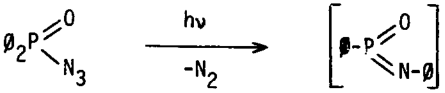

(8)

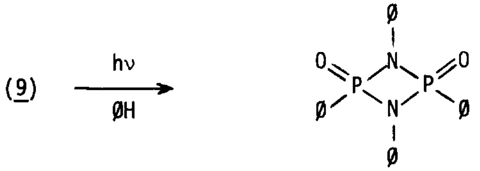
Compounds (1) and (2) were found to be stable (1-5) but most of these phosphorus entities have a very short lifetime. They have been postulated as synthetic intermediates (3-5) (6-12) or caracterized by trapping with α ethylenic ketones (6) (13) methanol (7) (14-15) or amines (8) (16).

Here we wish to report photolysis of the oxide of diphenylphosphine azide (9) which leads univoqually to the metaphosphonimidate (10), a new tricoordinated pentavalent phosphorus compound. Note that this type of rearrangement — migration - nitrogen loss — is wellknown in the carbon series (17).


(9) (10)

Compound (9) was irradiated overnight at 2537 Å, in benzene, in the absence of trapping agent or with an excess of alcohols, diols, amines, methyliodide, epoxyde or diene.

Thus photolysis of (9) without trapping agent gave phosphodiazetidine (11) (18) by head to tail dimerization of the metaphosphonimidate (10) in quantitative yield.



(11)

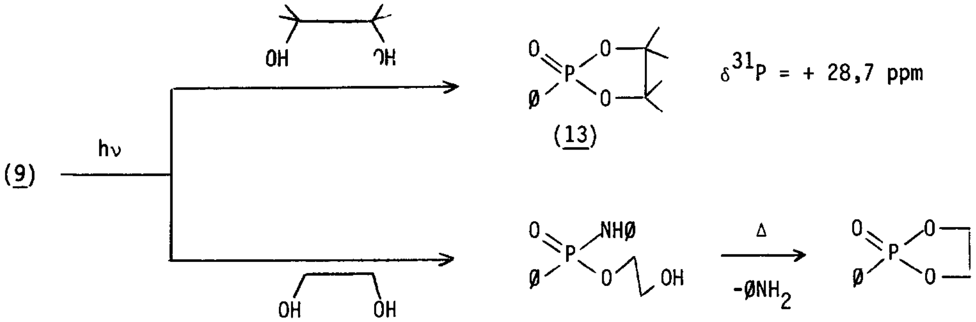
$\delta^{31}P$ = + 6 ppm
m.p = 290 °C

When (9)was irradiated in the presence of alcohol (methanol or ethanol) esters (12) (18) were obtained by addition of ROH on the phosphorus nitrogen double bond of (10)

(12)

$\delta^{31}P$ = + 19,6 ppm
m.p = 101 °C , R = CH_3
105 °C , R = C_2H_5

The cyclic derivative (13) (19) was obtained when photolysis was carried out with pinacol. Howewer the use of ethylene glycol allowed us to caracterize monoaddition product (14) which is slowly converted to dioxaphospholane (15) (20). Note that the rate enhancement of the reaction (14) to (15) is temperature sensitive.

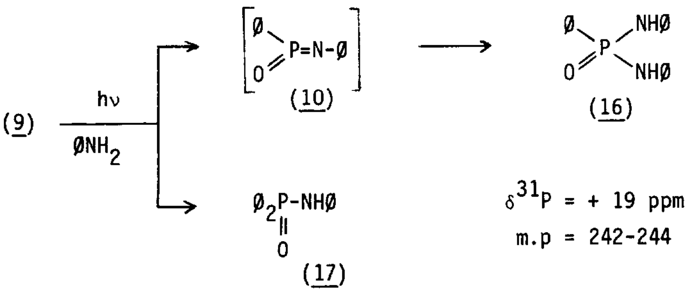


(13) $\delta^{31}P$ = + 28,7 ppm

(14) (15)

$\delta^{31}P$ = +19,8 ppm $\delta^{31}P$ = + 38,4 ppm

Two competitive reactions occured with aniline : addition of amine on the intermediate (10) with formation of (16) (21) and aminolysis of the starting phosphorus azide leading to compound (17) (22). This second reaction is self catalysed by the amine (23).



(10) (16) $\delta^{31}P$ = + 8,5 ppm

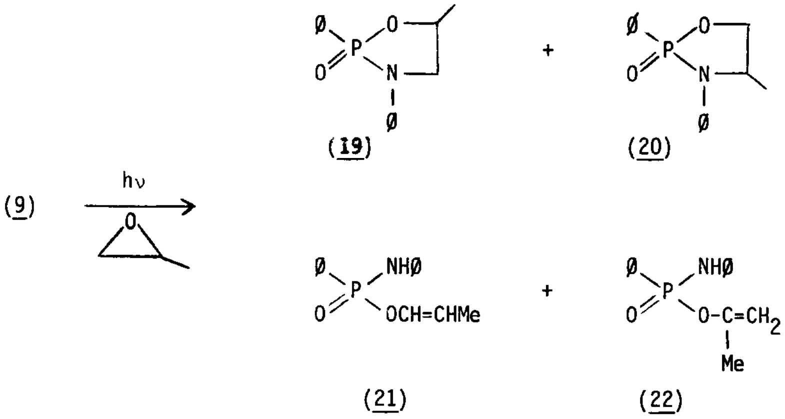
(17) $\delta^{31}P$ = + 19 ppm
m.p = 242-244 °C

Phosphorus species (10) reacts also with methyl iodide leading to the oxide of iodo phenyl (methylphenyl)amino phosphine (18)

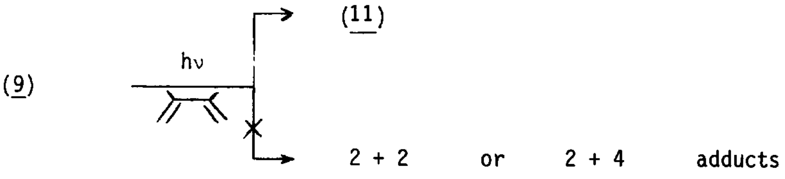
$\delta^{31}P = + 31$ ppm

$J_{P-N-CH_3} = 11{,}9$ Hz

In order to provide evidence for a ring insertion reaction, (9) was irradiated in the presence of propylene oxide. ^{31}P n.m.r spectroscopy showed two groups of signals : a wide peak at 30,8 ppm which can be attributed to 2-oxo-2-phenyl-1,3,2-oxazaphospholanes (19) and (20) ([23]) and another complex signal at + 18,6 ppm which is probably due to acyclic derivatives (21) and (22)



It is interesting to note that no trapping reaction occurs in the presence of dimethylbutadiene



These preliminary results indicate that the phosphorus nitrogen double bond of this tricoordinated pentavalent phosphorus derivative (10) has a marked polar character as in the tetracoordinated derivative. Attempts to caracterize this tricoordinated species (10) by low temperature ^{31}P n.m.r spectroscopy have so far been unsuccessfull. Efforts towards stabilization of this type of compound with bulky substituents are underway.

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