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PHOSPHORUS HETEROCYCLE SYNTHESIS BY $RPX_2 \cdot AlX_3$ ADDITION TO [1, n]DIENES VI

$RPX_2 \cdot AlX_3$ PHOSPHORYLATIONS IN THE PRESENCE AND ABSENCE OF WATER

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Abstract—The electrophilic addition of $RPX_2 \cdot AlX_3$ (1) (R=Ph or Me; X=Cl or Br) to [1, n]dienes was found to be an efficient and useful reaction for the synthesis of a variety of new phospha-heterocycles such as substituted phospholanes, dihalophosphorinanes, phosphorinenes, 3-phosphabicyclo[3.1.0]hexanes, 2-phosphabicyclo[2.2.1] heptanes, 2-phosphabicyclo[3.2.1]octanes and substituted phosphetanes. An ionic multistep mechanism, governed by the stability of the intermediate carbonium ions, is suggested. The phosphorylation reaction was found to be most sensitive to water and in its presence (even 0.1 eq.) it takes a different course. The products, results from hydrogen and RP(O)X addition to the double bond. The phosphorylation is initiated by an unusual protonation process which employs the specific catalytic properties of the $AlCl_3 \cdot H_2O$ complex ($HX + RPX_2$ in the presence or absence of $AlCl_3$ do not give any defined phosphorylation products but polymers). Some of the examined dienes give with water-doped $RPX_2 \cdot AlX_3$ phosphorylations and/or HX additions, involving in several cases participation of both double bonds to give intramolecular cyclisation products. These products may explain the substances obtained following phosphorylation of simple n-alkenes. Compound **16**, one of the new addition compounds, was found to cyclise to the 2-oxaphospholane system (**19**).

Phosphorylation of olefins with phosphorus halides in the presence of aluminum chloride was first reported by Jungerman in 1961.[1] However, the exact attachment of the P(O)Cl, or P(O)OH, grouping to the carbon chain was not established. It has been shown[1] that olefins react with $PX_3 \cdot AlX_3$ complexes in CH_2Cl_2 solution to give a 1:1 adduct, in varying yields depending on the olefin. Only in cases of highly branched olefins like 2,4,4-trimethylpentene-2 were the adducts fully characterized, resulting in the synthesis of the four membered phosphaheterocycle, namely the phosphetane. A similar reaction was observed with $PhPX_2$ and CH_3PX_2[2] however, except for the phosphetanes, no other well defined olefin products were reported. Moreover, when no phosphaheterocycle is produced nothing is known about the vicinal carbon atom† (the one adjacent to the phosphorylated olefin carbon).

The structure of the $RPX_2 \cdot AlX_3$ complex (1) is a matter of debate. Until recently is was assumed that when $R \neq X$ the complex possesses an ionic character ($\overset{+}{R}PCl \cdot AlCl_4^-$)[4] and that the $\overset{+}{R}PX$ cation is the species attacking the olefin.[5] This was based on electric conductance measurements in CH_2Cl_2 solution, which has shown that complexes with R=Ph and X=Cl or Br conduct, while if R is also a halide, they do not.[4] Very recently, however, it was suggested by Quin,[6] on the basis of ^{31}P-NMR measurements, that phosphonous dichlorides form molecular and not ionic complexes with $AlCl_3$. Quin suggests that "$AlCl_3$ serves to increase the electrophilic character of $RPCl_2$ through complexation; for PCl_3 where no complex is formed, $AlCl_3$ may serve to assist in the removal of chloride as the C–P bond is forming".[6]

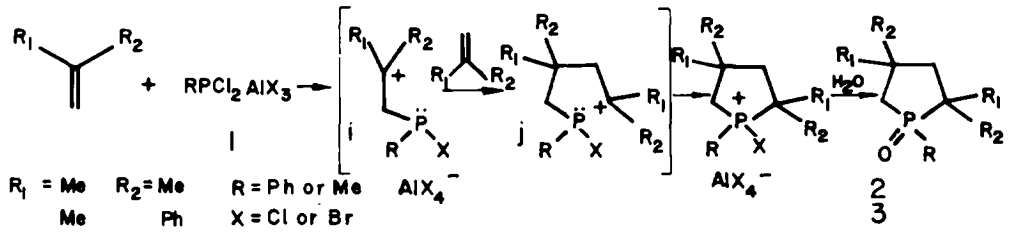
Whatever the structure of 1, the initially formed C–P bond will result in a carbonium ion on the vicinal olefin carbon atom; that complex 1 reacts as an electrophile can be seen also from the electrophilic substitution of benzene with $PCl_3 \cdot AlCl_3$.[7]

In a series of previous communcations,[8–12] we have described the phosphorylation reaction of 1,1-disubstituted olefins, various [1, n]dienes and vinyl cyclopropanes with the $RPX_2 \cdot AlX_3$ complexes. Phosphorylation additions, which resulted in a whole variety of phosphaheterocycles, are summarized in Schemes 1–4.

In the early stages of the work it was already revealed that absolute dryness is essential for obtaining good yields of the heterocycles. Moreover, in the presence of small amounts of water (0.1–1.0 equivalent) the reaction takes another course *vide infra*. A variety of compounds which are obtained under these "wet" conditions, and which will be discussed later, are summarized in Scheme 5.

Isobutylene and methylstyrene were two monoenes chosen for study of the phosphorylation reaction of simple olefins (see Scheme 1). These two alkenes were selected because of their ability to give stable *tert.* carbonium ions following the first addition step. Both olefins reacted with 1 to give, after quenching of the phosphorylation product in H_2O, crystallinic tetrasubstituted phospholanes 2 and 3, respectively in *ca.* 25 and 10% yield. The phospholanes were found to be accompanied by an unidentified polymeric material, as was found to be the case in most of these reactions, even the better ones. A three step mechanism is suggested for the phospholane synthesis (see Scheme 1), that is, (a) formation of ion i, (b) attack of i on a second molecule of the olefin to again give a *tert.* carbonium ion, j, and last, (c) cyclisation of j

†A reaction also occurs between ethylene and $RPX_2 \cdot AlX_3$; the products are more complex but depend in part on addition of a RPX fragment and halogen to the double bond;[3] a radical mechanism is suggested in this case.



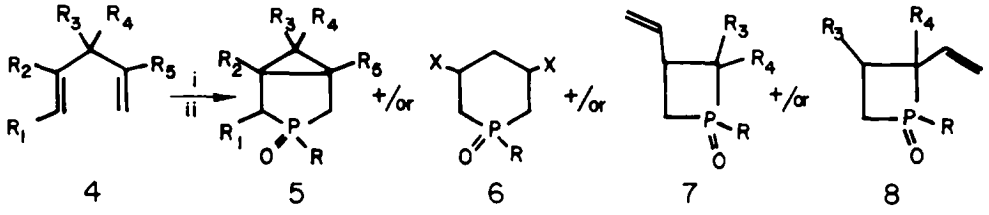
Scheme 1.

to the phospholanium ion. The multistep mechanism was first suggested on the basis that only the 2,2,4,4-tetra-substituted phospholane isomer was obtained. Even on employing $PhPBr_2 \cdot AlBr_3$ with methyl styrene no 3,3,4,4-isomer was detected. In a two step reaction which would involve a 1,3-dipolar addition of i to the second olefin molecule, a more highly substituted P-atom would have been expected to interfere strongly with the neighboring 1,1-methylene substituents and thus the 3,3,4,4-isomer would compete with the 2,2,4,4-one. The exact nature of ion i is still under investigation in order to determine to what extent the phosphorinanium form contributes.‡

‡The existence of ion i has been proved independently by its capture with dienophiles at low temperature.[13]

The above findings are in full agreement with the proposed mechanism of the phosphetane formation,[5] that is, formation of a carbonium ion in the first step followed by a CH_3(or other group) migration from C-3 to C-2 (the driving force of which is the stability of the newly formed *tert.* carbonium ion compared to the *sec.* ion), and finally, cyclization to the four membered ring.

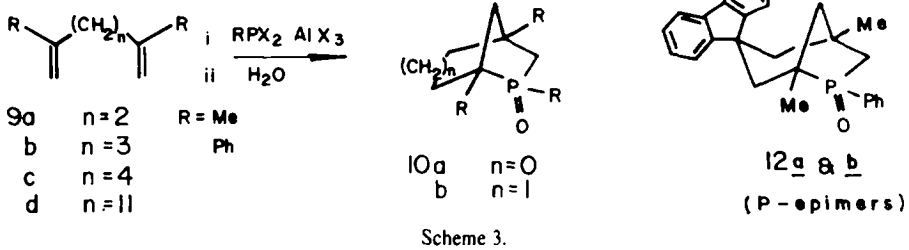
Attempts to synthesize other phospholanes starting from di- or even trisubstituted olefins (as e.g. 1-methyl-cyclohexene and 2-methyl-1-pentene) failed. The formation of a stable carbonium ion in the first phosphorylation step (*vide infra*) does not seem to be the only requirement for an efficient reaction. Oligo- and/or polymerisations reduce significantly the yields of the desired phosphorylation; the factors influencing the rela-



4a	$R_1=R_3=R_4=H$ $R_2=R_5=Me$	5a, 5b	-	-	-
b	$R_1=R_2=R_3=R_4=R_5=H$	-	6	-	-
c	$R_1,R_2=(CH_2)_4$ $R_3=R_4=R_5=H$	5c	-	-	-
d	$R_1=R_3=R_4=R_5=H$ $R_2=Me$	5d	-	-	-
e	$R_1=R_2=R_5=H$ $R_3=R_4=Me$	5e	-	7	-
f	$R_1=R_2=R_5=H$ $R_3=Me$ $R_4=Ph$	5f	-	-	8

i $RPX_2 \cdot AlX_3$
ii H_2O

Scheme 2. The reaction of 1,4-dienes with complex I.



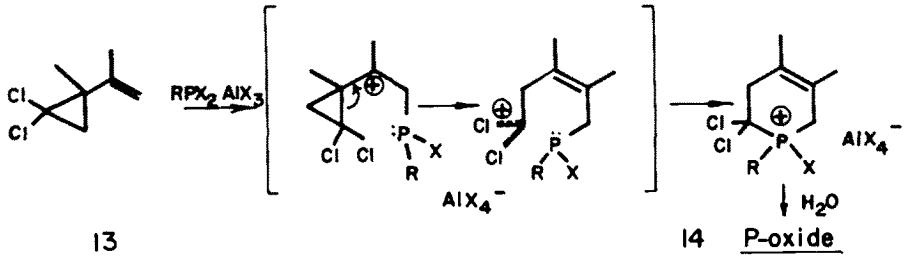
Scheme 3.

tive rates of the controlled phosphorylation vs the polymerization are as yet unknown.

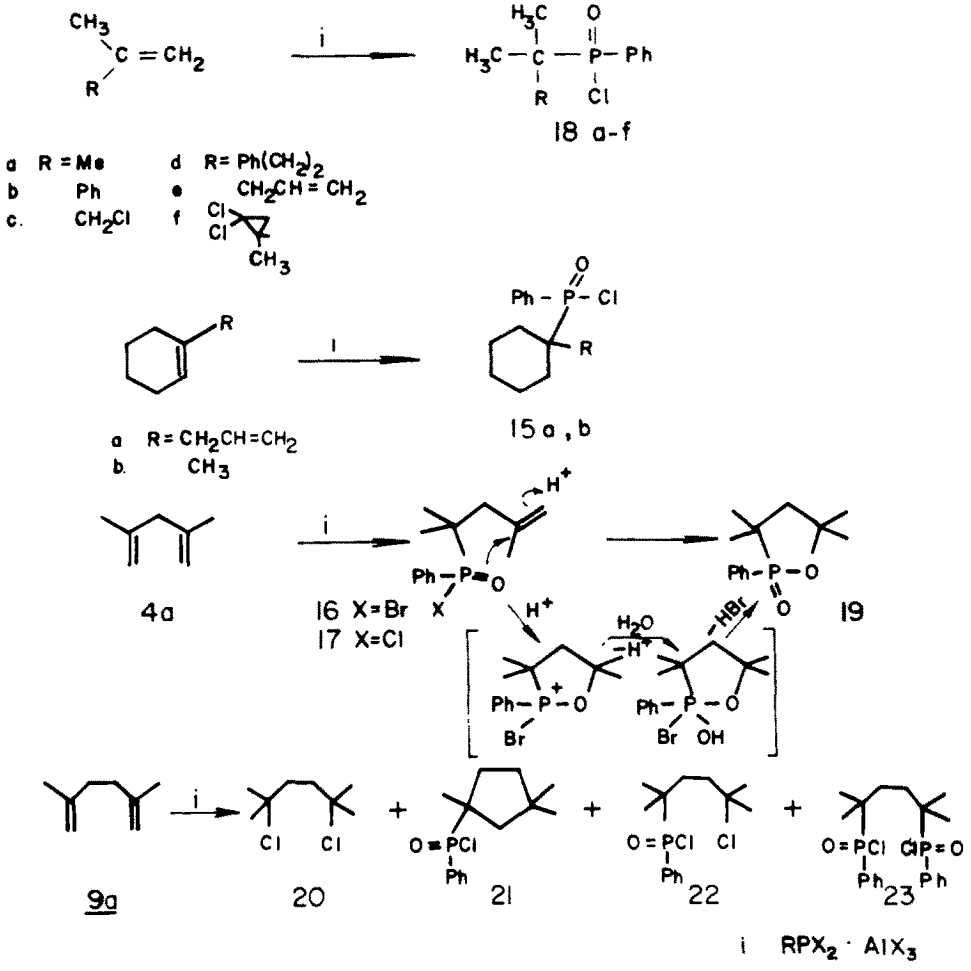
We thought it attractive to try and stabilise the initially formed carbonium ion by reacting it with a second, internally located double bond. The newly formed carbonium ion should then be able to react with the ^{III}P atom, as in the above cases, to give a cyclic phosphonium ion. Potentially, depending on the starting dienes, many different phosphaheterocycles can be prepared in this way. Schemes 2.and 3 summarize a whole series of reactions which were performed with [1, n]dienes (1,4;1,5 and 1,6 dienes **4**, **9a** and **9b**, respectiveyl; 1,7 and 1,14 dienes which were also tested, failed to give a heterocycle).

Reaction of 2,4-dimethyl-penta-1,4-diene (**4a**) with **1** (R=Me or Ph) gave in good yield, the two P-epimers of 3-phenyl (or methyl)-3-oxo-3-phosphabicyclo[3.1.0]hexane (**5a** and **5b**). Penta-1,4-diene (**4b**) on the other hand, gave in low yields two P-epimers of 3,5-dihalophosphorinane, **6**.†

†Compound **6** was obtained as the phosphine oxide most likely due to air oxidation during the prolonged purification process. The bromine atoms in both P-epimers are equatorial. The epimer with the δ3.30 dt(J = 12 and 3.0 Hz) signal is believed to be the one with the axial phenyl and equatorial oxygen while the other epimer with the δ4.50 dt(J = 12 and 3.5 Hz) signal is the second P-epimer. The difference in the vicinal to bromine proton signals, resulting from the upfield shift caused by the phenyl vs the paramagnetic shift of the P=O group.



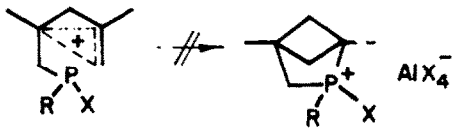
Scheme 4.



Scheme 5. The reaction of olefins with $XH_2O{\cdot}RPX_2{\cdot}AlX_3$.

From the above, as well as many other reactions, it is clear that for the success of these electrophilic additions, the initially formed carbonium ion must be stabilized as e.g. in the case of the *tert.* ions obtained from the $-C(Me)=CH_2$ terminus.‡ In the case of compound **4b** the quenching of the *sec.* carbonium ion with AlX_4^- (X=Br) seems to be faster than the intramolecular attack of the second double bond.§ 1-Allyl cyclohexene (**4c**) and 2-methylpenta-1,4-diene (**4d**) undergo essentially the same cyclisation as **4a**, to give the 2-phosphatricyclo[4.4.0^{4,6}]decane system (**5c**) and the bicyclophosphirane system (**5d**) respectively. Thus, it is clear that a single stable carbonium ion is sufficient to enable the second double bond participation in the reaction (to give compounds of type **5** rather than **6**).

It is interesting to note that although the intermediate homoallylic ion, which is obtained after the second double bond of the 1,4-diene interacts with the initially formed carbonium ion, can lead to either the 3-phosphabicyclo[3.1.0]hexane or to the 2-phosphabicyclo[2.1.1]hexane system, only the former one is obtained.[8,9] That an homoallylic cation can indeed be an intermediate in the above reaction, is evident from the results of the reaction between 3,3-dimethyl-penta-1,4-diene (**4e**) and complex **1** (Schemes 2 and 6). Compound **4e**, in spite of being unable to give a *tert.* carbonium ion *vide supra* in the first place, does not give a phosphorinane of type **6** but rather the phosphabicyclic compound **5e** and a phosphetane (**7**). The latter compound is obtained from a vinyl shift of the homoallyl cation to produce a *tert.* carbonium ion which after the C–P bond formation, results in the phosphetane **7** (Route 1, Scheme 6). The 3-methyl-3-phenyl-penta-1,4-diene (**4f**) on the other hand gives another phosphetane (**8**) following the phenyl migration (Route 2, Scheme 6). Obtaining **5e** can be explained by the 3,3 gem dimethyl group which prevents sterically, the quenching of the carbonium ion by the AlX_4^- ion while route 1 led through the vinyl shift to phosphentane **7**, route 2 leads through a 1,2 phenyl shift to phosphetane **8**.



†Several other 1,5-pentadienes (e.g. 4,5-dimethyl-2,6-octadiene and 1,6-diphenyl-1,5-hexadiene) which were tested gave only polymers. We have not yet found a way to influence the reaction route.

‡Stabilization of the carbonium ion by a rearrangement process is also possible as found in the case of compound **4e**.

§The initially obtained halide does not disturb the reaction because of the mild conditions; similarly isobutenylchloride gives the same reaction as isobutylene and 2-methyl-cyclohex-1-ene *vide infra.*

In order to study the scope of the reaction we turned to higher [1, n]diene homologues: the 2,5-dimethyl-1,5-hexadiene (**9a**) was found to give with complex **1**, the 1,4-dimethyl-2-phenyl (or methyl)-2-oxo-2-phosphabicyclo[2.2.1]heptane (**10a**) as the only bicyclic compound (Scheme 3). The fact that no bicyclo[3.2.0]heptane was obtained, supports once more, the proposed ionic multistep reaction mechanism; a mechanism which is governed by the intermediate carbonium ions stabilities.†

Next, the 2,6-diphenyl-1,6-heptadiene (**9b**) gave on reacting with **1** the higher homologue of **10a**, namely, the 1,4-diphenyl-2-methyl-2-oxo-2-phosphabicyclo[3.2.1] octane (**10b**). (Again no isomeric [3.3.0]octane could be detected). In this particular case we tried to change the course of the reaction by reacting 9,9-diisobutylene fluorene (**11**) with **1** but without any success, again, only the [3.2.1]octane system (**12**) was obtained. The P-configuration and conformations of the two P-epimers of **12**, which are of special interest because of the steric crowdedness, are under further investigation.

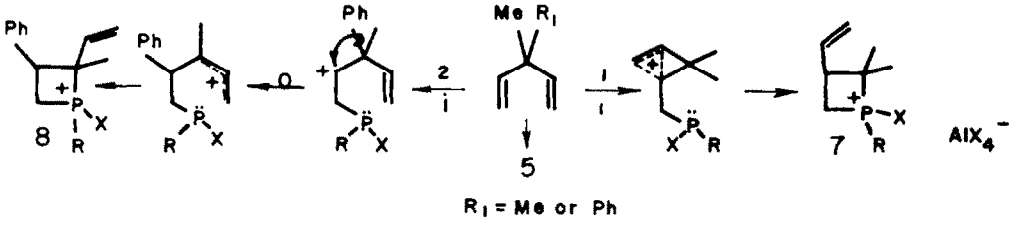
The phosphorylation of the still higher [1.7]diene homologue **9c** did not occur. The only product which was obtained from **9c**, by an acidic intramolecular cyclisation process, was 2,4-diphenyl-4-methylcyclohept-1-ene.[11] Attempts to react higher α,ω-homologue dienes as, e.g. the 1,14 diene, with complex **1** failed as well; only polymeric substances were obtained.

The phosphorylation reaction of vinylcyclopropane (**13**) by complex **1** further exhibits the latent synthetic potential of the discussed reaction.[12] 1,1-Dichloro-2-isopropenyl-2-methylcyclopropane (**13**) reacts with **1** to give 1-phenyl (or methyl)-1oxo-2,2-dichloro-4,5-dimethylphosphorin-4-ene (**14**). As above, an ionic multistep mechanism is suggested for the formation of **14**, that is, obtaining as before, at the first step, a *tert.* carbonium ion (by the attack of the olefin by **1**) followed by the cyclopropane ring opening to give the stabilized dihalocarbonium ion which then interacts with the P-atom to give the phosphorinene (see Scheme 4).

The cleavage of the cyclopropane in a single manner agrees with the multistep mechanism.[14]

The two functional sites of **14** enable interesting chemical transformations which are presently under investigation.

From the beginning of this research, we have noticed the formation of unpredictable phosphorylation products, as e.g. the formation of the phosphinic chloride **15a**, obtained as one of the products in the reaction of 1-allyl-cyclohexene with **1**. Formally compound **15a** is the addition product of a phosphorus moiety to one of the double bond carbon atoms and of a hydrogen to the vicinal C-atom. A similar process was also observed by Crews in the case of the phosphorylation of tetramethylethylene.[15] Quin, who reinvestigated the latter reaction suggests that the reaction starts by protonation of the double bond to give, at first, a carbonium ion



Scheme 6.

which then alkylates the phosphorus dichloride.[6] A second mechanism, involving a phosphiranium intermediate, as proposed earlier by Crews,[15] is not excluded either, although Quin believes it to be less probable. In the meanwhile, we have found a whole series of compounds which exhibit the same type of RP(O)Cl, H additions to a double bond.‡ See Scheme 5. As in the case of tetramethylethylene, the source of the hydrogen (which adds to the double bond), was found to be from a molecule of water initially present with complex **1**. For example, 2,4-dimethylpenta-1,4-diene (**4a**) was found to react with **1** prepared from freshly sublimed $AlBr_3$ under extreme conditions of dryness (under N_2 atm. in a glove box) to give in 80% yield the epimeric [3.1.0] pair (**5a** and **5b**). The remaining 20% is a polymeric unidentified substance (no traces of **16**, the RP(O)Br, H addition product could, however, be revealed). When 0.1 eq of H_2O were added to $PhPBr{\cdot}AlBr_3$ in CH_2Cl_2 (or CH_2Br_2), the yield of the bicyclophosphiranes (**5a** and **5b**) dropped to 60%. However, under these conditions a new compound (**16**) was produced in 10% yield, the rest being again the polymeric material. When D_2O was applied in the latter reaction d_1-**16** (in ~50%) was obtained; quenching of the former reaction, the one performed in the presence of 0.1 eq. H_2O, with D_2O did not cause deuterium incorporation. Compound **16** was determined by its spectroscopic data to be 1,1,3-trimethylbut-3-enyl phenylphosphinic bromide. Raising the amount of water to 1 equivalent gave a 40% yield of **16**, and, at the same time only 10% of the bicyclic compounds (**5a** and **5b**). The percentage of the polymeric material was raised, under the latter reaction conditions, to 50% (and even more when more water was present) and, at the same time the bicyclic compounds' yield dropped almost to zero. Similar results were obtained while using water-doped $PhPCl_2{\cdot}AlCl_3$ (the new addition product being in this case the phosphinic chloride **17**). It is thus clear that the added hydrogen, originates from water present with the complex in the first place. The above results may agree with the initial protonation mechanism (*vide supra*), however, further experiments have shown that even if the reaction starts by protonation, it is not a simple protonation. The presence of varying amounts of HBr (0.1–1 equivalent), together with $RPBr_2$ did not lead to **16**. The initial protonation mechanism is not excluded however by the latter results, as it is known that water with $AlCl_3$ gives a complex with special catalytic properties,[16] and it is this complex rather than simple protonation (if the protonation step is indeed the first step) that starts the reaction. Addition of varying small amounts of HX to $RPX_2{\cdot}AlX_3$ also failed to give anything but polymers. From the above data it can be concluded that AlX_3 is essential for the reaction to occur and that more than one mechanism of the phosphorylation addition can exist, depending on the reaction conditions. In the complete absence of water the reaction has to start from the $RPX_2{\cdot}AlX_3$ addition to the olefin to give ions of type **i**.

Whether such an ion is or not in equilibrium with a phosphiranium ion **I** is another question.[11] Ion **i** could be trapped by a dienophile (e.g. a thioisocyanate) when isobutylene was reacted with **1** at low temperatures.[13] To what extent ion **i** exists in the phosphiranium form is hard to predict. Further investigations of the manner of addition of **i** (or **I**) to various polar dienophiles may indicate on the preferred strucuture of the attacking ion entering the reaction, but will of course say nothing about the contributions of the various forms of the ion in the ground state. We hope that NMR studies including ^{31}P-NMR measurements of ion **i**/**I** will help clarify this problem.

It must be stressed that the existence of ion **i** does not exclude the special proton addition mechanism while using **1** in the absence of absolutely dry conditions. Scheme 5 summarises the various "wet" phosphorylation products (**15–23**). Full interpreted spectroscopic data which prove the structure of the various compounds are given in the Experimental section. A typical adduct is the product of **4a** with $PhPBr_2{\cdot}AlBr_3$, namely compound **16**; an oil, $C_{13}H_{18}POBr$, *m/e* 300, 302 [M^+, 25%], ^{1}H-NMR δ: 0.90s (3H, J_{PH} = 20 Hz), 0.95s (3H, J_{PH} = 20 Hz), 1.50s (3H, vinyl methyl), 2.0s (2H, J_{PH} = 9 Hz), 4.60 bs and 4.90q (J = 1.5 Hz) (2H, $=CH_2$), and 7.30–8.00 m (5H) the P(O)Ph group. Existence of the P(O)Br group was determined by boiling **16** with a 2% NaOMe methanol solution to give the characteristic P(O)OMe group (δ 3.60s, J_{PH} = 9 Hz).

Compound **16** is unstable and after several days it is completely transformed into compound **19**. Compound **19** is an oil, $C_{13}H_{19}PO_2$, according to elemental analysis and *m/e* 238 (M^+, 10%). ^{1}H-NMR δ: 0.95s (3H, J_{PH} = 20 Hz) 1.40s (3H, J_{P-H} = 20 Hz), 1.52s (3H), 1.60s (3H), 2.20 and 1.90 an ABP system (J_{AB} = 12 Hz, $J_{PA(or\ B)}$ = 12 Hz), and 7.30–8.00 m (5H) and P(O)Ph group. The ^{13}C-NMR clearly indicates an oxygen bearing carbon atom, δ 84.3 d (J_{PC} = 2 Hz). A C-atom adjacent to phosphorus appears at 37.6d (J_{PC} = 84 Hz); the large J_{PC} value pointing to a P(O)-O- moiety,[16] all other δ-values (Experimental) are in full agreement with the 2-oxophospholane structure (**19**). The suggested mechanism of the transformation is given in Scheme 5.

Interesting also are the four products which were obtained from **9a** with $PhPCl_2{\cdot}AlCl_3{\cdot}H_2O$. The structures of these compounds are in full agreement with the ones shown in Scheme 5, namely structures **20–23**. The various products are addition products of one or two equivalent of HCl and/or one or two P(O)PhCl, H units. Compound **21** results from protonation of one double bond, internal attack of the second double bond and, finally, quenching of the carbonium ion by alkylation of the RPX_2 molecule. The same type of reaction is also obtained with 1,5-dimethylencyclooctane which gives compound **24**.

It is clear from the above results that the reaction course differs significantly in the presence or absence of water. The latter conditions leading to phosphaheterocycles if their synthesis is achievable. The various products obtained under the "wet" reaction conditions may point to the different possible product types which may be obtained while adding complex **1** to n-alkenes which are unable to rearrange and form phosphaheterocycles.

Recently it was found that complex **1** can react not only with [1, n]dienes, but also with oxo and imino olefins in which the hetero atom replaces the second double bond, to give novel heterocycles. The latter results will be the subject of a forthcoming report.

EXPERIMENTAL

Melting points were taken on a Unimelt Thomas and Hoover's capillary m.p. apparatus and are uncorrected. IR Spectra were

‡The RP(O)Cl is always attached to the more substituted double bond carbon atom.

recorded on a Perkin–Elmer Infracord model 337 Spectrophotometer. NMR spectra were taken either on a Bruker WH 90 or a Jeol JNM-C-60 HL spectrometer (equipped with a P-decoupler) on 5-10% solutions in $CDCl_3$ containing TMS as an internal standard. All proton-multiplicities are the residual ones after P-irradiation. ^{13}C-NMR spectra were taken on a Bruker WH-90 (22.63 MHz) instrument in $CDCl_3$; all chemical shifts are reported with respect to TMS (δ_0). Mass spectra were recorded on a Dupont 21-491B spectrometer.

General procedure

Method A. To a stirred solution of $AlCl_3$ (freshly sublimed, 1.32 gr, 0.01 mole) and $PhPCl_2$ (1.78 gr, 0.01 mole) in dry CH_2Cl_2 (15 ml) at 0°C, was slowly added a solution of the diene, or the olefin (0.01 mole) in CH_2Cl_2 (10 ml) at 0°C. The reaction mixture was stirred under N_2 for 2 h and then, slowly poured on cold 10% $NaHCO_3$ solution. The aqueous solution was extracted several times with CH_2Cl_2, the combined CH_2Cl_2 phase dried over $MgSO_4$, and then evaporated to give a viscous oil which was then submitted to chromatography on a silicagel column. Elution with $CHCl_3$ and/or $CHCl_3$ with rising amounts of EtOAc (up to 15%) gave the products.

Method B. The same procedure as above (Method A) except for using unsublimed $AlCl_3$.

Method C. Same procedure as A except for addition of water, up to 1 eq. to the $AlCl_3$ in the CH_2Cl_2 solution, before adding the dihalophosphane.

The structure determinations of compounds: **2, 3, 5, 6, 7, 8, 10, 14, 15a** and **18a, b** and **f** are given in the previous reports.[8-12]

9,9-*Di* (2-*methallyl*) *fluorene* (**11**) was prepared following a procedure described by Makosza.[18] Fluorene was alkylated with methyallychloride to give an oil, **11**; ν_{max}^{neat} 2900, 1650, 1620 cm^{-1}, NMR, δ: 1.00s (6H), 2.82s (4H), 4.25bs (2H), 4.35bs (2H) and 7.30–8.00 m (8H). Mass spectra *m/e* 274 (M^+, $C_{21}H_{22}$).

1,4 - *Dimethyl* - 6 - (9 - *fluorene*) - 2 - *oxo* - 2 - *phenyl* - 2 - *phosphabicyclo*[3.2.1]*octanes* (**12a** *and the P-epimer* **12b**). Method A. **12a**; m.p. 220° (acetone) $\nu_{max}^{CHCl_3}$ 2900, 1600, 1470, 1440, 1410, 1380, 1340, 1170, 1130, 1100, 1000, 950, 890, and 820 cm^{-1}. NMR, δ: 0.85s (C_1-Me, J_{PH} = 12 Hz), 1.28s (C_4-Me, J_{PH} = 2 Hz), 1.92bs (4H), 2.30–2.50 m (2H), 3.00bs (1H), 3.30bs (1H) and 7.10–8.50 m (13H). ^{13}C-NMR, δ: 22.7q, 30.7dq (J_{PC} = 11 Hz), 36.8d (C_4, J_{PC} = 6 Hz), 38.9dt (C_3, J_{PC} = 60 Hz), 40.0d (C_1, J_{PC} = 66 Hz), 42.7t, 46.2dt (J_{PC} = 17 Hz), 49.2s (C_6) and 51.7t. Mass spectrum *m/e*, 398 (M^+, 50%), 320 (M^+-Ph, 80%), 221 (25%), 219 (25%), 205 (50%), 206 (25%), 178 (25%) and 119 (100%), λ_{max} (ethanol) 306 (330), 294 (960) and 268 (780).

12b–m.p. 110° (acetone), $\nu_{max}^{CHCl_3}$ 2900, 1630, 1450, 1400, 1380, 1250, 1150, 1110, 1100 and 960 cm^{-1}. NMR, δ: 1.38s (C_4-Me), 1.58s (C_1-Me, J_{PH} = 12 Hz), 2.10s (2H), 2.20–3.30 m (6H) and 6.70–8.00 m (13H). ^{13}C-NMR, δ: 21.5q, 31.2dq (J_{PC} = 9 Hz), 36.0d (C_4, J_{PC} = 4 Hz), 39.4dt (C_3, J_{PC} = 63 Hz), 39.7d (C_1, J_{PC} = 66 Hz), 41.8dt (J_{PC} = 4 Hz), 45.9dt (J_{PC} = 12 Hz), 49.1s (C_6) and 51.0t. Mass spectrum identical with that of **12a**, λ_{max} (ethanol) 306 (710), 294 (630) and 270 (1940).

1-*Methyl-cyclohexylphenylphosphinic chloride* (**15b**). Method B, an oil, 30% yield, ν_{max}^{neat} 2900, 1470, 1450, 1230, 1130 and 860 cm^{-1}. NMR, δ: 1.20s (Me, J_{PH} = 22 Hz), 1.50–1.70 m (10H) and 7.20–7.80 m (Ph). Mass spectrum *m/e* 258/256 (M^+, $C_{13}H_{18}POCl$, 3% and 10% respectively). 200 (10%), 190 (10%), 175 (15%) and 160 (PhPOHCl, 100%). The P(O)PhCl group was confirmed by the exchange of the chlorine atom by OMe, as described for compound **18d**; the product being an oil, ν_{max}^{neat} 2950, 2900, 1720, 1600, 1480, 1450, 1230, 1170, 1030, 860, 820, 770, 720, 700 and 600 cm^{-1}. NMR, δ: 1.10s (Me, J_{PH} = 18 Hz), 1.40–1.60m (10H), 3.60s (OMe, J_{PH} = 15 Hz) and 7.20–8.00m (Ph). Mass spectrum *m/e* 252 (M^+, $C_{14}H_{21}PO_2$).

1,1,3-*Trimethyl-3-butenylphenylphosphinic bromide* (**16**). Method B, employing $AlBr_3$, an oil 40% yield, $\nu_{max}^{CHCl_3}$ 2980, 1640, 1470, 1440, 1240, 1180, 1150, 1100 and 900 cm^{-1}. NMR, δ: 1.15s (Me, J_{PH} = 20 Hz), 1.20s (Me, J_{PH} = 20 Hz), 1.75d (Me, $^3J_{HH}$ = 1.5 Hz), 2.30s (2H, J_{PH} = 9 Hz), 4.60bs (1H), 4.90q (1H, Me–C=C–H, $^3J_{HH}$ = 1.5 Hz) and 7.30–8.00 m (Ph). ^{13}C-NMR. δ: 21.0q (2Me), 25.4q (Me), 41.7t (C_3), 42.4d (C_2, J_{PC} = 76 Hz), 117.0t (C_5) and 139.9d (C_4, J_{PC} = 16 Hz). Mass spectrum *m/e* 302/300 (M^+, 25%, 25%), 206/204 (PhP(O)HBr, 28%, 28%), 125 (PhPOH, 100%), and 108 (24%). Refluxing **16** with NaOMe/MeOH as described for **18d**, gave the P–OMe derivative, $\nu_{max}^{CHCl_3}$ 2900, 1440, 1300, 1160, 1120, 1030, 900 and 800 cm^{-1}. NMR, δ: 1.05s (Me, J_{PH} = 18 Hz), 1.10s (Me, J_{PH} = 18 Hz), 1.70bs (Me), 2.25s (2H, J_{PH} = 9 Hz), 3.60s (OMe, J_{PH} = 9 Hz), 4.60bs (1H), 4.90bs (1H) and 7.40–8.00 m (Ph). Mass spectrum *m/e* 252 (M^+, 50%), 237 (M^+–Me, 5%), 197 (24%) and 156 (MeOP(O)PhOH, 100%).

1,1,3-*Trimethyl-3-butenylphenylphosphinic chloride* (**17**). Method C, an oil, 40% yield, $\nu_{max}^{CHCl_3}$ 2900, 1470, 1450, 1210, 1100 and 910 cm^{-1}. NMR, δ: 1.18s (Me, J_{PH} = 21 Hz), 1.20s (Me, J_{PH} = 21 Hz), 1.75d (Me, J_{HH} = 1.5 Hz), 2.30s (2H, J_{PH} = 9 Hz), 4.65bs (1H), 4.90bs (1H) and 7.40–7.90 m (Ph). Mass spectrum *m/e* 258/256 (M^+, $C_{13}H_{18}POCl$, 10% and 30%, respectively), 243/241 (M^+–Me, 15% and 45%) and 160 (PhPOHCl, 100%).

2-*Chloro*-1,1-*dimethylethylphenylphosphinic chloride* (**18c**). Method B, an oil, 10% yield, ν_{max}^{neat} 2900, 1440, 1410, 1240, 1100 and 910 cm^{-1}. NMR, δ: 1.28s (Me, J_{PH} = 17 Hz), 1.30s (Me, J_{PH} = 17 Hz), 3.75s (2H, J_{PH} = 6 Hz) and 7.50–8.00 m (Ph). Mass spectrum *m/e* 250 (M^+, 10%), 215 (M^+–Me, 100%).

1,1-*Dimethyl-3-phenylpropylphenylphosphinic chloride* (**18d**). Method B, an oil, 35% yield, $\nu_{max}^{CHCl_3}$ 2900, 1440, 1410, 1210 and 1160 cm^{-1}. NMR, δ: 1.25s (Me, J_{PH} = 16 Hz), 1.30s (Me, J_{PH} = 16 Hz), 1.60–2.00 m (2H) 2.30–2.50 m (2H), 7.0s (Ph) and 7.5–8.0 m (Ph). ^{13}C-NMR, δ: 21.2q (2Me), 30.0dt (J_{PC} = 10 Hz), 37.9t, 42.1d (C_2, J_{PC} = 76 Hz). *Mass spectrum m/e* 308/306 (M^+, $C_{17}H_{20}POCl$, 3% and 10% respectively), 204/202 ('PrP(O)PhCl$^+$, 30% and 100%) and 160 (PhP(OH)Cl, 15%). The PhP(O)Cl group, suggested by the mass spectrometer was confirmed by the ability to replace the chlorine atom by an OMe following refluxing of **18d** in a 2% CH_3ONa/CH_3OH solution). The P-methoxy derivative gave the same NMR spectrum as **18d** except for an additional doublet at δ = 3.80 (OCH_3, J_{PH} = 12 Hz). Mass spectra *m/e* 302 (M^+, $C_{18}H_{23}O_2P$).

1,1-*Dimethyl-3-butenylphenylphosphinic chloride* (**18e**). Method C, an oil, 5% yield, $\nu_{max}^{CHCl_3}$ 2900, 1630, 1590, 1460, 1440, 1370, 1250, 1100, 1000, 920 and 800 cm^{-1}, NMR, δ: 1.20s (Me, J_{PH} = 20 Hz), 1.21s (Me, J_{PH} = 20 Hz), 2.35d (2H, J_{PH} = 12 Hz, $^3J_{HH}$ = 6 Hz), 5.20 m (2H), 5.60 m (1H) and 7.4–8.0 m (Ph). On irradiation of H-3 at δ 5.6 ppm the double doublet at δ 2.35 ppm changes into a doublet with J_{PH} = 12 Hz. Mass spectrum *m/e*: 244/242 (M^+, 10% and 30%), 201 (15%), 174 (15%), 164 (30%), 162 (45%), 161 (45%), 159 (15%), 158 (15%) and 125 (PhPOH, 100%).

1-*Oxo*-1-*phenyl*-3,3,5,5-*tetramethyl*-2,1-*oxaphospholane* (**19**). Compound **19** is obtained from compound **16** after the latter is left for several days in $CHCl_3$ solution (the transformation can be monitored in $CDCl_3$); an oil, $\nu_{max}^{CHCl_3}$ 2960, 1440, 1370, 1170, 1120, 960, 920, 900 and 850 cm^{-1}. NMR, δ: 0.90s (Me, J_{PH} = 16 Hz), 1.40s (Me, J_{PH} = 16 Hz), 1.50s (Me), 1.60s (Me), 1.98 and 2.26 (2H, an AB quartet, J_{AB} = 12 Hz) and 7.30–8.0 mm (5H); ^{13}C-NMR, δ: 24.5q, 26.4q, 30.7dq (J_{PC} = 5 Hz), 32.2q, 37.6d (C_5, J_{PC} = 84 Hz), 52.2dt (C_4, J_{PC} = 4 Hz), 84.3d (C_3, J_{PC} = 2 Hz); mass spectrum *m/e*: 238 (M^+, 10%), 223 (M^+–Me, 4%), 149 (9%), 99(15%), 98 (100%) and 97 (15%).

2,5 - *Dimethyl* - 2,5 - *dichlorohexane* (**20**), 1,3,3 - *Trimethyl-cyclopentylphenylphosphinic chloride* (**21**), 4 - *Chloro* - 1,1,4 - *trimethylpentylphenylphosphinic chloride* (**22**) *and* 1,1,4 - *Trimethyl* - 4 - *phenylphosphinyl* - *chloridepentylphenylphosphinic chloride* (**23**). Method C. The four compounds were separated on a silica gel column by eluants described below. Compound **20**, an oil, 5% yield, eluted with petrolether, NMR, δ: 1.40s (12H) and 1.7s (4H) CI-MS; *m/e* 182. Compound **21**, an oil, 20% yield, eluted with $CHCl_3$. ν_{max}^{neat} 3000, 1440, 1220, 1100, 750, 720 and 700 cm^{-1}. NMR, δ: 1.00s (Me), 1.10s (Me), 1.35s (Me, J_{PH} = 19 Hz), 1.50–2.00 m (4H), 2.00–2.50 m (2H) and 7.40–8.00 m (5H). ^{13}C-NMR, δ: 24.7q, 29.5q, 30.3q, 34.6t, 40.5dt (J_{PH} = 9 Hz), 44.4s, 48.5t, 49.5d (J_{PH} = 79 Hz). Mass spectrum *m/e* 272/270 (M^+, 1.5% and 5%), 205 (5%), 203 (10%), 201 (5%), 187 (40%) and 160 (PhP(O)HCl, 100%). Refluxing compound **21** in a 2% CH_3ONa/CH_3OH solution, gave the P–OMe derivative with the same NMR spectrum as **21** except for an additional doublet at δ = 3.7 (OMe, J_{PH} = 11 Hz). Mass spectrum *m/e* 266 (M^+, 12%),

251 (M^+–Me, 3%), 198 (5%), 197 (25%) and 156 (100%). Compound **22**, an oil, 5% yield, b.p. 90°/0.1 mm Hg, $\nu_{max}^{CHCl_3}$ 2900 1460, 1380, 1100 and 900 cm^{-1}. NMR, δ: 1.18s (Me, J_{PH} = 19 Hz), 1.22s (Me, J_{PH} = 19 Hz), 1.57s (2Me), 1.80s (4H, J_{PH} = 12 Hz) and 7.30–8.00 m (Ph). ^{13}C-NMR, δ: 21.4q ($2CH_3$), 31.3q, 32.5q, 39.6dt (J_{PC} = 12 Hz), 43.2t, 49.8d (J_{PC} = 68 Hz) and 70.4s. Mass spectrum *m/e* 272/270 (M^+–HCl, 3% and 10%), 219 (15%), 215 (20%), 202 (20%), 197 (20%), 160 (100%), 148 (20%) and 119 (60%); *m/e* (CI): 306 ($C_{14}H_{21}POCl_2$). Refluxing compound **22** in 2% CH_3ONa/CH_3OH solution gave the P–OMe derivative; NMR, δ: 1.05s (Me, J_{PH} = 19 Hz), 1.08s (Me, J_{PH} = 19 Hz), 1.55s (Me), 1.57s (Me), 1.70s (4H, J_{PH} = 11 Hz), 3.60s (OMe, J_{PH} = 12 Hz) and 7.50–8.00 m (Ph). Mass spectrum *m/e* 268/266 (M^+–HCl, 4%, 12%), 199 (12%), 198 (25%) and 166 (100%). Compound **23**, eluted with EtOAc, m.p. (acetonitrile) 195°C, $\nu_{max}^{CHCl_3}$ 2900, 1500, 1440, 1390, 1270 and 1100 cm^{-1}. NMR, δ: 1.20s (6H, J_{PH} = 18 Hz), 1.22s (6H, J_{PH} = 18 Hz), 1.70s (4H, J_{PH} = 12 Hz) and 7.50–8.00m (10H). *m/e* (C.I.): 430 ($C_{20}H_{26}P_2O_2Cl_2$). Exchange of the two chlorine atoms in **22** by two OCH_3 groups (refluxing **22** in 2% CH_3ONa/CH_3OH solution), gave an oil; $\nu_{max}^{CHCl_3}$ 2900, 1400, 1440, 1180, 1100 and 1020 cm^{-1}. NMR, δ: 1.00s (12H, J_{PH} = 15 Hz), 1.5s (4H, J_{PH} = 12 Hz), 3.50s (6H, J_{PH} = 12 Hz), and 7.50–8.00m (10H).

5-Methylbicyclo[3,3,1]*nonylphenylphosphinic chloride* (**24**). Method B, an oil, 5% yield, ν_{max}^{neat} 2900, 1400, 1440, 1100 cm^{-1}. NMR, δ: 0.90s (3H), 1.20–2.00 m (15H) and 7.40–8.00 m (5H). ^{13}C-NMR, δ: 21.8dt (C_3, C_7, J_{PC} = 16 Hz), 28.4dt (C_4, C_6, J_{PC} = 4 Hz), 29.8d (C_5, J_{PC} = 12 Hz), 33.0q (Me), 37.2t (C_2, C_8), 38.0dt (C_9, J_{PC} = 4 Hz), 42.7d (C_1, J_{PC} = 76 Hz). Mass spectrum *m/e* 298/296 M^+, 3%, 10%) and 160 (PhP(O)HCl, 100%).

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