Tetrahedron Vol. 47, No. 1, pp. 71-82, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

DIELS ALDER REACTIONS OF P-CHLORO (BISTRIMETHYLSILYL) METHYLENE PHOSPHINE.

Mustafa Abbari [1], Paul Cosquer [1], François Tonnard [2],
Yeung Yat Cheng Yeung Lam Ko [1] and Robert Carrié [1]*.

[1] Groupe de Recherches de Physicochimie Structurale, U.R.A. C.N.R.S. 704.
[2] Département de Physique cristalline, U.R.A. C.N.R.S. 804
[1] and [2] Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes Cédex, France.

(*Received in Belgium* 11 *September* 1990)

Abstract - The electrophilic dienophile, P-chloro (bistrimethylsilyl) methylene phosphine reacts with electron poor or rich dienes to give the [$4\pi + 2\pi$] cycloadducts whose structures are determined by NMR. The regiospecificity of the reaction is satisfactorily predicted by the second order perturbation theory.

Introduction

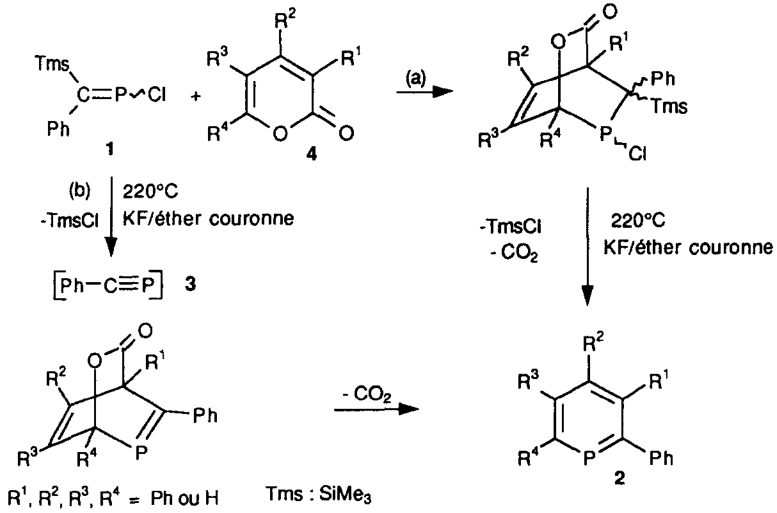
Diels Alder reactions involving phosphaalkenes as dienophiles have drawn much attention as shown by the number of articles and more particularly by two reviews [1,2] during the last decade.

The first example described by Arbuzov and co-workers [3] in 1978 shows that hexachlorocyclopentadiene adds on the P=C double bond of a diazaphosphole to give the [$4\pi + 2\pi$] cycloadduct. It has been shown that diazaphospholes react with 2,3-dimethylbutadiene [4] and cyclopentadiene [5]. In the latter case, the primary endo product isomerizes at a higher temperature to the exo product via a cycloreversion process. Mathey and his co-workers showed that [H] phospholes give, after 1,5 shifts, phosphadienes which may react as dienes or dienophiles [6]. They dimerize by a Diels Alder reaction [7] in an endo way [8]. The thermal behaviour of the adducts has been studied [9,10] and more particularly the reaction with different alkynes at over 200°C leads to phosphabenzenes. Heinicke and Tzchach have described the addition of two oxaphospholes and one oxaarsole with 2,3-dimethylbutadiene and tetrachloro orthoquinone [11,12].

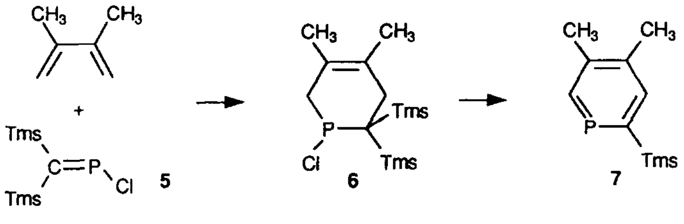
Open chain phosphaalkenes have been studied extensively. Bickelhaupt [13,14] and Navech [15] and their co-workers have shown that triaryl methylene phosphines and one aminophosphaalkene can react as dienophiles. The work done by Appel et al. [16-22] has given a better insight on the reactivity of P=C double bond compounds. Some interesting mechanistic problems occur during the course of their study. They have shown particularly that (i) the phosphorus atom can undergo an inversion during the cycloaddition without necessarily involving a cycloreversion [18] (ii) the kinetic endo adducts with cyclopentadiene are liable to transform into the exo adducts which are thermodynamically more stable, via a cycloreversion [21] (iii) the configuration of the phosphaalkene is maintained during the cycloaddition [22] (in the absence of inversion of the phosphorus atom).

The synthetic potentialities of the Diels Alder reaction was first used in this field by Märkl and coworkers [23] who prepared various phenylphosphabenzenes **2** from phosphaalkene **1**. They consider that these compounds 2 are obtained via pathway (b) thus figuring **1** as a synthetic equivalent of phosphaalkyne 3. The same sequence of reactions can be observed by using a cyclopentadienone instead of α-pyrone **4** with extrusion of carbon monoxide in the last step.

Remark : Taking our own work into account and in particular the greater reactivity of compounds of type **1** relatively to those of type **3** in the Diels-Alder reactions [24], it seems to us that pathway (a) is more probable.



We have also shown [25] that the addition of phosphaalkene **5** with 2,3-dimethylbutadiene leads to a 30 % yield of phosphabenzene **7** after the reaction with KF and [18] crown-6 ether.

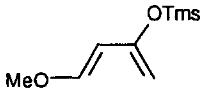


Only a few functionalized phosphabenzenes are known [26-30], so, it is interesting to us to find a general route to these compounds in two steps : (i) the reaction of electron rich or poor functionalized dienes with **5** leading to Diels Alder adducts. (ii) the aromatisation of these adducts leading to functionalized phosphabenzenes.

Three short papers [31,32,33] show that the syntheses of these last compounds are possible this way. The present article will only deal with the first step, i.e. the addition of phosphaalkene **5** to different dienes. The obtention of phosphabenzenes will be described in a second article.

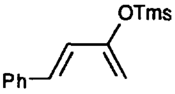
Results

The electron rich or poor dienes **8a-8g** react regiospecifically with phosphaalkene **5**. A mixture of two diastereoisomers [a different relative configuration between phosphorus and the cyclic asymetric carbon(s) atom(s)] is sometimes obtained. Generally, the purification of adducts **9** is difficult due to their instability.

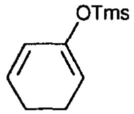


8a

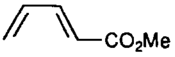
8b



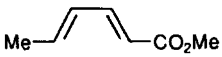
8c



8d



8e

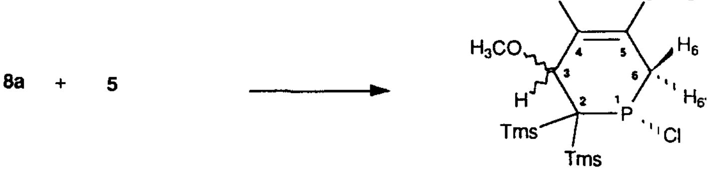


8f

8g

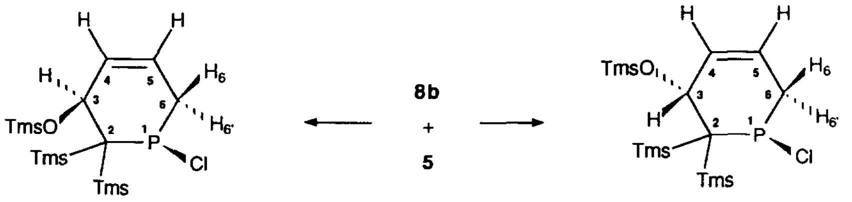
The determination of their structure(s) was established on the basis of their NMR data. It was particularly difficult The number of coupled nuclei required high field NMR together with repeated selective decoupling. The sense of addition was determined without any ambiguity. In certain cases, it was not possible to ascertain the relative configuration of the different asymmetric atoms.

1 - Diene 8a. The reaction carried out at room temperature is exothermic and after one hour, adduct **9a** is obtained quantitatively (^{31}P NMR $\delta = 114$ ppm). It is not possible to purify the latter by distillation. The corresponding phosphabenzene is obtained under this condition (slowly at room temperature). The NMR data, ^{31}P, ^{1}H and ^{13}C, allow us to establish the structure of **9a**. Thus, the ^{13}C NMR shows that carbon 6 with two hydrogen atoms is bound to phosphorus ($^{1}J_{PC6} = 36$ Hz and $^{2}J_{PC3} = 5.7$ Hz only). The ^{1}H NMR also confirms the proposed structure : H_6' ($\delta = 2.00$ ppm) is in the cis position with respect to the lone pair of the phosphorus atom, $^{2}J_{PH6'} = 24.7$; H_6 ($\delta = 2.60$ ppm with $^{2}J_{PH6} = 6.8$ Hz) [34]. First impressions lead us to believe that the coupling constant ($^{3}JPH_3 = 2.0$ Hz) enables the relative configuration of phosphorus and carbon 3 [35] to be determined but this is not so because : (i) only one isomer is obtained and (ii) we have no information about the conformation of the molecule.



9a

2 - Diene 8b. After the reaction has proceeded for 15 hours at room temperature a 1:4 mixture of two diastereoisomers A and B is obtained (67 % yield after distillation).



9b' or 9b" — **9b" or 9b'**

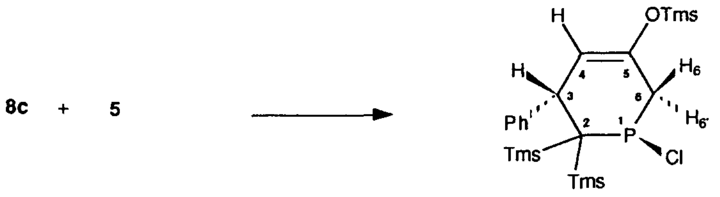
1st diastereoisomer, A, 20 %, δ^{31}P = 129.9 ppm.

2nd diastereoisomer, B, 80 %, δ^{31}P = 120.6 ppm

When the reaction is monitored at -20°C by ^{31}P NMR, we observe that after one hour's reaction, phosphaalkene 5 is not completely transformed and isomer A is predominant (5/A/B : 28/63/9 %).

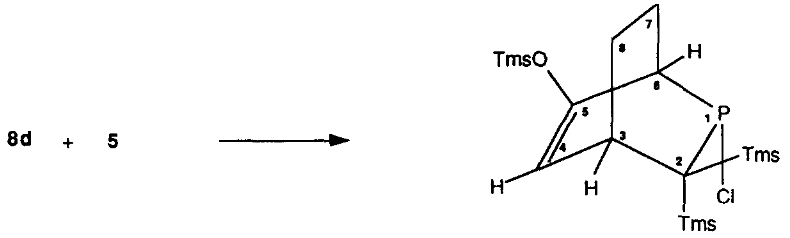
After 7 days at -20°C, isomerization leads to the same mixture as the one obtained at room temperature (15 hours). The mixture distilles without any decomposition. The isomerization does not occur via a cycloreversion (diene **8b** has a very low boiling point). The isomerization seems to occur by the inversion of the phosphorus atom as already mentioned and not discussed[18]. The structures of the adducts are established on the basis of their ^{1}H, ^{31}P and ^{13}C NMR spectra. Thus, the large coupling constants, $^{1}J_{PC6}$ = 38.2 and 29.9 Hz and $^{2}J_{PH6'}$ = 34 and 25 Hz simultaneously for **9b'** and **9b"** show that phosphorus is bound to the carbon atom with two hydrogens while $^{3}J_{PH3}$ = 2.0 and 2.5 Hz in the two diastereoisomers do not lead to the determination of the relative configuration between phosphorus and carbon 3.

3 - Diene 8c. After 24 hours at room temperature, only one diastereoisomer **9c** is obtained almost quantitatively. The purification of this compound by distillation is not possible due to decomposition. The orientation of addition was determined as in the previous examples ($^{1}J_{PC6}$ = 36.0 Hz). The relatively large value of the coupling constant, $^{3}J_{PH3}$ = 7.8 Hz is in favour of the relative configuration of carbon 3 and the phosphorus atom as represented in **9c** (i.e. H3 and the lone pair of the phosphorus atom are in trans relationship) by analogy with adducts **9f'** and **9f"** obtained from methyl sorbate **8f**, as we shall see later.



9c

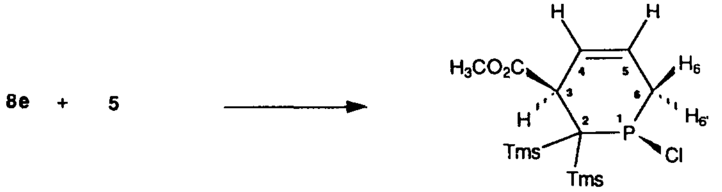
4 - Diene 8d. After 15 hours at room temperature, the total transformation of the starting diene leads to only one diastereoisomer (m.p. = 85°C).



9d

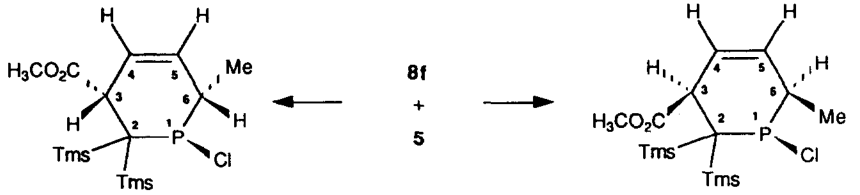
The structure and hence the sense of addition is established on the basis of the coupling constants : $^1J_{PC6}$ = 35.0 Hz and $^2J_{PH6}$ = 14.7 Hz. The coupling constant $^2J_{PC7}$ = 21.0 Hz is in favour of the stereochemistry shown (the CH_2-CH_2 bridge is in cis position with the lone pair of phosphorus [36]) while the coupling constants, $^4J_{H4H6}$ = 2.2 Hz and $^3J_{H3H4}$ = 7.8 Hz show that the trimethylsilyloxy group is linked to carbon 5.

5 - Diene 8e. After 2 hours without any solvent, the reaction of the phosphaalkene **5** leads to adduct **9e** with about 10 % unidentified impurities (^{31}P NMR). The coupling constant $^1J_{PC6}$ = 36.0 Hz between phosphorus and carbon 6 with two geminal hydrogen atoms shows the orientation of addition. The relative configuration of atoms 1 and 3 (H_3 and lone pair of phosphorus in cis) is determined by analogy with results obtained with diene **9f** ($^3J_{PH3}$ = 2.8 Hz).



9e

6 - Diene 8f. A 4:6 mixture of two diastereoisomers **9f'** and **9f''** respectively is obtained quantitatively after 12 hours' reaction at room temperature.



9f' 40 % $\delta^{31}P$ = 144.1 ppm **9f''** 60 % $\delta^{31}P$ = 145.4 ppm

Attempts to purify this mixture by distillation lead to cycloreversion (methyl sorbate **8f** was characterized by ^1H NMR). For the two isomers, **9f'** and **9f''**, the carbon atom substituted with the methyl group is bound to the phosphorus atom, which is proved by the coupling constants $^2J_{PH6}$ = 3 and 24 Hz and $^3J_{PH}$ (CH_3 linked to carbon 6) = 20.4 and 16.6 Hz. The values observed for $^2J_{PH6}$ show without any ambiguity that the lone pair of phosphorus is in the trans position relative to H_6 in **9f'** ($^2J_{PH6}$ = 3.0 Hz) and in the cis position with **9f''** ($^2J_{PH6}$ = 24.0 Hz). The relative configuration of carbon 3 and 6 (H_3 and H_6 in cis) is derived from the concerted process of the Diels-Alder reaction, thus defining completely the stereochemistry of **9f'** and **9f''** (**9f'** : $^3J_{PH3}$ = 10.2 Hz and **9f''** : $^3J_{PH3}$ = 2.0 Hz), i.e. a large coupling constant $^3J_{PH3}$ implies a trans relationship between hydrogen and phosphorus.

7 - Diene 8g. After refluxing for 40 hours in benzene, the diene completely disappears. The expected adduct **9g** is unstable and leads to a mixture of a phosphine and functionalized phosphabenzenes in different proportions which depend on the experimental conditions. This will be discussed in another article.

8 - Theoretical approach : Reactivity and regiospecificity . The simplest and most popular method for discussing the theory of cycloaddition reactions (reactivity, regioselectivity...) is the second order perturbation theory [37-39]. The calculated second order perturbation energy $E^{(2)}$ corresponds to an attractive interaction between all occupied π molecular orbitals (MO) of one molecule with all unoccupied MO of the other, the two species being considered as approaching in two parallel planes [40]. The molecular orbital energies and atomic orbital coefficients in the molecular orbital are calculated in the CNDO/2 approximation [41] and the distance between the two parallel planes of the interacting molecules is taken as 3 Å.

The geometry of phosphaalkene is chosen in the following way : (i) The molecule is considered to be planar. (ii) The usual lengths are taken from literature [42] and in particular the C-Si bond length is assumed to be 1.84 Å. (iii) The P-Cl bond length (2.05 Å) and the Cl-P=C bond angle (104°5) are taken from Nixon's work [43]. (iv) The P=C bond length (1.66 Å) represents the average of the values from the literature [43,44]. (v) The P-C-Si bond angles are assumed to be 115° (the literature average value) [45].

The geometry of the dienes is obtained from standard parameters in the literature [42], while that of **8d** is optimized using calculations by the MNDO method [46]. The energies of the frontier orbitals are shown in figure 1. It appears that phosphaalkene **5** behaves as an electrophile in every case and reacts more easily with electron rich dienes. The second order perturbation energies $E^{(2)}$, are calculated for the two possible orientations (pathway 1 or 2) [47]. The results are given below (in Kcal/mole) and are in perfect agreement with the experimental observations. The orientation of addition is that for which the absolute value of $E^{(2)}$ is the greatest.

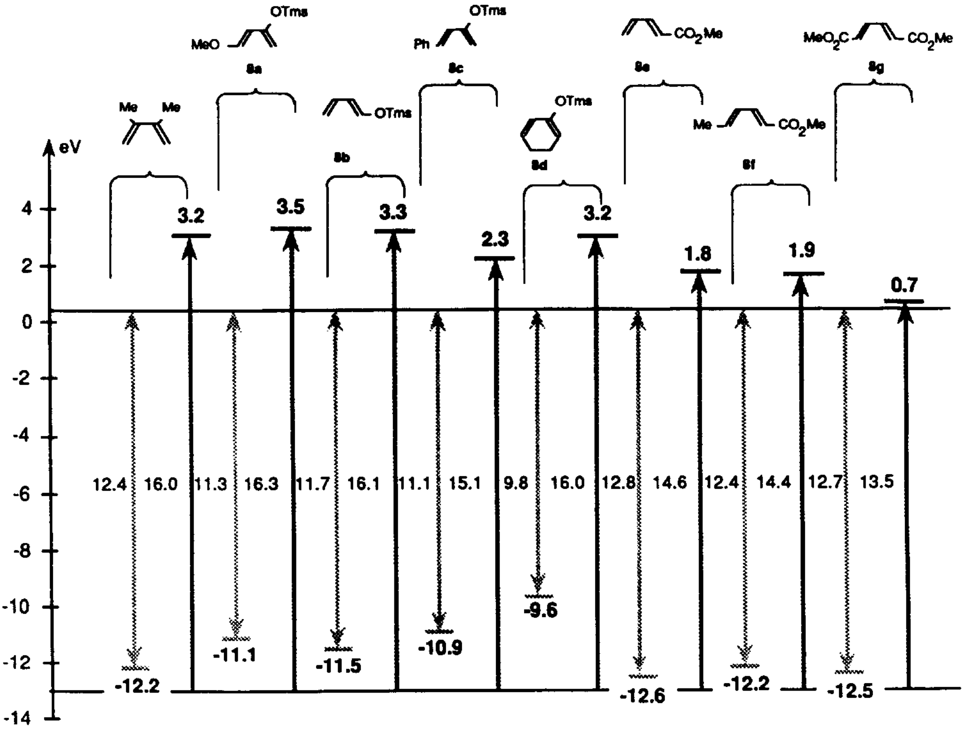
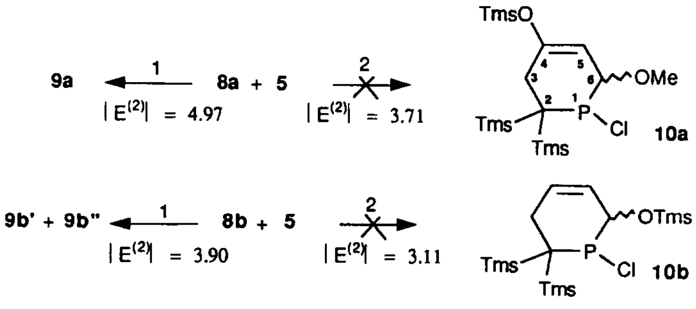
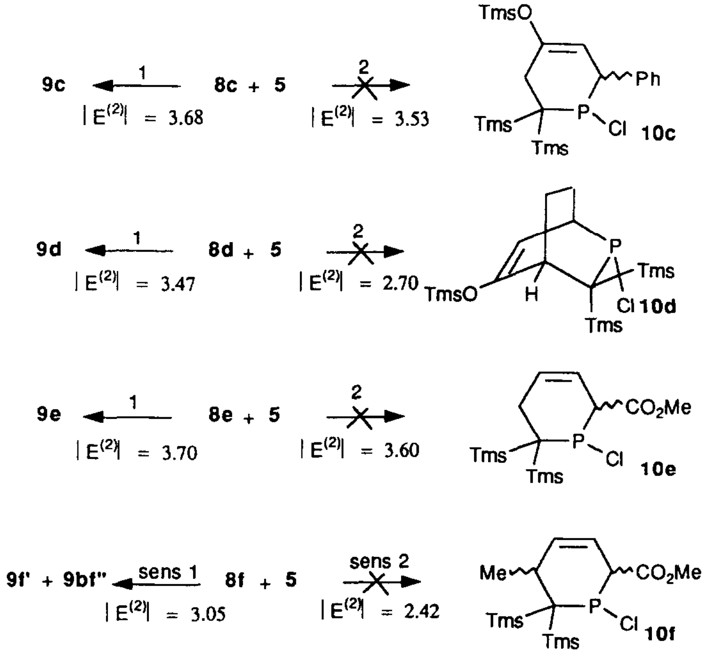

eV
4
2
0
-2
-4
-6
-8
-10
-12
-14
Me Me
MeO OTms
8a
OTms
8b
Ph OTms
8c
OTms
8d
CO2Me
8e
Me CO2Me
8f
MeO2C CO2Me
8g
3.2
3.5
3.3
2.3
3.2
1.8
1.9
0.7
12.4 16.0
11.3 16.3
11.7 16.1
11.1 15.1
9.8 16.0
12.8 14.6
12.4 14.4
12.7 13.5
-12.2
-11.1
-11.5
-10.9
-9.6
-12.6
-12.2
-12.5

Figure 1


9a
1
8a + 5
2
| E(2)| = 4.97
| E(2)| = 3.71
TmsO
OMe
Tms
Tms
P
Cl
10a
9b' + 9b"
1
8b + 5
2
| E(2)| = 3.90
| E(2)| = 3.11
OTms
Tms
Tms
P
Cl
10b



Experimental Section

The NMR spectra are performed on a Bruker AM 300 of the Centre de Mesures de l'Université de Rennes (300, 121.5 and 75.5 MHz for ^{1}H, ^{31}P and ^{13}C respectively)* with many selective decoupling ^{31}P-^{1}H, ^{1}H-^{1}H and ^{1}H-^{13}C. The chemical shifts δ are given in parts per million (ppm) with respect to tetramethylsilane (TMS) as the internal reference for ^{1}H and ^{13}C NMR and to 85 % phosphoric acid as the external reference for ^{31}P NMR, the + sign being for lower field signals. The coupling constants, J, are given in Hertz.

The mass spectra are recorded on a Varian Mat 311 (Centre de Mesures Physiques de l'Université de Rennes). The energy of the electron beam is 70 eV, the intensity of the emitting current 300 µA and the accelerating voltage 3 kV. The precise masses are determined by the Peak Matching Technique.

Chromatography columns are achieved with Merck 60 silica gel (230-400 mesh) or Aldrich's fluorisil (100-200 mesh).

---

* The authors thank Dr. S. Sinbandhit for his helpful suggestions and criticisms.

I - Preparation of dienes 8

This is achieved by methods already described in the literature [48].

8a [49]. b.p. = 31-34°C/0.1-0.2 mm Hg ; Yield = 77 %. ^{1}H NMR (CCl_4, lock $CHCl_3$), δ : 0.40 (s, $Si(C\underline{H}_3)_3$, 9H) ; 3.90 (s, OCH_3, 3H) ; 4.00 and 4.10 (2s, large, CH_2) ; 5.90 (d, $^3J_{HH}$ = 12.3, 1H) ; 7.50 (d, $^3J_{HH}$ = 12.3, 1H).

8b [50-52]. b.p. = 70-80°C/760 mm Hg ; Yield = 60 %. ^{1}H NMR (CCl_4, lock $CHCl_3$), δ : 0.35 (s, $Si(C\underline{H}_3)_3$, 9H) ; 4.70-5.10 (m, 2H) ; 5.50-6.75 (m, 2H)) ; 6.50 (d, $^3J_{HH}$ = 12.0, 1H).

8c [53-54]. b.p. = 109-110°C/2.5 mm Hg ; Yield = 56 %. ^{1}H NMR (CCl_4, lock dioxanne), δ : 0.35 (s, $Si(C\underline{H}_3)_3$, 9H) ; 4.40 and 4.45 (2s, $=CH_2$, ^2J 0, 2H) ; 6.52 and 6.82 (AB system, J_{AB} = 16.0 trans configuration of the double bond) ; 7.10 - 7.60 (m, C_6H_5, 5H).

8d [53,54]. b.p. = 66-68°C/15 mm Hg ; Yield = 64 %. ^{1}H NMR (CCl_4, lock dioxanne), δ : 0.30 (s, $Si(C\underline{H}_3)_3$, 9H) ; 2.00 - 2.30 (m, 4H) ; 4.70 - 4.90 (m, 1H) ; 5.50 - 6.00 (m, 2H).

8e 2,4-pentadienoic acid is prepared as described [55]. m.p. = 71-72°C, yield = 51 %. Its esterification to **8e** is achieved in the following way : A solution of 40 mmoles of diazomethane in 200 ml of diethyl ether is added, in small increments to a cold solution (0°C) of 4 g (40 mmoles) of the acid in 50 ml of diethyl ether whilst keeping the mixture agitated by using a magnetic stirrer. After drying with $MgSO_4$, and eliminating the solvent, diene **8e** is distilled. b.p. = 70-80°C/15 mm Hg, Yield = 82 %. ^{1}H NMR ($CDCl_3$), δ : 3.72 (s, $CO_2C\underline{H}_3$, 3H) ; 5,48 (broad d, $^3J_{HH}$ = 10.0, $^2J_{HH}$ = 1, 1H) ; 5.60 (broad d, $^3J_{HH}$ = 16.0, $^2J_{HH}$ = 1, 1H) ; 5.90 (one part of AB system, $^3J_{HH}$ = 15.0, $=C\underline{H}CO_2CH_3$), 6.45 (dt, $^3J_{HH}$ = 16.0, coupled with the protons at 5.48 and the proton at 7.29 ppm, $^3J_{HH}$ = 10.0 in both cases, 1H) ; 7.29 (one part of split AB system, $^3J_{HH}$ = 15.0, $^3J_{HH}$ = 10.0).

8f. A solution of 25 g (223 mmoles) of sorbic acid (commercially available) in 100 ml of methanol (1.6 mmoles) with 2-3 drops of concentrated sulphuric acid is refluxed for 4 hours. After cooling, the organic phase is washed with 100 ml of water. The aqueous phase is treated with diethylether (3 x 50 ml). The organic phase together with the ethereal extracts are dried with $MgSO_4$, overnight. After filtration, the diethyl ether is distilled and the diene is purified by vacuum distillation. b.p. = 70-80°C/15 mm Hg, Yield = 82 %. ^{1}H NMR ($CDCl_3$), δ : 1.90 (d, $C\underline{H}_3$, $^3J_{HH}$ = 5.0) ; 3.70 (s, $CO_2C\underline{H}_3$) ; 5.70 (part of AB system, $^3J_{HH}$ = 15.0) ; 6.0 - 6.3 (2H) and 7.0 - 7.5 (1H) (first order analysis is not possible for these olefinic protons).

Dimethylmuconate is a commercial product and phosphaalkene **5** is prepared from dichloromethane as previously described [57].

II - 4π+ 2π cycloadditions

A 50 ml Schlenk's flask is previously flame-dried under vacuum and flushed with argon. m' (mg) of diene **8** is added to m (mg) of phosphaalkene using a pipette or syringe. An argon atmosphere is maintained throughout the addition. The reaction is continued as described below.

Reaction of diene 8a. A solution of 441 mg (0,35 ml, 2 mmoles) of **8a** in 4 ml of dry benzene (distilled over Na/benzophenone). The reaction is fast and exothermic. After one hour at room temperature, only one adduct is formed (δ ^{31}P = 114). The product is not purified. It aromatizes slowly at room temperature. Mass spectrum : calculated mass for $C_{12}H_{25}O_2PSi_2\,^{35}Cl$: 323.083 ; found : 323.083 (M -Me_3Si]$^+$). NMR : ^{31}P (C_6H_6), δ : 114.0. ^{1}H (CD_2Cl_2), δ : 0.06, 0.18 and 0.19 [3s, $Si(C\underline{H}_3)_3$] ; 2.00 ($H_{6'}$, $^2J_{PH}$ = 24.7, $^2J_{HH}$ = 15.2, $^4J_{HH}$ = 1.9, $^5J_{HH}$ = 1.7) ; 2.60 (H_6, $^2J_{PH}$ = 6.8, $^2J_{HH}$ = 15.2, $^4J_{HH}$ = 1.7, $^5J_{HH}$ = 0.5) ; 3.17 (s, $OC\underline{H}_3$) ; 3.62 (H_3, $^2J_{PH}$ = 2.0, $^3J_{HH}$ = 2.8, $^5J_{HH}$ = 1.7 and 0.5) ; 4.84 (H_4, $^3J_{PH}$ = 2.0, $^3J_{HH}$ = 2.8,

$^4J_{HH}$ = 1.7 and 1.9). ^{13}C (CD_2Cl_2), δ : 32.2 (C_2, $^1J_{PC}$ = 79.0) ; 36.0 (C_6, $^1J_{PC}$ = 36.0, $^1J_{CH}$ = 129.0 and 136.0, $^3J_{CH}$ = 6.5) ; 56.2 ($O\underline{C}H_3$, $^1J_{CH}$ = 141.0, $^3J_{CH}$ = 4.0) ; 80.6 (C_3, $^2J_{PC}$ = 5.7, $^1J_{CH}$ = 142.0) ; 103.3 (C_4, $^3J_{PC}$ = 9.8, $^1J_{CH}$ = 158.0) ; 148.4 (C_5).

Reaction of diene 8b. m = 800 mg (1.67 mmoles) ; m' = 600 mg (4.40 mmoles). After 15 hours at room temperature, the excess diene is removed under vacuum. A 1:4 mixture of two diastereoisomers **9b'** and **9b"** respectively (δ ^{31}P = 120.6 and 129.9) is obtained. It is possible to distill this mixture (b.p. = 115-120°C/0.1 mm Hg). Yield = 67 %. Mass spectrum : calculated molecular mass for $C_{14}H_{32}OPSi_3{}^{35}Cl$: 366.118, found : 366,119.

Minor diastereoisomer, A, 20 % : NMR : ^{31}P : δ : 129.9. ^1H (CD_2Cl_2), δ : 1.65 ($H_{6'}$, $^2J_{PH}$ = 25.0, $^2J_{HH}$ = 15.0, $^3J_{HH}$ = 3.00, $^4J_{HH}$ = 3.0, $^5J_{HH}$ = 2.0) ; 2.76 (H_6, $^2J_{PH}$ = 0, $^2J_{HH}$ = 15.0, $^3J_{HH}$ = 7.8, $^4J_{HH}$ =1.0) ; 4.16 (H_3, $^3J_{PH}$ = 2.5, $^3J_{HH}$ = 2.7, $^4J_{HH}$ = 2.4, $^5J_{HH}$ = 2.0) ; 5.72 (H_4, $^3J_{HH}$ = 9.6 and 2.7, $^4J_{HH}$ = 3.0 and 1.0) ; 5.92 (H_5, $^3J_{HH}$ = 9.6 and 3.0, $^4J_{HH}$ = 2.4. ^{13}C (CD_2Cl_2). δ : 29.9 (C_6, $^1J_{PC}$ = 34.7) ; 35.0 (C_2, $^1J_{PC}$ = 84.0) ; 72.0 (C_3, $^2J_{PC}$ = 7.0) ; 124.8 et 134.7 (C_4 andC_5).

Major isomer : NMR, B, 80 % : ^{31}P, δ : 120.6 ; ^1H (CD_2Cl_2), δ : 2.27 ($H_{6'}$, $^2J_{PH}$ = 0, $^2J_{HH}$ = 18.7, $^3J_{HH}$, $^4J_{HH}$ and $^5J_{HH}$ = 3.0) ; 2.71 ($H_{6'}$, $^2J_{PH}$ = 34.0, $^2J_{HH}$ = 18.7,$^3J_{HH}$ = 5.2, $^4J_{HH}$ =1.3) ; 4.80 (H_3, $^3J_{PH}$ = 2.0, $^3J_{HH}$ = 2.5, $^4J_{HH}$ = 3.0, $^5J_{HH}$ = 3.0) ; 5.46 (H_5, $^3J_{HH}$ = 10.5, 5.2 and 3.0, $^4J_{HH}$ = 3.0) ; 5.88 (H_4, $^3J_{HH}$ = 10.5 and 2.5, $^4J_{HH}$ = 1.3 and 3.0). ^{13}C (CD_2Cl_2), δ : 31.5 (C_6, $^1J_{PC}$ = 38.2, $^1J_{CH}$ = 128.0 and 132.0) ; 32.4 (C_2, $^1J_{PC}$ = 73.1) ; 70.7 (C_3, $^2J_{PC}$ = 10.0, $^1J_{CH}$ = 148.0) ; 124.3 (C_5, $^2J_{PC}$ = 4.0, $^1J_{CH}$ = 160.0) ; 135.1 (C_4, $^3J_{PC}$ = 3.0, $^1J_{CH}$ = 158.0).

Reaction of diene 8c. m = 847 mg (3.77 moles) ; m' = 823 mg (3.77 moles). 2 ml of benzene, freshly distilled over Na/benzophenone, were added to the resulting solution. After 24 hours at room temperature, the reaction is quasi-quantitative (only one isomer is detected). Attempts to purify the product by distillation lead to its degradation. Mass spectrum : calculated molecular mass for $C_{20}H_{36}OSi_3P\,{}^{35}Cl$: 442.150 ; found : 442.150. NMR : ^{31}P (C_6H_6). δ : 111.6. ^1H (CD_2Cl_2), δ : 0.10, 0.12 ($^3J_{PH}$ = 0.8) and 0.18 [$Si(C\underline{H}_3)_3$] ; 2.62 (H_6, $^2J_{PH}$ = 11.0, $^2J_{HH}$ = 15.0) ; 2.63 ($H_{6'}$, $^2J_{PH}$ = 24.1, $^3J_{HH}$ = 15.0, $^5J_{HH}$ = 3.0) ; 3.91 (H_3. $^3J_{PH}$ = 7.8, $^3J_{HH}$ = 4.7, $^5J_{HH}$ = 3.0) ; 5.00 (H_4, $^4J_{PH}$ = 4.0, $^3J_{HH}$ = 4.7). ^{13}C (CD_2Cl_2), δ : 34.7 (C_6, $^1J_{PC}$ = 36.0, $^1J_{CH}$ = 130.0, $^3J_{CH}$ = 6.0) ; 34.7 (C_2, $^1J_{PC}$ = 78.5) ; 47.7 (C_3, $^2J_{PC}$ = 4.0, $^1J_{CH}$ = 127.0) ; 112.0 (C_4, $^1J_{CH}$ = 154.0) ; 127.3 ; 128.1 ; 131.8 and144 .0 (aromatic carbons).

Reaction of diene 8d. m = 360 mg (1.6 mmoles), m' = 287 mg (2.3 mmoles). The resulting mixture is diluted with 1 ml of CH_2Cl_2 (distilled over P_2O_5) and kept at room temperature overnight. Only one product is detected by ^{31}P NMR. After solvent stripping under vacuum, the adduct cristallizes (m.p. = 85°C). Yield = 80 %. Every attempt at purifying the product fails. Mass spectrum : calculated molecular mass for $C_{16}H_{34}OP^{35}ClSi_3$: 392.134 ; found : 392.133. NMR : ^{31}P (C_6H_6), δ : 128.8. ^1H (CD_2Cl_2), δ : 0.92 - 1.03 and 1.50 - 1.70 (two multiplets, 4H. H_7 and H_8) ; 2.88 (H_3, $^3J_{PH}$ = 2.2, $^3J_{HH}$ = 7.8) ; 2.99 ($H_{6'}$, $^2J_{PH}$ = 14.7, $^3J_{HH}$ = 5.5, ^3J ou $^4J_{HH}$ = 2.2) ; 5.89 (H_4, $^3J_{HH}$ = 7.8). ^{13}C (CD_2Cl_2), δ : 20.0 (C_7, $^2J_{PC}$ = 21.0) ; 28.1 (C_8) ; 30.9 (C_2, $^1J_{PC}$ = 80.0) ; 35.9 (C_3, $^3J_{PC}$ = 4.0) ; 41.8 (C_6, $^1J_{PC}$ = 35.0) ; 107.2 (C_4, $^3J_{PC}$ = 7.5), $^1J_{CH}$ = 163) and 148.6 (C_5).

Reaction of diene 8e. m = 850 mg (3.78 mmoles), m' = 424 mg (3.78 mmoles). After two hours, at room temperature (whilst stirring magnetically), the reaction is nearly quantitative. The analysis of the pale yellow solution by ^{31}P NMR shows the formation of only one adduct together with about 10 % of unidentified impurities (δ ^{31}P = 131, 28, 23 and 6). NMR : ^{31}P (C_6H_6), δ : 111.9. ^1H (CD_2Cl_2), δ : 0.22 and 0.34 [2s, $Si(C\underline{H}_3)_3$] ; 2.21 (H_6, $^2J_{PH}$ = 0, $^2J_{HH}$ = 19.1, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.8, $^5J_{HH}$ = 3.1) ; 2.39 ($H_{6'}$, $^2J_{PH}$ = 30.0, $^2J_{HH}$ = 19.1, $^3J_{HH}$ = 3.1, $^4J_{HH}$ = 2.3, $^5J_{HH}$ = 1.4) ; 3.90 (H_3, $^3J_{PH}$ = 2.8, $^3J_{HH}$ = 2.4, $^4J_{HH}$ =

3.0, $^5J_{HH}$ = 3.1 and 1.4) ; 5.48 (H_5, $^3J_{HH}$ = 10.8, 5.1 and 3.1) ; 5.89 (H_4, $^3J_{HH}$ = 10.8 and 2.4, $^4J_{HH}$ = 2.3 and1.8). ^{13}C (CD_2Cl_2). δ : 23.4 (C_2, $^1J_{PC}$ = 73.8) ; 29.6 (C_6, $^1J_{PC}$ = 36.0) ; 42.0 (C_3, $^2J_{PC}$ = 24) ; 54.7 ($CO_2\underline{C}H_3$) and 174.9 ($\underline{C}O_2CH_3$).

Reaction of diene 8f : m = 516 mg (2.3 mmoles), m' = 287 mg (2.3 mmoles). 1 ml of benzene distilled over Na/benzophenone is added to the mixture of the two reactants. The solution is kept at room temperature and left to react overnight. A 2:3 mixture of two diastereoisomers, **9f'** and **9f"** respectively, is obtained. Distillation of the crude product leads to cycloreversion with the formation of methyl sorbate and phosphaalkene **5**. Mass spectrum : calculated molecular mass for $C_{14}H_{28}O_2P^{35}ClSi_2$: 350.105 ; found : 350.106.

Minor diastereoisomer (40 %). **9f'**. NMR : ^{31}P (C_6H_6), δ : 144.1. ^1H (CD_2Cl_2). δ : 0.05 and 0.07 ($[Si(C\underline{H}_3)_3]$, $^4J_{PH}$ = 1.7 and 2.3) ; 1.36 ($C\underline{H}_3$, $^3J_{PH}$ = 20.4, $^3J_{HH}$ = 7.7) ; 2.55 (H_6, $^2J_{PH}$ = 3.0, $^3J_{HH}$ = 7.7 and 3.0, $^4J_{HH}$ = 3.7, $^5J_{HH}$ = 2.7) ; 3.29 (H_3, $^3J_{PH}$ = 10.2, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 3.0, $^5J_{HH}$ = 2.7) ; 3.49 (s, $CO_2C\underline{H}_3$) ; 5.44 (H_5, $^3J_{PH}$ = 5.5, $^3J_{HH}$ = 9.7 and 3.0, $^4J_{HH}$ = 3.0) ; 6.02 (H_4, $^4J_{PH}$ = 1.3, $^3J_{HH}$ = 9.7 and 4.8). ^{13}C (CD_2Cl_2), δ : 3.3 and 4.6 ($[Si(CH_3)_3]$, $^3J_{PC}$ = 5.3 and 9.0) ; 17.4 ($C\underline{H}_3$. $^2J_{PC}$ = 34.4) ; 30.6 (C_2, $^1J_{PC}$ = 85.0) ; 40.9 (C_6, $^1J_{PC}$ = 37.4, $^1J_{CH}$ = 130) ; 44.9 (C_3, $^2J_{PC}$ 0, $^1J_{CH}$ = 131) ; 51.8 ($CO_2\underline{C}H_3$) and 174.7 ($\underline{C}O_2CH_3$).

Major isomer (60 %). **9f"**. NMR : ^{31}P (C_6H_6), δ : 145.4. ^1H (CD_2Cl_2), δ : 0.35 and 0.37 ($[Si(C\underline{H}_3)_3]$, $^4J_{PH}$ = 0.6 and 0.8) ; 1.42 (CH_3, $^3J_{PH}$ = 16.6, $^3J_{HH}$ = 7.0) ; 1.79 (H_6, $^2J_{PH}$ = 24.0, $^3J_{HH}$ = 3.6, $^4J_{HH}$ = 2.6, $^5J_{HH}$ = 2.0) ; 2.73 (H_3, $^3J_{PH}$ = 2.0, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 2.5, $^5J_{HH}$ = 2.0) ; 3.42 (s, $CO_2C\underline{H}_3$) ; 5.50 (H_5, $^3J_{PH}$ = 2.8, $^3J_{HH}$ = 8.8 and 3.6, $^4J_{HH}$ = 2.5) ; 5.85 (H_4, $^4J_{PH}$ = 0.6, $^3J_{HH}$ = 8.8 and 4.7, $^4J_{HH}$ = 2.6). ^{13}C (CD_2Cl_2), δ : 3.7 and 5.6 ($[Si(C\underline{H}_3)_3]$), $^3J_{PC}$ = 11.3 and 4.5) ; 16.1 ($C\underline{H}_3$. $^2J_{PC}$ = 16.0) ; 32.2 (C_2. $^1J_{PC}$ = 90.0) ; 35.4 (C_6, $^1J_{PC}$ = 34.7, $^1J_{CH}$ = 128) ; 45.3 (C_3, $^2J_{PC}$ = 3.0, $^1J_{CH}$ = 129) ; 51.8 ($CO_2\underline{C}H_3$) and 174.1 ($\underline{C}O_2CH_3$).

The authors wish to express their thanks to Patrick Roby for his useful suggestions in their revision of the english text.

References

1 Arbuzov, B.,A. ; Dianova, E.,N. Phosphorus and Sulfur, **1986**, *26*, 203-251 and references therein.
2 Markovski, L.,N. ; Romanenko, V.,D. Tetrahedron, **1989**, *45*, 6019-6090.
3 Arbuzov, B.,A. ; Dianova, E.,N. ; Samitov, Y.,Y. Dokl. Akad. Nauk. SSSR, **1978**, *244*, 1117, english translation, p. 59-62.
4 Yeung Lam Ko, Y.,Y.,C. Thèse de 3ème Cycle, Rennes, 1981.
5 Yeung Lam Ko, Y.,Y.,C. ; Carrié, R. Communication "International Conference on Phosphorus Chemistry", Nice, France, 1983.
Yeung Lam Ko, Y.,Y.,C. ; Toupet, L. ; De Sarlo, F. ; Carrié, R. Bull. Soc. Chim. Fr., **1986**, 115-118.
6 Mathey, F. ; Mercier, F. ; Charrier, C. ; Fischer, J. ; Mitschler, A. J. Am. Chem. Soc., **1981**, *103*, 4595-4597.
7 De Lauzon, G. ; Charrier, C. ; Bonnard, H. ; Mathey, F. Tetrahedron Lett., **1982**, *23*, 511-514.
8 De Lauzon, G. ; Charrier, C. ; Bonnard, H. ; Mathey, F. ; Fischer, J. ; Mitschler, A. J. Chem. Soc. Chem. Comm., **1982**, 1272-1273.
9 Charrier, C. ; Bonnard, H. ; Mathey, F. J. Org. Chem., **1982**,*47*, 2376-2379.
10 Charrier, C. ; Bonnard, H. ; De Lauzon, D. ; Mathey, F. J. Am. Chem. Soc., **1983**, *105*, 6871-6877.
11 Heinicke, J. ; Tzschach, A. Tetrahedron Lett., **1983**, *24*, 5481-5484.
12 Hausen, H.,D. ; Weckler, G. Z. Naturf., Teil B, 1, **1984**, *39*, 628-631.
13 Klebach, T.L. ; Lourens, R. Wisse, J. ; Bickelhaupt, F. Communication Symposium de Halle, R.D.A., **1979**.
14 Van der Knapp, A. ; Klebach, T.C. ; Visser, F. ; Bickelhaupt, F. Pos, P. ; Baerends, E.,J. ; Stam, C.,M. ; Konijn, M. Tetrahedron, **1984**, *40*, 765-776.
15 Meriem, A. ; Majoral, J.P. ; Revel, M. ; Navech, J. Tetrahedron Lett., **1983**, *24*, 1975-1978.

16 Appel, R. ; Korte, S. ; Malstenberg, M. ; Knoch, F. Chem. Ber., **1982**, *115*, 3610-3617.

17 Appel, R. ; Zimmermann, R. Tetrahedron Lett., **1983**, *24*, 3591-3594.

18 Appel, R. ; Knoch, F. ; Zimmermann, R. Chem. Ber., **1985**, *118*, 814-824.

19 Appel, R. ; Casser, C. ; Knoch, F. Chem. Ber., **1984**, *117*, 2693-2702.

20 Appel, R. ; Casser, C. ; Kunze, H. Chem. Ber., **1984**, *117*, 3151-3159.

21 Appel, R. ; Casser, C. Chem. Ber., **1985**, *118*, 3419-3423.

22 Appel, R. ; Menzel, J. ; Knoch, F. Chem. Ber., **1985**, *118*, 4068-4072.

23 Märkl, G. ; Jin, G.,Y. ; Silbereisen, E. Angew. Chem. Int. Ed., **1982**, *21*, 370-371.

24 Yeung Lam Ko, Y.,Y.,C. Thèse de Doctorat d'Etat, Rennes, 1986.

25 Yeung Lam Ko, Y.,Y.,C. ; Carrié, R. J. Chem. Soc. Chem. Comm., **1984**, 1640-1641.

26 Märkl, G. "Houben Weyl", Methoden der Organische Chemie, Ed. Regitz, M. ; Thieme G., Verlag, Stuttgart **1982**, E1, 72-105.

27 Märkl, G. ; Adolin, G. ; Kees, F. ; Zander, G. Tetrahedron Lett., **1977**, 3445-3448.

28 Märkl, G. ; Hock, K. Tetrahedron Lett., **1983**, 2645-2648.

29 Märkl, G. ; Hock, K. Tetrahedron Lett., **1983**, 5051-5054.

30 Märkl, G. ; Hock, K. Tetrahedron Lett., **1983**, 5055-5058.

31 Pellon, P. ; Yeung Lam Ko, Y.,Y.,C. ; Cosquer, P. ; Hamelin, J. ; Carrié, R. Tetrahedron Letters, **1986**, *27*, 4299-4302.

32 Yeung Lam Ko, Y.,Y.,C. ; Cosquer, P. ; Pellon, P. ; Hamelin, J. ; Carrié, R.Phosphorus and Sulfur, **1987**, *30*, 523-526.

33 Le Floch, P. ; Mathey, F. Tetrahedron Lett., **1989**, *30*, 817-818.

34 Albrand, J.,P. ; Gagnaire, D. ; Picard, M. ; Robert, J.,B. Tetrahedron Lett., **1970**, 4593-4596.

35 Bentrude, W.,G. ; Setzer, W.,N. ; "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis", Verkade, J.,G. and Quin, L., N. Ed., VCH Publishers Inc., Deerfield Beach Florida, **1987**, ch. 11, 365-389 and references therein.

36 Breen, J.,J. ; Featherman, S.,I. ; Quin, L.,D. ; Stocks, R.,C. J. Chem. Soc. Chem. Comm., **1972**, 657-658.

37 Dewar, M.,J.,S. J. Am. Chem. Soc., **1952**, *29*, 3341-3367.
Herndon, W.,C. Chem. Rev., **1972**, *72*, 157- and references therein.
Hudson, R.,F. Angew. Chem. Int. Ed., **1973**, *12*, 36-56.

38 Klopman, G. "Chemical Reactivity and Reactions Paths", Wiley, New York, **1974**.

39 Martelli, J. ; Tonnard, F. ; Carrié, R. ; Sustmann, R. Nouv. J. Chim., **1978**, *2*, 609-613.

40 Huisgen, R. J. Org. Chem., **1976**, *41*, 403-419 and references therein.

41 Pople, J.,A. ; Beveridge, D.,L. Approximate Molecular Orbital Theory", Mc Graw Hill, New York, 1970 and references therein.

42 Sutton, L.,E. "Tables of Interatomic Distances Configuration in Molecule and Ions", Special Publications, Chem. Soc., London (1958-1965).

43 Hopkinson, M.,J. ; Kroto, H.,W. ; Nixon, J. ; Simmons, N.,P.,C. J. Chem. Soc. Chem. Comm., **1976**, 513-515.

44 Appel, R. ; Barth, V. ; Knoch, F. Chem. Rev., **1983**, *116*, 938-950.
Appel, R. ; Knoch, F. ; Laubach, B. ; Sievers, R. Chem. Ber., **1983**, *116*, 1873-1879.
Appel, R. ; Casser, C. ; Immenkeppel, M. ; Knoch, F. Angew. Chem. Int. Ed., **1984**, *11*, 895-896.

45 Cowley, A.,H. ; Jones, R.,A. ; Lasch, J.,G. ; Norman, N.,C. ; Stewart, C.,A. ; Stuart, A.,L. ; Atwood, J.,L. ; Hunter, W.,E. ; Zhang, H.,M. J. Am. Chem. Soc., **1984**, *106*, 7015-7020.
Appel, R. ; Kundgen, V. ; Knoch, F. Chem. Ber., **1985**, *118*, 1352-1370.

46 Dewar, M.,J.,S. ; Thiel, W. J. Am. Chem. Soc., **1977**, *99*, 4899-4906.

47 Details are available on request.

48 Abbari, M. Thèse de l'Université de Rennes, 1989.

49 Danishefsky, S. ; Kitahara, T. J. Am. Chem. Soc., **1974**, *96*, 7807-7808.

50 French patents : 1 436 58 (1965) et 88 358 (1967). Chem. Abst., **1968**, *68*, 49733j.

51 Fleming, I. ; Godhill, J. ; Paterson, I. Tetrahedron Lett., **1979**, 3205-3208.

52 Belanger, J. ; Landry, N.,C. ; Parl, J.,R. et Jankowski, J. J. Org. Chem., **1982**, *47*, 3649-3652.

53 Girard, G. ; Conia, J.,M. Tetrahedron Lett., **1974**, 3327-3328.

54 Rubottom, G.,M. ; Gruber, J.,M. J. Org. Chem., 1977, *42*, 1051-1056.

55 Schneider, M.,P. ; Goldbach, M. J. Am. Chem. Soc., **1980**, *102*, 6114-6116 .

56 De Boer, T.,J. ; Backer, H. J. "Organic Syntheses", J. Wiley and Sons, New York, London, 1963, Col. Vol. IV, 250-253.

57 Appel, R. ; Westerhaus, A. Tetrahedron Letters, **1981**, *22*, 2159-2160.
Thoraval, J.,Y. ; Nagai, W. ; Yeung Lam Ko, Y.,Y.,C. ; Carrié, R. Tetrahedron, **1990**, sous presse.