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CYCLOADDITIONS OF DISUBSTITUTED DIAZO COMPOUNDS TO P-CHLORO (BISTRIMETHYLSILYL) METHYLENE PHOSPHINE.

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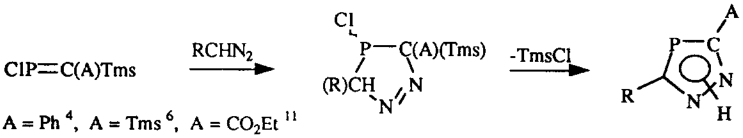
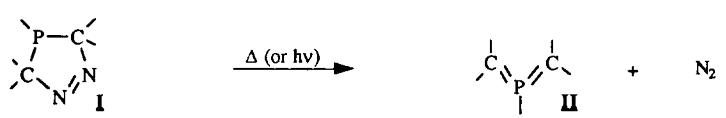
Summary - Disubstituted diazo compounds rapidly add to P-chloro (bistrimethylsilyl) methylene phosphine at low temperature. ^1H, ^{31}P and ^{13}C NMR allow the characterization of the resulting cycloadducts and the establisment of the stereochemistry of the resulting cycloadducts which are potential precursors of σ^3 λ^5 bis methylene phosphorane by nitrogen extrusion.

The reactions of diazocompounds with phosphaalkenes are relatively well investigated [1-13]. They occur with the formation of a P-N or P-C bound via a Staudinger-type reaction or by $4\pi + 2\pi$ cycloadditions [5-10]. In the latter case, the adducts are thermally unstable and undergo further transformation in two distinct ways (generally) :

- (i) those which are able to eliminate molecules such as TmsCl to form aromatic phosphorus heterocycles.



- (ii) those (I) which extrude nitrogen to form $\sigma^3\lambda^5$ bis methylene phosphoranes II.



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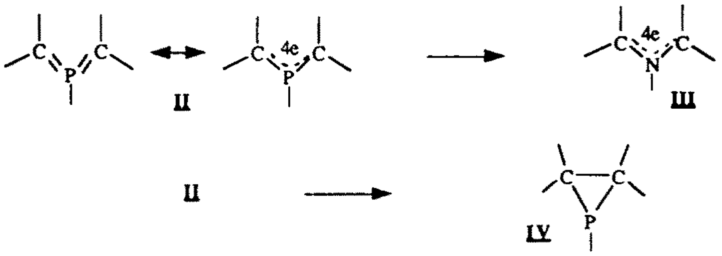
The work of Schoeller and Niemann [14] shows that (i) specy II presents four delocalized electrons over three atoms and (ii) the effect of the d electrons of the phosphorus atom on the electronic distribution of II is not very important.

Another way of representing $\sigma^3\lambda^5$ bis methylene phosphoranes is shown below. The structural analogy of II with azomethine ylids III [15] is quite striking. Can we then expect compounds II to show some typical properties of 1.3 dipoles ? The electrocyclisation of II to phosphiranes IV is known [14,16], but only one example has been reported in which a phosphorus 1,3 dipole such as II could have generated and trapped by cycloaddition to the -P=C double bond[3].



Three methods for the synthesis of II have been described.

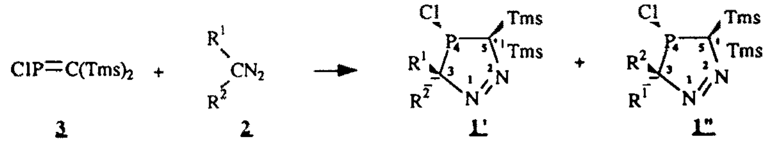
(i) carbenoid addition to phosphaalkene [17] (ii) from dichlorophosphine [18] (iii) thermolysis of cycloadducts I.

This article only deals with the formation of compounds I from P-chloro (bis trimethylsilyl) methylene phosphine and disubstituted diazo compounds and their structural determination. The thermolysis of I will be described in a forthcoming paper.

Results and discussion

I - Reactivity of diazo compounds

Diazo compounds 2 react quantitatively with phosphaalkene 3 [19] leading to the diastereoisomeric cycloadducts 1' and 1''.



Due to the thermal instability of compounds 1 the reactions were monitored by ^{31}P NMR and performed at -50°C in a NMR tube under an nitrogen atmosphere. In order to avoid the decomposition of the products, the spectra were recorded at -70°C.

The ratio of 1'/1'' and their respective ^{31}P chemical shifts are given in table 1.

Table 1

Ratio of the diastereoisomers **1'** and **1"** and their $\delta^{31}P$ (CD_2Cl_2).

Diazocompounds	R^1	R^2	1'/1"	$\delta^{31}P$ (1')	$\delta^{31}P$ (1")
2a	Me	Ph	58/42	92.0	88.1
2b	Et	Ph	71/29	94.1	88.8
2c	iPr	Ph	80/20	95.2	88.1
2d	tBu	Ph	100/0	95.0	-
2e(a)	Ph	Ph		86.1	
2f	Me	$pMeC_6H_4$	59/41	93.2	89.6
2g	Me	$pMeOC_6H_4$	50/50	91.5	89.4
2h	Me	$pClC_6H_4$	45/55	91.9	88.6
2i	Me	$mMeC_6H_4$	78/22	91.0	86.8
2j	MeCO	Me	40/60	84.4	82.6
2k(b)	PhCO	PhCO	-	-	-
2l(c)	$-CH_2(CH_2)_2CO-$		23/77	83.5	78.6
2m(c)	$-CH_2(CH_2)_3CO-$		24/76	87.3	74.8

(a) Single compound (**1'**≡**1"**). (b) No reaction at -50°C. (c) See text for the stereochemistry of **1l'**, **1l"**, **1m'** and **1m"**.

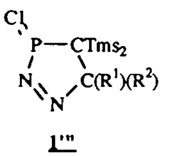
The reaction of **3** is almost instantaneous at -50°C with acyclic and cyclic diazo compounds **2a**-**2i**, **2l** and **2m** except in the case of **2j** (80 % conversion after 30 mins) and **2k** (no reaction). At room temperature **2k** reacts with **3** and forms several unidentified products as shown by ^{31}P NMR.

The difference in reactivity of diazo compounds **2a**-**2m** can be qualitatively discussed in terms of second order perturbation theory [20]. It has been shown that phosphaalkene **3** is a very electrophilic specy characterized by a very low LUMO [21]. The predominant orbital interaction during this cycloaddition is that arising between the HOMO of the nucleophilic diazo compounds **2** and the LUMO of phosphaalkene **3**. The introduction of electron withdrawing substituents in diazo compounds lowers their HOMO's, hence decreasing their reactivity towards **3**.

II - Structural determination of cycloadducts 1' and 1"

A) From acyclic diazocompounds 2a-2j

The ^{31}P, ^1H and ^{13}C NMR data are given in tables 1, 2 and 3 respectively. It should be noted that some signals are sometimes difficult to assign, especially those of the Tms groups, since, besides the two diastereoisomers **1'** and **1"**, some decomposition products are also observed.



1'''

The orientation of addition is readily established by ^{13}C NMR which allows us to exclude structure **1'''**. The fact that the coupling constant of the phosphorus atom and the cyclic carbon atom substituted by R^1 and R^2 is between 54 and 73 Hz confirms structure **1'** or **1"** for the adducts. Such large values are only compatible with a $^1J_{PC}$ and not with a $^2J_{PC}$ [22] if an inverse addition is observed (compounds **1'''**).

The determination of the stereochemistry of adducts **1'** and **1"** is based on the criteria used to establish rigid structures of phosphorus compounds [22] : $^2J_{PH}$ and $^2J_{PC}$ are significantly greater when either the H or C atom is in cis position with the lone pair of phosphorus.

Table 2 : ^1H NMR data of compounds **1'** and **1"** (δ(ppm), J(Hz) ; -70°C) in CD_2Cl_2.

Compounds	R^1	R^2	$Si(CH_3)_3(^4J_{PH})$	$R^1(J_{PH})$	R^2
1a'	Me	Ph	0.30 (0) -0.23(0)	2.12(0)	6.92 to 7.95
1a"			0.30(0) -0.23(0)	1.83(17.9)	6.92 to 7.95
1b'	Et	Ph	0.34(0) 0.13 (0)	2.53(0) 1.24(0)	7.18 to 7.86
1b"			-0.12(0) 0.13(0)	2.31(0) 1.16(17.1)	7.18 to 7.86
1c'	iPr	Ph	0.07(0) -0.34(0)	2.54 $C\underline{H}(CH_3)_2$ (0) 1.31(6.4) $CH(C\underline{H}_3)_2$	7.15 to 7.71
1c"			(a)	(b) $C\underline{H}(CH_3)_2$ 1.09 (6.5) $CH(CH_3)_2$	7.15 to 7.71
1d'	tBu	Ph	0.38(0) 0.02(0)	1.35 $C(CH_3)_3$	7.02 to7.37
1e'	Ph	Ph	-0.33(0) 0.40(0)	7.20 to 7.89	7.80 to 7.89
1f'	Me	$pMeC_6H_4$	-0.80(1.3) 0.37(0)	2.08(5.5)	7.13 to 7.39 2.15 CH_3
1f"			0.30(1.3) 0.33(0)	1.80(17.8)	7.17 to 7.39 2.73 CH_3
1g'	Me	$pMeOC_6H_4$	0.07 (0) 0.38(0)	2.05(3.0)	7.11 to 8.40 3.78 OCH_3
1g"			-0.94(0) 0.27(0)	1.78(18.1)	7.11 to 7.40 3.75 OCH_3
1h'	Me	$pClC_6H_4$	-0.21(1.4) (a)	2.06(5.3)	7.10 to 7.36
1h"			+0.28(1.3) (a)	1.80(17.6)	7.10 to 7.36
1i'	Me	$mMeC_6H_4$	-0.17 0,41	2.16(0)	7.09 to 7.45 2.37 CH_3
1i"			0.13 0.33	1.88(17)	7.09 to 7.45 2.35 CH_3

(a) Those signals could not be assigned. (b) Due to the complexity of the signal and the low ratio of this compound, this signal could not be assigned.

Table 3 : ^{13}C data of compounds **1'** and **1"** (δ (ppm), J(CH_3) -70°C) in CD_2Cl_2.

Com-pounds	R^1	R^2	δC_3 ($^1J_{PC}$)	δC_5 ($^1J_{PC}$)	δR^1 ($^2J_{PC}$)	$\delta R^{2(a)}$ ($^2J_{PC}$)	$\delta Si(CH_3)_3$ ($^3J_{PC}$)
1a'	Me	Ph	108.9(56)	95.9(82)	28.5(1)	144.2(33)	(b)
1a"			108.4(56)	96.8(83)	25.8(11)	140.9(6)	(b)
1b'	Et	Ph	113.7(56)	95.6(83)	11.4(0) 32.9(3.2)	141.1(32)	(b)
1b"			112.6(56)	94.7(82)	10.9(14) 33.8(53)	138.3(0)	(b)
1c'	iPr	Ph	117.5(59)	95.4(80)	20.4(0)$^{(c)}$ 25.5(0)$^{(c)}$ 35.1(3)	137.7(33)	2.67(0) 0.50(7)
1c"			120.7(61)	94.9(81)	(b) 38.7(37)	136.7(0)	(b)
1d''	tBu	Ph	118.4(73)	93.2(85)	25.79C(<u>C</u>H_3)$_3$ 41.51<u>C</u>(CH_3)$_3$	139.4(38)	0.80(0) 0.10(0)
1e	Ph	Ph	117.2(60)	97.3(83)	141.6$^{(d)}$ (34)	140.6(0)	1.7(0) -0.4(7)
1f'	Me	$pMeC_6H_4$	108.8(56)	96.2(82)	28.2(3.7)	141.0(34)	2.10(0) 0.25(8.6)
1f"			108.5(56)	96.8(83)	25.8(52)	140.3(0)	2.50(0) 1.42(9.3)
1g'	Me	$pMeOC_6H_4$	108.1(54)$^{(e)}$	96.5(83)	28.3(0)	135.6(33)	(b) 0.30(9)
1g"			107.9(55)$^{(e)}$	95.7(82)	25.5(53)	131.1(0)	(b) 1.50(9.1)
1h'	Me	$pClC_6H_4$	108.0(56)$^{(f)}$	96.9(83)	28.5(3.2)	142.9(34)	2.25(0) 0.22(8.6)
1h"			107.8(56)$^{(f)}$	96.5(83)	25.7(49)	139.6(0)	2.11(0) 1.43(8.9)
1i'	Me	$mMeC_6H_4$	108.5(56)	95.7(81)	28.4(0)	143.3(32)	2.22(0) 0.28(7.6)
1i"			107.9(56)	96.2(82)	25.6(52)	140.3(0)	2.63(0) 1.51(8.7)

(a) Carbon from R^2 bonded to C3. (b) It was not possible to determine the chemical shifts of these carbon atoms. (c) Two diastereotopic methyl groups. (d) Ipso carbon of R^1 bonded to C3. (e) and (f) These signals can be inverted.

For example, in the case of 2d (R^1 = tBu, R^2 = Ph) only one diastereoisomer is obtained. By using the criteria described above it was possible to precise the stereochemistry of this single isomer : the coupling constant between the phosphorus atom and the quaternary carbon of the t-butyl group, $^2J_{PC}$, being about 0, it can be concluded that this group is trans to the phosphorus lone pair (structure **1'd**). This was further confirmed by the large value of the coupling constant between phosphorus and the ipso carbon of the phenyl group, $^2J_{PC}$ = 38 Hz.

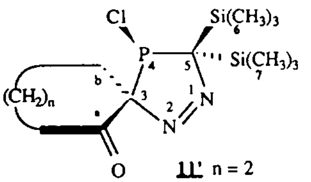
The stereochemistry of all the other adducts is similarly determined.

Remark : The ratio of the two diastereoisomers depends on the size of the substituents. In the case of **2a**-**2d** (R^1 = Me, Et, iPr and t.Bu ; R^2 = Ph), the amount of **1'** increases with the size of R^1. We have not yet found a rational explanation for this phenomena.

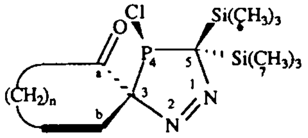
R^1	Me	Et	isoPr	tBu
Diazo compound	**2a**	**2b**	**2c**	**2d**
% of **1'**	58	71	80	100

B) From cyclic diazocompounds 2l and 2m

2l and **2m** react with phosphaalkene **3** to yield a mixture of **1'/1''** (23/77) and **1m'/1m''** (24/76) respectively.



1l' n = 2
1m' n = 3



1l'' n = 2
1m'' n = 3

Table 4

^{13}C NMR data : δ (J_{PC}) of compounds **1l'**, **1l''**, **1m'** and **1m''** (CD_2Cl_2, -70°C).

Compounds	C_3	C_5	C_6	C_7	C_a	C_b	$(CH_2)_n$
1l'	113.3 (64.4)	97.4 (83.1)	2.1 (0)	0.5 (10.3)	206.6 (0)	33.3 (40.8)	38.0 (0) 21.2 (2.5)
1l''	115.5 (62.2)	97.1 (84.7)	-0.2 (0)	-0.5 (12.8)	209.7 (31.3)	33.0 (0)	37.4 (0) 20,9 (0)
1m'	116,7 (64.1)	95.9 (83.0)	2.2 (0)	0.9 (8.7)	201.2 (0)	34.6 (36.5)	44.2(0) 26.7 (0) 24.3 (5.6)
1m''	117.6 (64.9)	95.4 80.7)	3.3 (0)	0.6 (10)	206.5 (34.0)	36.3 (0)	43.5 (0) 28.0 (0) 24.7 (0)

The chemical shift of carbon atoms C_3 and C_5 as well as the coupling constants J_{PC} (see table 4) are in agreement with the above structures. The stereochemistry of those spiro compounds is similarly determined by using the criteria previously described.

Thus, the structures of the minor diastereoisomers are **1l'** and **1m'** : the coupling constant between the carbonyl carbon Ca and phosphorus atom are about 0 (Ca and the phosphorus lone pair are in trans position) while the large values of $^{2}J_{PCb}$ about 35-40 Hz confirm that Cb and the phosphorus lone pair are well in cis position.

Inversely, the following coupling constants are found in **1l"** and **1m"** : $^{2}J_{PCa} = 31.3$ (**1l"**) and 34.0 (**1m"**) ; $^{2}J_{PCb'} = 0$ (**1l"** and **1m"**). Ca and Cb are therefore in a cis and trans relationship to the phosphorus lone pair, respectively.

C) Remarks concerning the high field ^{31}P NMR spectra

When the ^{31}P spectrum is recorded at low field (32.38 MHz), only one signal is observed for each diastereoisomer, while two signals are detected when the spectrum is recorded at high field (121.50 MHz). This is due to the presence of the two isotopic chlorine atoms ^{35}Cl and ^{37}Cl (see figure 1).

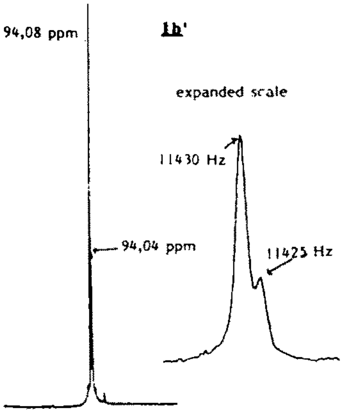
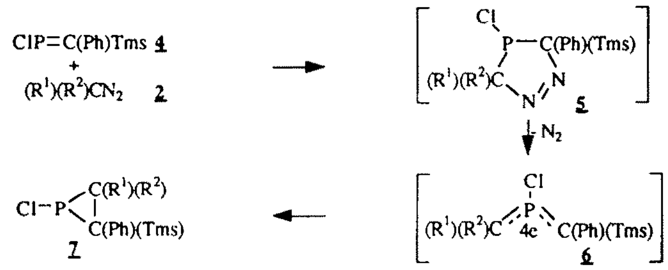


Figure 1

This isotopic chlorine effect has already been reported for the ^{13}C spectra [23]. It seems interesting to us to point out this phenomena because it should be of wider scope and applicability, particularly in the structural determination of phosphorus compounds. It should allow to establish whether a phosphorus atom is bound or not to a chlorine atom. This isotopic effect has alco been observed in other phosphorus compounds (σ^2 or σ^3) which were eventually complexed to tungsten *

Note : Märkl et al reported the reaction of disubstituted diazo compounds **2** with phosphaalkene **4** forming phosphiranes **7** but the postulated intermediates **5** and **6** have not been characterized.



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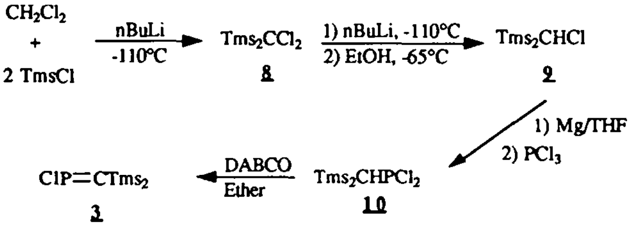
* Details are available from the authors.

Experimental

All reactions are performed under an argon (or sometimes nitrogen) atmosphere except for the synthesis of diazocompounds **2** and the apparatus dried just before use.

I - Preparation of phosphaalkene 3

This compound reported in 1981 by Appel and Westerhaus [19] with few experimental details, is prepared in four steps :



Compound **8** is prepared according to a literature procedure [24] ($E_{0.2}$ = 42-44°C, 64 % yield).The bistrimethylsilyl chloromethane **9** [25] is obtained from **8** in 70 % yield (the overall yield of **9** from CH_2Cl_2 is about 45 %).

a) Dichlorophosphine 10 [19]

3.0 g (123 mmoles) of magnesium dust are flame-dried under vacuum. After cooling at room temperature, 60 ml of dry THF are introduced into a two necked flask (a nitrogen inlet, a dropping funnel and a condenser) via canula technique. 4 ml of compound **9** are added to the reaction mixture which is then heated to reflux to initiate the formation of the Grignard reagent. As soon as a vigorous reaction sets in, heating is stopped and the rest of compound **9** (21 g in all, 108 mmoles) is added dropwise so as to maintain the reaction mixture at reflux (ca. 30 mins). After 3 hours' reflux and cooling at room temperature, the filtered grignard reagent is carefully added during 1.5 hours to a cold solution of 12 ml (137 mmoles) of PCl_3 in 12 ml of THF at 0°C. 50 ml of dry diethyl ether are added and the reaction mixture stirred overnight. After filtering and washing the white solid with 3 x 30 ml of dry diethyl ether, the solvents are removed under reduce pressure and the residue (28 g) distilled to give **10** (23.1 g, 82 % yield, $E_{0.2}$ = 66-69°C). **10** was obtained by Lappert et al. [26].

b) Phosphaalkene 3

A solution of 17.2 g (65.9 mmoles) of dichlorophosphine **10** in 30 ml of dry diethylether is added dropwise to a mixture of 8 g (81.4 mmoles) of freshly sublimed DABCO in 125 ml of dry diethyl ether during 1 hour. A white precipitate is formed and stirring is pursued during 14 hrs at room temperature. After filtering and washing the solid with 40 ml of dry diethyl ether, the solvent is removed under reduced pressure (0.1-0.2 mm de Hg) and the excess DABCO sublimed at 45-50°C. The residue is then distilled with an oil-bath (t < 100°C) to afford **3** as a yellow green oil (10.6 g ; $E_{0.1\text{-}0.2}$ = 37-43°C ; 72 % yield).

II - Synthesis of diazocompounds

They are prepared by oxidation [27] of the corresponding hydrazone by activated manganese dioxide [28]. The hydrazones are obtained by reacting a large excess (10 equivalents) of hydrazine hydrate with the appropriate ketone [29] (65-85 % yield).

The relatively unstable diazo compounds can only be kept for a few days at - 15°C. The yields ranging from 75-90 % are assessed by back titrating the excess benzoic acid (added to a known quantity of the diazo compound) with sodium hydroxide.

General procedure for the oxidation of hydrazone

Activated manganese dioxide (40 mmoles) are added over 10 mins to a mixture of hydrazone (10 mmoles), anhydrous magnesium sulphate (40 mmoles) and dichloromethane (30 ml) at 0°C and the reaction mixture stirred 4 more hours at 0°C. After filtering the solid, the solvent from the filtrate is removed under reduced pressure at 0°C to avoid any decomposition. The diazo compounds thus obtained are used immediately.

Note : Diphenyldiazomethane [30], a more stable diazo compound, is a solid which can be recrystallized from pentane.

Diazo compounds **2l** and **2m**

1-Formyl 2-oxo cyclopentane **11** and 1-formyl 2-oxo cyclohexane **12** are prepared from cyclopentanone and cyclohexanone respectively.

11, E_{15} = 33-34°C, 70 % yield [31]. **12**, $E_{0.8}$ = 54-56°C, 65 % yield [32].

The diazocompounds **2l** and **2m** are prepared by reacting tosylazide with **11** and **12** [31] respectively. (80-90 % yield after distillation).

2l. E_1 = 35-40°C ; ^{13}C NMR, δ ($CDCl_3$, ppm) : 201.9 ($\underline{C}=O$) ; 59.7 ($\underline{C}=N_2$) ; 26.6, 26.3 and 21.8 (3 $\underline{C}H_2$).

2m : E_1 = 65-70°C ; ^{13}C NMR, δ ($CDCl_3$, ppm) : 194.1 ($\underline{C}=O$) ; 63.3 ($\underline{C}=N_2$), 36.7, 22.4, 22.3 and 21.9 (4 $\underline{C}H_2$).

III - Formation of adducts **1**

The acyclic diazo compounds are characterized by a deep pink colour. They decolorize upon addition to a solution of phosphaalkene **3**, thus indicating that the reaction is instantaneous.

Procedure : A solution of the diazo compound in CH_2Cl_2 is added to a cold solution (-50°C) of phosphaalkene **3** in CH_2Cl_2 (2 ml per 100 mg of **3**) and continued until a colour change occurs. The solvent used for ^{1}H and ^{13}C NMR is CD_2Cl_2.

Stable diazo compounds are weighed and added in stoechiometric amounts to phosphaalkene **3** under the conditions described above.

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