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DIELS-ALDER REACTION WITH PHOSPHAALKENES.
SYNTHESIS OF FUNCTIONALIZED λ^3 PHOSPHABENZENES.

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Summary - The reaction of phosphaalkenes (**1** and **2**) with 1,3 dienes such as methyl sorbate and 1-methoxy 3-trimethylsilyloxy-1,3 butadiene leads to functionalized λ^3 phosphabenzenes **6**, **9**, **12**, **13** and **16** after aromatization of the primary adducts. The aromatization may occur either spontaneously or after chemical transformations. The reversible cycloaddition has allowed the synthesis of isomeric phosphabenzenes **6** and **9**. Diels-Alder reaction with phosphaalkenes appears to be a general method for the obtention of functionalized λ^3 phosphabenzenes.

Functionalized λ^3 phosphabenzenes are still scarce compared to alkyl or aryl ones (1). Märkl and coworkers have prepared some with a trimethylsilyloxy, hydroxy, halogen , keto or amino groups (2). However, no general method has been described. The Diels Alder reaction should provide an easier and wider access to functionalized phosphabenzenes after aromatization of the primary adducts, with the possibilities of introducing the functionality either with the diene or with the phosphaalkene or both. Märkl *et al.* (3) have already shown that the reaction of $Cl\text{-}P{=}C(TMS)Ph$ with α-pyrones or cyclopentadienones could lead to alkyl or/and aryl phosphabenzenes. Furthermore, we have shown that the adduct from **1** and 2,3 dimethylbutadiene (4) could be aromatized. However, drastic conditions were used and yields were rather low.

Our first results with phosphaalkenes **1** prepared by Appel's procedure (5) and **2** (generated *in situ* in an original way) are reported here.

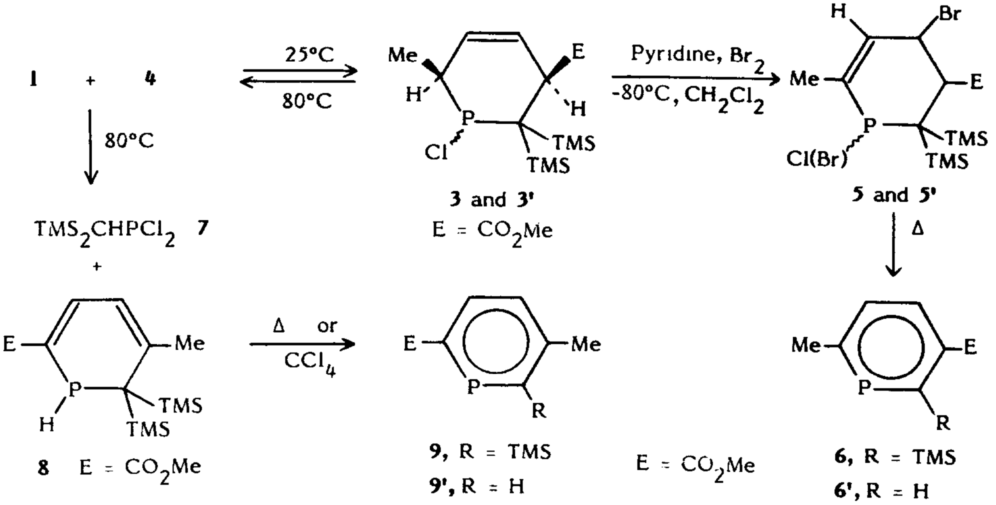
$Cl\text{—}P{=}C(TMS)_2$ $\quad\quad$ $Cl\text{—}P{=}C(TMS)E$

1 $TMS = Me_3Si$ $\quad\quad$ **2** $E = CO_2Et$

1 is an excellent dienophile reacting with electron-poor or -rich dienes in almost quantitative yield (NMR).

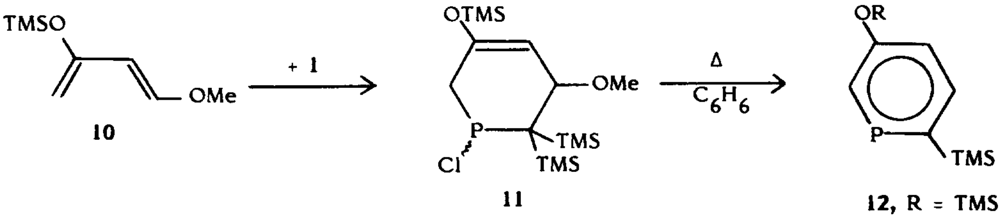
A 1/1 mixture of two diastereoisomers **3** and **3'** is obtained at room temperature (12 hrs) from **1** and methyl sorbate **4** (scheme 1).

Scheme 1



Addition of pyridine perbromide in CH_2Cl_2 to a cold solution (-80°C) of **3** and **3'** leads to a 1/1 mixture of chloro- and bromo-phosphines **5** and **5'** which is thermolyzed in vacuum above 250°C to yield a 4/1 mixture of **6** and **6'** (42 %/**1**). Heating at reflux a benzene solution of the kinetic adducts **3** and **3'** for 15 hours yields a 1/1 mixture (^{31}P NMR) of dichlorophosphine **7** (5) and secondary phosphine **8**, via cycloreversion, Diels-Alder reaction with inverse addition, dehydrochlorination and 1,5 hydrogen shift. **8** is converted to phosphabenzene **9** either by thermolysis under vacuum (**9** is contaminated with 20% of **9'**) or in refluxing CCl_4 (yield = 32%/**4**). When heating a mixture of **3** and **3'** with Danishefsky's diene **10**(6), the cycloreversion is shown by trapping **1** with **10**, more reactive than methylsorbate, to yield **12** and **13** (see after). **6** and **9** may be protodesilylated by excess formic acid in refluxing CCl_4. The reaction of **1** with **4** shows the synthetic potentiality of the reversible Diels-Alder reaction in that it enables the synthesis of one isomer or another (**6** or **9**) depending on the experimental conditions.

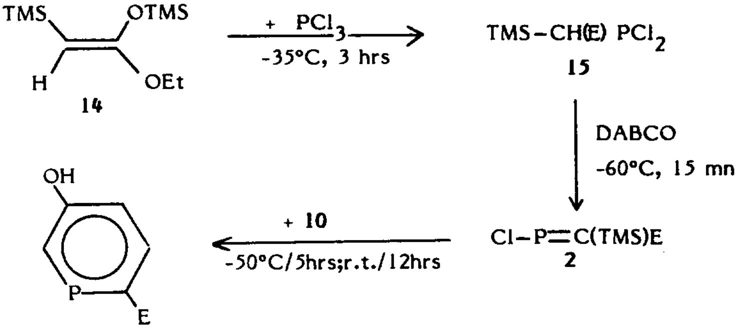
Heating adduct **11** obtained from **1** and **10**, in benzene at reflux for 4 hrs, leads to a 9/1 mixture of phosphabenzenes **12** and **13** as shown by ^{31}P NMR (yield = 54 %/**1** after distillation, $E_{0.1}$ = 110-130°C).



10 **11** **12**, R = TMS **13**, R = H

13 is obtained pure (F = 54-57°C) after methanolysis of the mixture.

The introduction of the functionality in the dienophile necessitates the preliminary synthesis of the functional phosphaalkene **2** which is generated *in situ* by the following sequence :



14

16 E = CO_2Et

Treating the silylated ketene acetal, **14** (7) with PCl_3 yields the dichlorophosphine **15** which is dehydrochlorinated with DABCO to give phosphaalkene **2** which is trapped by Danishefsky's diene leading to **16** after aromatization (one pot reaction, yield 70 %/**14**, F = 135°C). When the reaction is carried out without diene at -60°C, the observed signal at $\delta = 213$ ppm (^{31}P NMR) may correspond to **2**.

The structure of products **3**, **3'**, **5**, **5'**, **6**, **6'**, **8**, **9**, **9'**, **11**, **12**, **13**, **14**, **15** and **16** have been established on the basis of their spectroscopic data (^1H, ^{31}P, ^{13}C NMR and Mass)(8).

This note shows that the Diels Alder reaction with phosphaalkenes **1** and **2** leads to functionalized λ^3 phosphabenzenes. The cycloaddition step is an easy one while the difficulty lies in finding easy experimental conditions for the aromatization of the primary cycloadducts. The mechanism of aromatization in certain cases is not clearly understood at the present time and is under actual study. The extension of this strategy to other dienes or phosphaalkenes is under way.

References and Notes

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2 - G. MÄRKL, G. ADOLIN, F. KEES and G. ZANDER, Tetrahedron Letters, 1977, p. 3445. G. MÄRKL and K. HOCK, Ibid., 1983, p. 2645, 5051, 5055.

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4 - Y.Y.C. YEUNG LAM KO and R. CARRIÉ, J. Chem. Soc., Chem. Comm., 1984, p. 1640.

5 - R. APPEL and A. WESTERHAUS, Tetrahedron Letters, 1981, p. 2159.

6 - S. DANISHEFSKY and T. KITAHARA, J. Am. Chem. Soc., 1974, 96, 7807.

7 - Same method as described for analogous ketene acetals by C. AINSWORTH and YU-NENG KUO, J. Organometallic Chem., 1972, 46, 73.

8 - Only the main characteristics are given here (δ in ppm, J in Hz) :

3 (CCl_4/C_6D_6) : ^{31}P : 144.1 ; ^{1}H : 2.55, $^{2}J_{PH}$ = 3.0 ($C\underline{H}CH_3$, proton in trans position to the lone pair).

3' (CCl_4/C_6D_6) : ^{31}P : 145.1 ; ^{1}H : 1.79, $^{2}J_{PH}$ = 24.0 ($C\underline{H}CH_3$, proton in cis position to the lone pair).

5 and **5'** (C_6D_6) : ^{31}P : 85.3 and 90.0 ; ^{1}H : 1.78, $^{3}J_{PH}$ = 12.4 and 1.77, $^{3}J_{PH}$ = 12.4 ($C\underline{H}_3$) ; 5.16 and 5.26 ($C\underline{H}Br$) ; 6.01 and 6.05 ($=C\underline{H}$) ; mass spectrum : m/z : 472 ($C_{14}H_{27}O_2PSi_2{}^{79}Br_2$) and 428 ($C_{14}H_{27}O_2PSi_2{}^{35}Cl^{79}Br$).

6 (CCl_4/CD_2Cl_2) : ^{31}P : 237 ; ^{1}H : 2.73, $^{3}J_{PH}$ = 14 ($C\underline{H}_3$).

6' (CCl_4/CD_2Cl_2) : ^{31}P : 207 ; ^{1}H : 2.80, $^{3}J_{PH}$ = 15 ($C\underline{H}_3$) ; 9.40, $^{2}J_{PH}$ = 37 (1H).

8 (CCl_4/CD_2Cl_2) : ^{31}P : -98.4, $^{1}J_{PH}$ = 185 ; ^{1}H : 2.08 ($C\underline{H}_3$) ; 4.05, $^{1}J_{PH}$ = 185 ($P\underline{H}$) ; 6.02, $^{3}J_{HH}$ = 6.7 ; 7.24, $^{3}J_{PH}$ = 5.3 (2 olefinic protons).

9 (CCl_4/C_6D_6) : ^{31}P : 252 ; ^{1}H : 2.68 ($C\underline{H}_3$).

9' (CCl_4/C_6D_6) : ^{31}P : 223 ; ^{1}H : 2.19 ($C\underline{H}_3$) ; 8.30, $^{2}J_{PH}$ = 39 (1H).

11 (CCl_4/C_6D_6) : ^{31}P : 114 ; ^{1}H : 2.00, $^{2}J_{PH}$ = 24.7, $^{2}J_{HH}$ = 15.2 (H_A) ; 2.60, $^{2}J_{PH}$ = 6.8 (H_B) ; ^{13}C : 32.2, $^{1}J_{PC}$ = 79 ($\underline{C}TMS_2$) ; 36.0, $^{1}J_{PC}$ = 36 ($\underline{C}H_2$).

12 (CCl_4/C_6D_6) : ^{31}P : 237 ; ^{1}H : 7.93 , $^{2}J_{PH}$ = 34.5 (1H) ; ^{13}C : 142.5, $^{1}J_{PC}$ = 61 ($\underline{C}H$) ; 161.6, $^{1}J_{PC}$ = 55 ($\underline{C}TMS$).

13 (CCl_4/C_6D_6) : ^{31}P : 236 ; ^{1}H : 7.95, $^{2}J_{PH}$ = 34.0 (1H).

14 ($CDCl_3/CHCl_3$) : ^{1}H : 3.08 ($\equiv CH$).

15 : ^{31}P (THF/C_6D_6) : 185 ; ^{1}H ($CDCl_3/CHCl_3$) : 3.25, $^{2}J_{PH}$ = 10.0 ($C\underline{H}$).

16 : ^{31}P (THF/C_6D_6) : 217 ; ^{1}H ($CDCl_3$) : 8.02, $^{2}J_{PH}$ = 38 (1H).

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