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REACTION OF ALUMINUM HALIDE σ COMPLEXES OF CYCLOBUTADIENES WITH PHOSPHONOUS DICHLORIDES. PREPARATION OF PHOSPHOLIUM SALTS AND PHOSPHOLE OXIDES.

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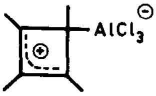
Abstract: Some highly substituted phospholium salts and phosphole oxides have been prepared *via* a ring expansion reaction of aluminum halide σ complexes of cyclobutadienes with phosphonous dichlorides.

Aluminum halide σ complexes of cyclobutadienes were first described more than a decade ago[1]. These complexes, e.g. 1, 2[2] and 3[3], are easily prepared from aluminum halides and alkynes. Their synthetic utility appears in various reactions: Dewarbenzenes[4], bicyclohexenes[5], Dewarpyridones[6], pyridines[7], cyclopentadienes[8], pyrroles[9,10] and a number of other derivatives[8b,9] are obtained upon the reaction with appropriate reagents. We now report preliminary results of a novel reaction of these complexes with phosphonous dichlorides to yield phospholium salts, which on hydrolysis afford phosphole oxides. The phosphole ring system[11], although known for many years, has been the subject of many investigations[12] of both synthesis and chemical behaviour.



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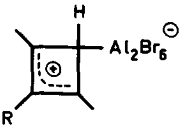
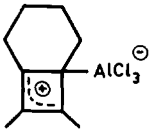


2a R=H
2b R=CH$_3$



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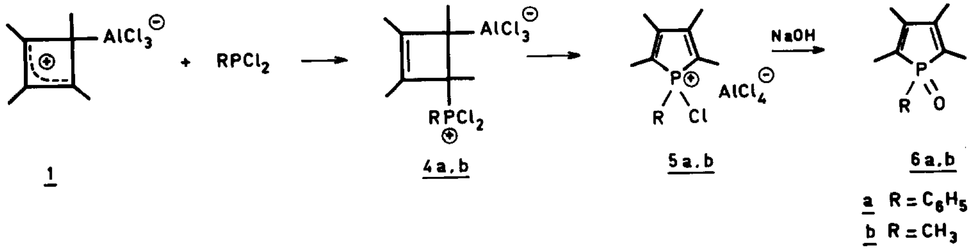
$\boxed{—\equiv CH_3}$

Complex 1 reacted with phenyl phosphonous dichloride[13] in CH_2Cl_2 at -50°C; ^1H-, ^{13}C- and ^{31}P-NMR spectroscopic data were in accord with quantitative formation of phospholium salt 5a (based on the stoichiometry of the reaction and the symmetry of the product as may be concluded from the ^{1}H- and ^{13}C-NMR data[14a]). After aqueous work-up of the reaction mixture and crystallization of the product from ether/pentane pure phosphole oxide 6a[15a] was obtained in 78% overall yield (based on 2-butyne). The structure assignment for phosphole oxide 6a is based on micro-elemental analysis and spectroscopic data[15a]. When methyl phosphonous dichloride is used in the reaction with complex 1[14b] the corresponding phosphole oxide 6b[15b] is isolated in 66% overall yield (Scheme 1). This procedure for the preparation

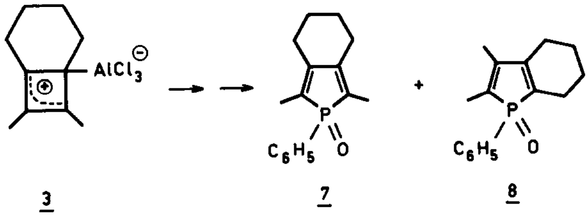
Scheme 1



of P-alkyl phosphole oxides is likely to be general: t-butyl phosphonous dichloride also affords the expected phosphole oxide[16] (yield > 60%).

No identifiable products could be isolated from the reactions of complexes 2a and 2b with phenyl phosphonous dichloride. The reaction of complex 3 with phenyl phosphonous dichloride afforded, after aqueous work-up, a mixture of two isomeric phosphole oxides 8 and 9 in the ratio 3 : 1, respectively[17] (Scheme 2).

Scheme 2



In order to obtain more insight in the mechanistic details of the formation of the phospholium salts, the reaction of 1 with phenyl phosphonous dichloride was followed by ^{1}H-NMR spectroscopic measurements at various temperatures. Indications for the intermediacy of a cyclobutene derivative 4a (Scheme 1) in the reaction of 1 to 5a were found in the ^{1}H-NMR spectrum at -60°C: four transient CH_3 absorptions are observed at 1.15 (br.s), 1.65 (br.d, J_{PH}= 10 Hz), 1.95 (br.s) and 2.25 ppm (br.d, J_{PH}= 28 Hz).

In summary a novel but straightforward route to the highly substituted phosphole ring system has been found.

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13. Procedure for complexes 1 and 3 : A solution of 2-butyne (20 mmol) or 2,8-decadiyne (10 mmol) in CH_2Cl_2 (15 ml) is added dropwise to a stirred suspension of $AlCl_3$ (1.4 g, 10.5 mmol) in CH_2Cl_2 (15 ml) at 0^oC. Complex formation is completed by stirring for an additional 30 min. at room temperature. The solution is cooled to -50^oC and a solution of the phosphonous dichloride (11 mmol) in CH_2Cl_2 (20 ml) is added dropwise. The reaction mixture is allowed to warm to $+15^oC$ in 1 hr. and cooled to -50^oC again, at which temperature a solution of DMSO (2g) in CH_2Cl_2 (20 ml) is added. Subsequently this reaction mixture is added to a vigorously stirred mixture of 150 ml 1 N NaOH/150 ml CH_2Cl_2 (0^oC), followed by extraction of the organic layer with a satd. NaCl solution (2x70 ml). After drying over K_2CO_3 and evaporation of the solvent the crude phosphole oxide(s) is obtained.
14. NMR spectra of 5a and 5b have been recorded in $CH_2Cl_2/CDCl_3$ (1/1) solutions; ^{31}P-chemical shifts have been measured relative to $(NPCl_2)_3$ at + 19.90 ppm and converted to 80% H_3PO_4 at 0.00 ppm.

a. Salt 5a: ^{1}H-NMR: 2.14 (dq,J_{PH}=15.9 Hz,J_{HH}=0.8 Hz,6 H), 2.34 (br.s,6 H), 7.7-8.2 (m,5 H); ^{13}C-NMR: 8.6(dq,J_{PC}=12.8 Hz,J_{CH}=131 Hz), 15.1(dq,J_{PC}=18.5 Hz, J_{CH}=130 Hz), 113.2(d,J_{PC}=82.5 Hz), 117.8(d,J_{PC}=82.1 Hz), 130.6(dd,J_{PC}=14.8 Hz, J_{CH}=169 Hz), 131.1(dd,J_{PC}=14.1 Hz,J_{CH}=169 Hz), 136.5 (dd,J_{PC}=3.4 Hz,J_{CH}=165 Hz), 159.3(d,J_{PC}=33.6 Hz); ^{31}P-NMR: +69.3 ppm.

b. Salt 5b: ^{1}H-NMR: 2.27(d,J_{PH}=15 Hz,6 H), 2.31(br.s,6 H), 2.59(d,J_{PH}=12.3 Hz,3 H); ^{13}C-NMR: 8.8(dq,J_{PC}=13.3 Hz,J_{CH}=131 Hz), 11.0(dq,J_{PC}=54.4 Hz,J_{CH}=137 Hz), 14.8 (dq,J_{PC}=18.4 Hz,J_{CH}=130 Hz), 117.3(d,J_{PC}=81.5 Hz),158.2(d,J_{PC}=33.9 Hz); ^{31}P-NMR: +78.2 ppm.

15.a. Phosphole oxide 6a: ^{1}H-NMR ($CDCl_3$): 1.81(d,J_{PH}=11.9 Hz,6 H), 1.95(br.s,6 H), 7.3-7.7(m,5 H); ^{13}C-NMR ($CDCl_3$): 9.5 (dq,J_{PC}=12.0 Hz,J_{CH}=129 Hz), 13.0(dq, J_{PC}=16.2 Hz,J_{CH}=127 Hz), 126.2(d,J_{PC}=98.0 Hz), 128.6(d,J_{PC}=90.7 Hz), 128.6 (dd,J_{PC}=11.4 Hz,J_{CH}=166 Hz), 130.4(dd,J_{PC}=10.4 Hz,J_{CH}=164 Hz),131.5(dd,J_{PC}= 2.7 Hz,J_{CH}=165 Hz), 146.8(d,J_{PC}=29.3 Hz); ^{31}P-NMR ($CDCl_3$): +46.4 ppm;IR (CH_2Cl_2): 1150, 1200 cm^{-1} (P=O); mp 128-129 °C; MS: M^+ at m/e 232; analysis: calcd. for $C_{14}H_{17}OP$: C 72.40 %, H 7.38 %, P 13.34 %, found C 72.14 %, H 7.37 %, P 13.31 %.

b. Phosphole oxide 6b: ^{1}H-NMR ($CDCl_3$): 1.44(d,J_{PH}=12.4 Hz,3 H), 1.85(dq,J_{PH}= 2.4 Hz,J_{HH}=0.9 Hz,6 H), 1.92(dq,J_{PH}=11.6 Hz,J_{HH}=0.9 Hz,6 H); ^{13}C-NMR ($CDCl_3$): 9.2(dq,J_{PC}=12.1 Hz,J_{CH}=126 Hz), 11.1(dq,J_{PC}=62.6 Hz,J_{CH}=127 Hz), 12.4(dq, J_{PC}=15.8 Hz,J_{CH}=127 Hz), 125.2(d,J_{PC}=96.7 Hz), 144.4(d,J_{PC}=29.4 Hz); ^{31}P-NMR ($CDCl_3$): +51.0 ppm; IR (CH_2Cl_2): 1135,1180 cm^{-1} (P=O); mp 91-93°C; MS: exact mass calcd. for $C_9H_{15}OP$ at m/e 170.086, found 170.086.

16. Only the NMR spectroscopic data for 1-t-butyl-2,3,4,5-tetramethylphosphole 1-oxide were determined: ^{1}H-NMR ($CDCl_3$): 1.17(d,J_{PH}=15.3 Hz,9 H), 1.88(br.s, 6 H), 1.94(d,J_{PH}=10.9 Hz,6 H); ^{13}C-NMR ($CDCl_3$): 11.9(dq,J_{PC}=10.7 Hz,J_{CH}=129 Hz), 13.2(dq,J_{PC}=15.2 Hz,J_{CH}=127 Hz), 24.2(q,J_{PC}<2 Hz,J_{CH}=128 Hz), 31.4(d,J_{PC}=63.3 Hz), 121.7(d,J_{PC}=89.5 Hz), 150.3(d,J_{PC}=26.8 Hz); ^{31}P-NMR ($CDCl_3$): +72.1 ppm.

17. The ratio of both isomers has been determined by GLC and ^{13}C-NMR. The major isomer 8 could be purified by crystallization from ether. Phosphole oxide 8: ^{1}H-NMR ($CDCl_3$): 1.68(m,4 H), 1.75(d,J_{PH}=12.2 Hz,6 H), 2.44(br.s,4 H), 7.35-7.70(m,5 H); ^{13}C-NMR ($CDCl_3$): 8,9(dq,J_{PC}=11.8 Hz,J_{CH}=125 Hz),22.3(t,J_{PC}<1 Hz, J_{CH}=126 Hz), 25.4(dt,J_{PC}=15.8 Hz,J_{CH}=123 Hz), 125.2(d,J_{PC}=99.4 Hz), 128.5(dd, J_{PC}=11.4 Hz,J_{CH}=163 Hz), 128.8(d,J_{PC}=90.2 Hz), 130.3(dd,J_{PC}=10.5 Hz,J_{CH}=162 Hz), 131.3(dd,J_{PC}=2.8 Hz,J_{CH}=160 Hz), 147.0(d,J_{PC}=28.0 Hz); IR (CCl_4): 1165,1195 cm^{-1} (P=O); mp 117-118 °C; MS: exact mass calcd. for $C_{16}H_{19}OP$ at m/e 258.117, found 258.118. Chemical shift values of the sp^3 carbon atoms of isomer 9 have been deduced from the ^{13}C-NMR spectrum of a 1 : 1 mixture of 8 and 9: 8.8(J_{PC}=11.5 Hz), 11.7(J_{PC}=15.8 Hz), 20.5(J_{PC}=8.9 Hz), 21.1(J_{PC}=8.1 Hz), 21.5(J_{PC}<1 Hz), 24.3 (J_{PC}=14.1 Hz).

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