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# SYNTHESIS OF PHOSPHIRENIUM SALTS

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Abstract: Phosphirenium salts, a compound type not previously described, have been prepared by the reaction of alkynes with phosphonous dichlorides in the presence of aluminum trichloride.

During the past several years the search for unsaturated three-membered ring heterocycles has met with remarkable success; examples are selenirene 1[1] and thiirene 2[1] as well as selenirenium ion 3[2] and thiirenium ion 4[3], all of which have now been characterized. Although reports on phosphirene derivatives[4] have appeared, the postulated structures for these compounds have not been demonstrated unambiguously by spectroscopic evidence[5]. Very recently, however, Mathey et. al.[6] prepared phosphirene metal carbonyl complexes 5, the structure of which (M=W, $R=R^1=C_6H_5$) was proven by X-ray analysis. This observation prompts us to report our preliminary results on the synthesis of phosphirenium salts, obtained by formal addition of "R$\overset{\oplus}{\text{P}}$Cl" to alkynes. The "R$\overset{\oplus}{\text{P}}$Cl" ion has already been shown to be capable of addition to alkenes[8], a reaction in which phosphiranium type intermediates have been suggested.

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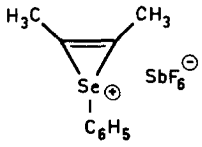

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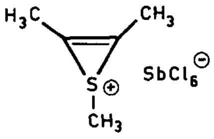

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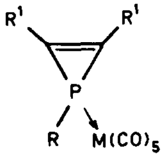

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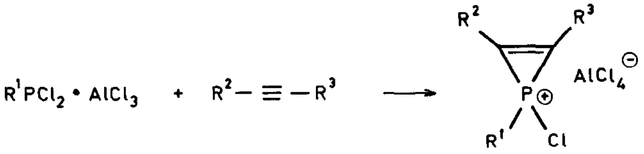
After addition of a 1 molar solution of 2-butyne (1 equiv.) in methylene chloride to a 1 molar solution of methylphosphonous dichloride/aluminum trichloride (1:1) in methylene chloride at -30$^\circ$C a colorless solution is obtained, which contains, as determined from the $^1$H-NMR spectrum, a new compound, which exhibits two sharp doublets (J = 22.9 and 18.0 Hz) in the ratio 2:1. Crystallization of this product at low temperature from methylene chloride yields a white solid hygroscopic material[9]. The $^1$H-, $^{13}$C- and $^{31}$P-NMR data (Tables 1 and 2) for the addition product are fully in accord with our assignment of phosphirenium salt 6a (see below). The $^{27}$Al-NMR spectrum unambiguously demonstrates the presence of the $AlCl_4^\ominus$ ion by a narrow (5.2 Hz; lit.[10] 15.1 Hz) absorption at 102.9 ppm (lit.[10]:102.4 ppm).



| | $R^1$ | $R^2$ | $R^3$ | yield[11] (%) |
|---|---|---|---|---|
| 6a | $CH_3$ | $CH_3$ | $CH_3$ | > 90 |
| 6b | $CH_3$ | $CH_3$ | H | 70 |
| 6c | $CH_3$ | H | H | 60 |
| 6d | $C_6H_5$ | $CH_3$ | $CH_3$ | 90 |
| 6e | $C_6H_5$ | $CH_3$ | H | 70 |
| 6f | $C_6H_5$ | H | H | 50 |

Some structural variation with regard to the alkyne and the phosphonous dichloride is possible; in all instances the formation of phosphirenium salts 6 has been demonstrated by NMR spectroscopy. In the case of 6c and 6f considerable byproduct formation lowers the yield of these products as compared to the almost quantitative formation of 6a (isolated yield after crystallization 92.4%).

The evidence for the phosphirenium structure is based on the spectroscopic data summarized in Tables 1 and 2. First the large values of the coupling constants $^1J_{=CH}$ (232 to 241 Hz) in 6b, 6c, 6e and 6f are comparable to those found in cyclopropenes[12] (213-255 Hz) and cyclopropenium ions[12] (around 260 Hz). Second, the absorptions in the $^{31}$P-NMR spectra in 6a-f show upfield shifts (-57.3 to -69.2 ppm), which have been observed also in other small ring phosphorus compounds[13] (e.g. phosphiranes around

-200 ppm). Third the values of the chemical shifts of phenyl-$C_1$ and $^1J_{PC_1}$ in 6d, 6e and 6f (aver. 115 ppm, 114 Hz) are in agreement with those in phosphonium salts[14], e.g. $(C_6H_5)_3\overset{\oplus}{P}R$ (118 ppm, 90 Hz), compare to $(C_6H_5)_3P$ (137.1 ppm, 12.4 Hz). Last, but not least, the values found for the coupling constants between phosphorus and the ring carbons and between phosphorus and the protons directly attached to the ring carbons have the same order of magnitude as those predicted by calculations[15]: $^1J_{PC,calcd}$= 4.1 and -1.0, $^1J_{PC,exp.}$= 6.6 to 15.3; $^2J_{PH,calcd}$= 2.6 and 3.3, $^2J_{PH,exp.}$= 10.4 to 12.2.

Table 1: $^{31}P$- and $^1H$-NMR data[a] of phosphirenium salts 6a-f

| Salt | $\delta_{^{31}P}$[b,c] | $=C-CH_3$ ($^3J_{PH}$) | $P-CH_3$ ($^2J_{PH}$) | $C_6H_5$ | $=CH$ ($^2J_{PH}$) |
|---|---|---|---|---|---|
| 6a | -57.3 | 2.60 (d, 22.9) | 2.92 (d, 18.0) | — | — |
| 6b[d] | -62.2 | 2.70 (d, 23.2) | 2.90 (d, 18.1) | — | 8.89 (d, 10.5) |
| 6c | -68.4 | — | 3.26 (d, 18.3) | — | 9.51 (d, 12.2) |
| 6d | -58.0 | 2.69 (d, 23.1) | — | 7.6-8.3 (br) | — |
| 6e[e] | -57.9 | 2.95 (d, 22.9) | — | 7.6-8.2 (br) | 9.00 (d, 10.4) |
| 6f | -69.2 | — | — | 7.4 8.2 (br) | 9.28 (d, 11.5) |

a. Spectra are recorded in $CH_2Cl_2$ or $CD_2Cl_2$ solutions at room temperature, except for 6b, 6d and 6f (below -30°C).

b. $^{31}P$ chemical shifts have been measured relative to $(NPCl_2)_3$ at 19.90 ppm[16] and converted to 80% $H_3PO_4$ at 0.00 ppm.

c. $^{31}P$-$^1H$ coupled spectra of 3a, 3b and 3c show the splittings to be expected from the $^1H$-NMR spectra.

d. Long-range couplings: $^4J_{HCPCH}$ = 0.9 Hz ; $^4J_{HCCCH}$ = 1.3 Hz.

e. Long-range coupling: $^4J_{HCCCH}$ = 1.4 Hz.

Table 2 : $^{13}C$-NMR data of phosphirenium salts 6a-f[a,b]

| Salt | $=C-CH_3$ ($^2J_{PC}$ : $^1J_{CH}$) | $P-CH_3$ ($^1J_{PC}$ : $^1J_{CH}$) | $C=C$ ($^1J_{PC}$ : $^1J_{CH}$) | $C_1$ ($^1J_{PC}$) | $C_o$ ($^2J_{PC}$ : $^1J_{CH}$) | $C_m$ ($^3J_{PC}$ : $^1J_{CH}$) | $C_p$ ($^4J_{PC}$ : $^1J_{CH}$) |
|---|---|---|---|---|---|---|---|
| 6a | 11.2<br>(2.1 ; 135) | 19.3<br>(57.6 ; 140) | 145.8<br>(7.4 ; —) | — | — | — | — |
| 6b | 13.4<br>(1.7 ; 134) | 18.9<br>(61.1 ; 140) | 133.7 154.1<br>(12.5 ; 232) ; (6.6 ; —) | — | — | — | — |
| 6c | — | 18.9<br>(64.1 ; 141) | 142.8<br>(13.2 ; 241) | — | — | — | — |
| 6d | 11.2<br>(1.6 ; 134) | — | 143.0<br>(8.9 ; —) | 116.6<br>(109.1) | 132.6<br>(16.5 ; 168) | 129.8<br>(20.4 ; 168) | 135.8<br>(5.3 ; 168) |
| 6e | 13.5<br>($<2^{b}$ ; 135) | — | 131.0 152.6<br>(14.5 ; 234) ; (8.5 ; —) | 114.6<br>(114) | 132.7<br>(14.5 ; 170) | 129.8<br>(14.5 ; 169) | 136.2<br>(5.3 ; 160) |
| 6f | — | — | 141.2<br>(15.3 ; 238) | 114.8<br>(118.7) | 133.2<br>(17.2 ; 172) | 130.6<br>(21.5 ; 168) | 137.2<br>(5.5 ; 173) |

a. $^{13}C$ chemical shifts have been measured relative to $CH_2Cl_2$ at 53.4 ppm and converted to $(CH_3)_4Si$ at 0.00 ppm
b. See note a) at Table 1

Investigations concerning the detailed structure of "R$\overset{\oplus}{P}$Cl"[7] and the chemistry of the phosphirenium salts are in progress.

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