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Aliphatic Phosphenium Cation Featuring A P-S Bond

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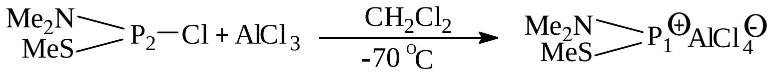
Abstract: The first aliphatic phosphenium cation featuring a P-S bond, (dimethylamino)(methylthio) phosphenium cation **1**, has been prepared by treatment of the (dimethylamino)(methylthio) chlorophosphines **2** with the stoichiometric quantity of $AlCl_3$ in CH_2Cl_2 solution, and characterized by ^1H, ^{13}C, ^{27}Al and ^{31}P NMR spectroscopy.

Keywords: Phosphenium cation; chlorophosphine; ^{31}P NMR spectroscopy.

The first stable phosphenium cation was found in 1972[1]. Their extensive chemistry were respectively reviewed by Cowley[2] in 1985 and by Sanchez[3] in 1990. Recent interest has focused on the role of functionallization of the phosphorus center in the stability and reactivity[4-6]. Burford reported that the dithiaphospholidinium[6] cation is unstable at low temperature. Our objective is to explore stability of N-P^+-S phosphenium cations. We have reported the synthesis of two 1, 3, 4, 2-thiadiazaphospholinium cations[7,8]. Present approach results in the first synthesis of persistent aliphatic phosphenium cation, **1**, [(dimethylamino(methylthio)chlorophosphenium], featuring a S-P bond.

A mixture of 3 mmol of (dimethylamino)(methylthio)chlorophosphines **2** and equimolar quantities of $AlCl_3$ in 20 ml of CH_2Cl_2 was stirred for 4 hrs at -70℃. The ^{31}P NMR at 120 MHz showed that phosphenium cation **1** are formed and persistent, ^1H and ^{13}C NMR supported the structure of **1**. The ^{27}Al NMR at 78 MHz disclosed the formation of $AlCl_4^-$.



The ^{31}P chemical shift of **1** is 429.0 ppm, indicative of phosphenium cation as a sole product. The phosphorus nucleus is about 257 ppm downfield of that of **2**. ^{27}Al (102.60 ppm), ^1H and ^{13}C NMR data for **1** support its cationic structure. δ ^1H and δ ^{13}C data listed in experimental part showed that protons and carbon nuclei in **1** were significantly deshielded from those in **2**. These can be ascribed to the presence of positive charge in **1**.

The cation **1** is noteworthy because it is the first aliphatic phosphenium cations to feature a P-S bond. It is also significant in that the value of its ^{31}P chemical shift is rather larger than those of known N-P^+-N (ca. 260 ppm) and N-P^+-Cl (ca. 325 ppm) phosphenium cations. This trend is a reflection of the relative inferior π-donor ability of RS group to R_2N group and to Cl.

Experimental

All experiments were conducted under an atmosphere of dry oxygen-free nitrogen. NMR spectra were recorded on Brucker AM300 spectrometers.

Preparation of (dimethylamino(methylthio)chlorophosphenium 1: A solution of **2** (3.0 mmol) in 10 ml of CH_2Cl_2 was poured in small portions onto a vigorously stirred suspension of $AlCl_3$ (ca. 3.0 mmol) in 10 ml of CH_2Cl_2. The mixture was stirred for 4 hrs at -70℃. After granular $AlCl_3$ has disappeared, a colorless solution was formed. About 0.5 ml of filtrate was measured on ^{27}Al, ^{31}P NMR. After CH_2Cl_2 and other volatile components in filtrate were removed off under vacuum, the solutions of **1** in CD_2Cl_2-$CDCl_3$ were examined on ^{1}H and ^{13}C NMR. $\delta\ ^1$H (ppm): 2.98 (d, $^3J_{PSCH}$=10.5 Hz, 3H, Me), 3.1 (d, $^3J_{PNCH}$=10.6 Hz, 3H, Me), 3.2 (d, $^3J_{PNCH}$=11 Hz, 3H, Me). $\delta\ ^{13}$C: 35.44 (d, $^2J_{PSC}$=26.3 Hz), 39.17 (d, $^2J_{PNC}$=21.4 Hz), 42.65 (d, $^2J_{PNC}$=44.7 Hz). $\delta\ ^{27}$Al : 102.60 ($\Delta\nu$ <15 Hz). $\delta\ ^{31}$P: 429.0.

(Dimethylamino)(methylthio)chlorophosphines 2 was synthesized according to the reported procedure.[9] For **1** (54%), bp 80℃/5 mmHg. δ^1H (ppm): 2.65(d, $^3J_{PSCH}$=9.8 Hz, 3H, SMe), 2.75(d, $^3J_{PNCH}$=9.0 Hz, 6H, NMe_2). $\delta\ ^{31}$P (ppm): 172.0. IR (cm^{-1}): 670, 790, 945, 1020, 1140, 1205, 1258, 1380, 1455, 2950. Anal. Calcd for C_3H_9ClNPS: C, 22.86; H,5.76; N, 8.89. Found: C, 22.75; H, 5.82, N, 8.80.

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