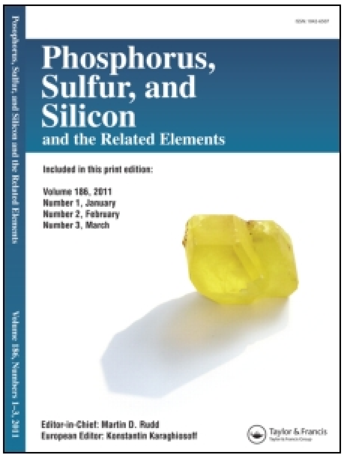

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IMPROVED SYNTHESIS OF DIALKYLTHIOXAPHOSPHORANESULFENYL CHLORIDES AND BROMIDES

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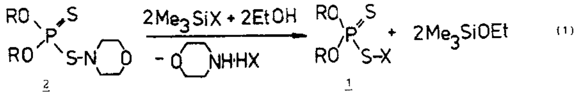
Dialkylthioxaphosphoranesulfenyl chlorides and bromides can be conveniently prepared in the reaction of the corresponding thioamides with hydrogen chloride generated in situ with trimethylsilyl chloride and ethanol. Stability of the chlorides and bromides obtained by this method is high and the yields are quantitative.

Phosphoranesulfenyl halides of the general formula RR'P(Z)YX ($Z = O, S, Se$; $Y = S, Se$; $X = Cl, Br$) are of great practical and theoretical interest.[1,2] Convenient methods of synthesis of oxaphosphoranesulfenyl chlorides ($Z = O$, $Y = S$, $X = Cl$)[3] are available. Recently the synthesis of thioxaphosphoranesulfenyl chlorides and bromides ($Z = S$, $Y = S$, $X = Cl, Br$),[4–6] as well as their seleno analogs[6–8] was accomplished.

Almasi and Hantz[9,10] described the synthesis of dialkoxythioxaphosphoranesulfenyl chlorides **1** based on the reaction of sulfenamides **2** with hydrogen chloride which is introduced into reaction medium. However, such a way of conducting this reaction between **2** and hydrogen chloride causes that the final outcome is not reproducible. According to our experience low yields and low purity of dialkoxythioxaphosphoranesulfenyl chlorides are observed. However, the method of Almasi is still an attractive alternative route for the synthesis of sulfenyl halides, and specially those containing a chiral center at the phosphorus atom RR'P*(S)SX.[6] In this paper we describe a significant modification of the Almasi method which allows the synthesis of required sulfenyl chlorides and bromides in high yields and high purity.

RESULTS

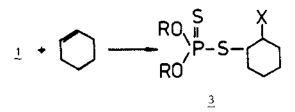
The sulfenamides **2** are readily available by a number of methods[5,9,11,12] and can be resolved in the case of compounds containing the chiral phosphorus center.[6] In contrast to the original Almasi's procedure,[9] hydrogen chloride, or hydrogen bromide is formed in situ by the reaction of the corresponding trimethylsilyl halide with the equivalent amount of the ethanol. Under such condition, the reaction of hydrogen halide gives the sulfenyl compounds **1** in quantitative yield, according to the ^{31}P NMR spectroscopy. The solvents of choice for the reaction are low boiling hydrocarbons. The sulfenyl halides **1** are readily separated from amine hydrohalides and trimethylsilyl ethyl ether. The isolated sulfenyl halides



(1)

2a, R = Et; **2b**, R = iPr; **2c**, R = Neo; **1a**, R = Et, X = Cl; **1b**, R = iPr, X = Cl; **1c**, R = Neo, X = Cl; **1d**, R = iPr, X = Br; **1e**, R = Neo, X = Br

are of high purity according to ^{31}P NMR spectroscopy and can be directly used for further transformations. The structures and high purity of the sulfenyl halides **1** were confirmed by their addition to the cyclohexene. The adducts **3** were fully characterized by their spectral properties and elemental analysis.



(2)

The attempt to obtain sulfenyl iodides $(RO)_2P(S)SI$ by the same procedure led to the formation of disulfides $[(RO)_2P(S)S]_2$ **4** and elemental iodine. According to the ^{31}P NMR spectra the chemical shifts of **4** are only slightly different from the shifts of **4** prepared by an independent method. This would indicate some interaction between **4** and elemental iodine. There were no signals in the ^{31}P NMR spectra which could be ascribed to sulfenyl iodides.[13]

EXPERIMENTAL

The solvents and reagents were purified by conventional methods before use. All b.ps. and m.ps. are uncorrected. ^{1}H NMR spectra were recorded on Tesla BS-487C. Bruker MSL-300 spectrometers, ^{31}P NMR spectra were recorded on Jeol JNM-FX60 and Bruker MSL-300 spectrometers.

Preparation of dialkoxythioxaphosphoranesulfenyl halides. General procedure. To a solution of the corresponding dialkoxythioxaphosphoranesulfenamide **2** (0.01 M) in 50 ml of dry hexane was added 0.92 g (0.02 M) ethanol at temp. 15–10°C. The resulting solution was treated with stirring at temp. 15–20°C with (0.02 M) trimethylsilylhalide in 5 ml dry hexane. Amine hydro halide precipitates immediately. The sulfenyl halide (**1**) are formed with 100% yield which was confirmed by the integration from ^{31}P NMR spectra. The amine hydrohalides were removed by filtration and the evaporation of the residual liquid at 5°C/5 mmHg gave the sulfenyl halides as oily liquids. These undergo the reaction with cyclohexene to give 1-halogeno-2-(S-dialkoxythiophosphoro)cyclohexane which were fully characterized.

Diethoxythioxaphosphoranesulfenyl chloride (**1a**). Yield 2.2 g (100%); ^{31}P NMR 78.5 ppm (hexane).

1-Chloro-2-(S-diethoxythiophosphoro)cyclohexane (**3a**). Yield 3.02 g (100%); oil $n_D^{20} = 1.5212$; ^{31}P NMR 91.7 ppm (hexane); ^{1}H NMR ($CDCl_3$) 1.2995 ppm (t, 6H, $J_{H-H} = 7$ Hz, CH_3—CH_2—O—), 1.33–1.80 ppm (m, 6H, cyclohexane), 2.13–2.34 ppm (m, 2H, cyclohexane), 3.39–3.44 ppm (m, 1H, cyclohexane), 4.04–4.16 ppm (m, 1H, cyclohexane), 4.0–4.16 ppm (m, 4H, CH_3—CH_2—O—). Found: C, 39.48; H, 6.68; P, 9.91; S, 19.36; Cl, 11.44. Calcd. for $C_{10}H_{20}PO_2S_2Cl$: C, 39.66; H, 6.66; P, 10.23; S, 21.77; Cl, 11.71.

Diisopropoxythioxaphosphoranesulfenyl chloride (**1b**). Yield 2.48 g (100%); ^{31}P NMR 75.4 ppm (CH_2Cl_2).

1-Chloro-2-(S-diisopropoxythiophosphoro)cyclohexane (**3b**). Yield 3.3 g (100%); oil $n_D^{20} = 1.5139$; ^{31}P NMR 89.7 ppm ($CDCl_3$); ^1H NMR ($CDCl_3$) 1.3590 ppm (d, 12H, $J_{H-H} = 6$ Hz $(CH_3)_2CH—O—$), 1.500–1.8622 ppm (m, 6H, cyclohexane), 2.1644–2.4464 ppm (m, 2H, cyclohexane), 3.5388–3.6280 ppm (m, 1H, cyclohexane), 4.2077–4.3156 ppm (m, 1H, cyclohexane), 4.8335 ppm (hept., 2H, $J_{H-H} = 6$ Hz $(CH_3)_2CH—O—$). Found: C, 43.14; H, 7.20; P, 9.20; S, 18.38; Cl, 10.64; Calcd. for $C_{12}H_{24}PO_2S_2Cl$ C, 43.56; H, 7.31; P, 9.36; S, 19.38; Cl, 10.70.

Dineopentoxythioxaphosphoranesulfenyl chloride (**1c**). Yield 3.04 g (100%); ^{31}P NMR 79.1 ppm (CH_2Cl_2).

1-Chloro-2-(S-dineopentoxythiophosphoro)cyclohexane (**3c**). Yield 3.5 g (90%) crystallized from ethanol m.p. 51°C; ^{31}P NMR 91.6 ppm (CH_2Cl_2); ^1H NMR ($CDCl_3$) 0.94 ppm (s, 18H, $(CH_3)_3CCH_2—O—$) 2.1696–2.3665 ppm (m, 2H, cyclohexane), 3.4943–3.5433 ppm (m, 1H, cyclohexane), 3.6485–3.7935 ppm (m, 4H, $(CH_3)_3CCH_2—O—$), 4.15–4.22 ppm (m, 1H, cyclohexane). Found: C, 48.73; H, 8.42; P, 8.19; S, 16.13; Cl, 9.25; Calcd. for $C_{16}H_{32}PO_2S_2Cl$: C, 49.65; H, 8.33; P, 8.01; S, 16.56; Cl, 9.16.

Diisopropoxythioxaphosphoranesulfenyl bromide (**1d**). Yield 3.23 g (100%); ^{31}P NMR 70.0 ppm (CH_2Cl_2).

1-Bromo-2-(S-diisopropoxythiophosphoro)cyclohexane (**3d**). Yield 2.62 g (70%); ^{31}P NMR 89.0 ppm (CH_2Cl); oil $n_D^{20} = 1.5293$; b.p. 98°C/0.01 mmHg; ^1H NMR ($CDCl_3$) 1.36 ppm (d, 12H, $J_{H-H} = 6$ Hz, $(CH_3)_2CH—O—$), 1.70–1.96 ppm (m, 6H, cyclohexane), 2.20–2.49 ppm (m, 2H, cyclohexane), 3.69–3.75 ppm (m, 1H, cyclohexane), 4.55–4.57 ppm (m, 1H, cyclohexane), 4.78–4.91 ppm (hept., 2H, $J_{H-H} = 6$ Hz, $(CH_3)_2CH—O—$). Found: C, 38.07; H, 6.21; P, 8.24; S, 14.79; Br, 21.21. Calcd. for $C_{12}H_{24}PO_2S_2Br$: C, 38.40; H, 6.45; P, 8.25; S, 17.08; Br, 21.29.

Dineopentoxythioxaphosphoranesulfenyl bromide (**1e**). Yield 3.49 g (100%); ^{31}P NMR 74.4 ppm (CH_2Cl_2).

1-Bromo-2-(S-dineopentoxythiophosphoro)cyclohexane (**3e**). Yield 3.4 g (80%); ^{31}P NMR 91.9 ppm (CH_2Cl), m.p. 46°C crystallized from ethanol; ^1H NMR ($CDCl_3$) 0.98 ppm (s, 18H, $(CH_3)_3CCH_2—O—$), 1.48–1.95 ppm (m, 6H, cyclohexane), 2.26–2.47 ppm (m, 2H, cyclohexane), 3.66–3.78 ppm, (m, 1H, cyclohexane), 3.79–3.93 ppm (m, 4H, $(CH_3)_3CCH_2—O—$), 4.48–4.50 ppm (m, 1H, cyclohexane). Found: C, 44.92; H, 7.26; P, 7.70; S, 15.15; Br, 17.80. Calcd. for $C_{16}H_{32}PO_2S_2Br$: C, 44.54; H, 7.48; P, 7.18; S, 14.82; Br, 18.52.

Reaction of **2c** *with hydrogen iodide.* Reaction of **2c** (0.01 M) with trimethylsilyl iodide (0.02 M) and ethanol (0.02 M), HI generated in situ, performed under exactly the same conditions, gave however bis(dineopentoxythiophosphoryl)disulfide **4** ($\delta^{31}P$ 86.0, yield 100%, which compared favourably with the $\delta^{31}P$ 84.4 of the authentic sample prepared by reaction of sulfuryl chloride with 0.0-dineopentyltriethylammonium phosphorodithioate.

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