REACTION OF SECONDARY PHOSPHINES WITH SULFONYL CHLORIDES

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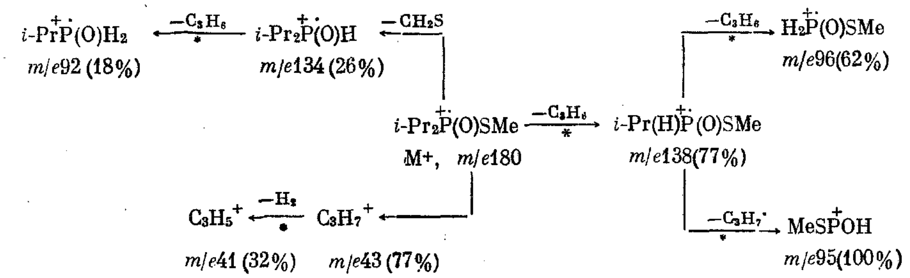
The attempted synthesis of sulfonylphosphines by reacting secondary phosphines with sulfonyl chlorides (A) gave the sulfonyl derivatives of phosphine oxides, and specifically the esters of dialkylthiolphosphinic acids (Table 1), for example:

$$i\text{-}Pr_2PH + MeSO_2Cl \xrightarrow[Et_2O]{A.\,C_5H_5N} i\text{-}Pr_2P(O)SMe \xleftarrow[MeONa/MeOH]{B.\,MeI} i\text{-}Pr_2P(O)SH$$

The structure (I) was proved by counter synthesis (B). The molecular weights of (I) and (III) were determined by mass spectrometry, and the fragmentation of (I) is shown in the scheme (the relative intensity of the peaks at 30 eV is given in parentheses)



The assignment of the signals in the NMR spectra is confirmed via the decoupling from ^{31}P (Figs. 1 and 2). Compounds (I)-(III) are similar in all of the parameters of their NMR spectra (Table 1). The values of the SSCC [spin-spin coupling constants] of the phosphorus and protons of the substituents correspond to a tetracoordinated phosphorus, while the values of the chemical shifts of the MeS groups correspond to a discoordinated sulfur. In addition, the NMR spectrum of (III) testifies to the purity of the compound (see Fig. 2), which excludes the alternate structure of the sulfinyl oxide that should be present in the mixture of diasteromers.

The formation of the sulfonylphosphine or sulfinylphosphine oxide cannot be recorded by changing the order of mixing the reactants. The slow addition of diisopropylphosphine and pyridine to the sulfonyl chloride in CCl_4 at −20°C gives a reaction mixture whose NMR spectrum corresponds to (I). As a result, similar to tertiary phosphines and phosphites [1], secondary phosphines react with sulfonyl chlorides as reducing agents, with apparently the initial formation of sulfenyl chlorides.

EXPERIMENTAL

All of the experiments were run in a dry argon atmosphere, without the admittance of atmospheric oxygen and moisture.

Methyl Ester of Diisopropylthiolphosphinic Acid (I). a. A mixture of 2.36 g (0.02 mole) of diisopropylphosphine and 1.6 g (0.02 mole) of pyridine in 25 ml of ether was stirred at 20° and treated with a solution of 2.1 g (0.02 mole) of methanesulfonyl chloride in 10 ml of ether. After 1 h the obtained precipitate was filtered and washed with ether. After removal of the ether in vacuo the residue was distilled. We obtained 0.73 g of (I) (see Table 1).

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TABLE 1

Compound	Formula	Yield, %	bp, °C (p, mm of Hg)	δ, ppm				J, Hz				
				$Me_A(H_A)$	$Me_B(H_B)$	HCP (Me_3C)	Me (C_6H_4Ph)	Me_ACH (MeCP)	Me_BCH (H_AH_B)	Me_AP (H_ACP)	Me_BP (M_BCP)	MeSP
(I)	$i\text{-}Pr_2P(O)SMe$	40,5 (a) 52,5 (b)	70—71 (2) 76—77 (3,5)	1,27	0,97	1,97	2,14	6,6	7,0	16,9	17,2	9,0
(II)	$i\text{-}Pr_2P(O)SC_6H_4Me\text{-}p$	98,9	123 (1,0)	1,22	0,95	1,95	2,2 (7,05)	6,7	7,1	16,5	17,2	—
(III)	$Me_3C(PhCH_2)P(O)SMe$	95,7	114—115 (2) mp 56,5—57,0	(3,41)	(3,08)	(1,2)	1,67 (7,25)	(16,5)	(12,8)	(11,1)	(9,0)	9,7

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*JNM-C-60 HL (JEOL) NMR spectrometer, ^1H 60 MHz (in CCl_4 from TMS); ^{31}P 24.3 MHz (pure specimen from 85% H_3PO_4) for (I) $\delta_{^{31}P}$ — 72.0 ppm.

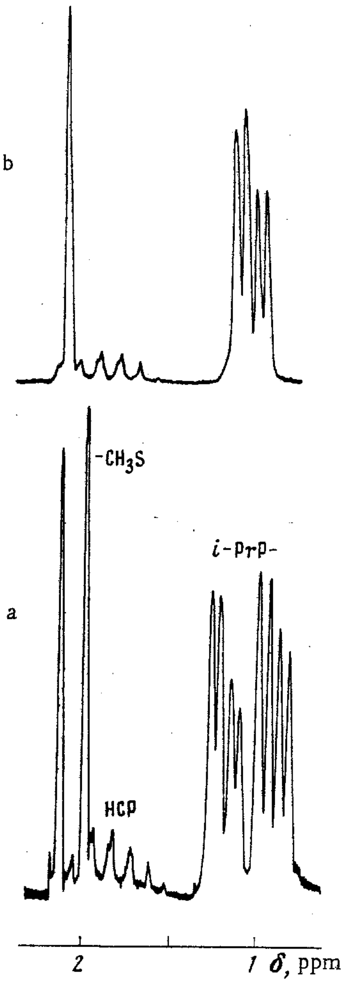

Fig. 1

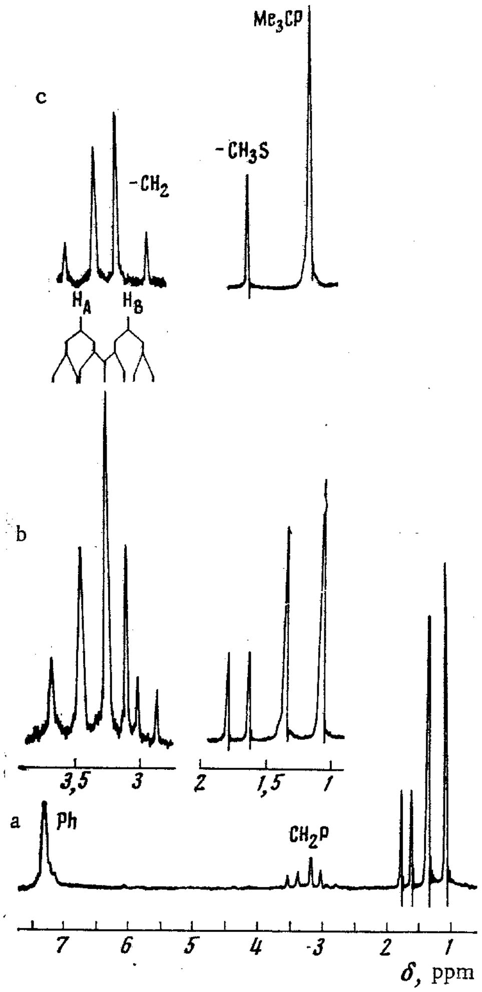

Fig. 2

Fig. 1. NMR spectrum of (I) (60 MHz in Ph_2O from TMS): a) normal; b) with decoupling from ^{31}P. The spectrum does not change in the range 20-200°.

Fig. 2. NMR spectrum of (III) (60 MHz in CCl_4 from TMS): a) total; b) upfield portion; c) the same, with decoupling from ^{31}P.

b. To a solution of 3.15 g (0.018 mole) of diisopropylthiophosphinic acid [3] (dried over P_2O_5 in vacuo) in 15 ml of methanol were added 0.018 mole of sodium methylate in 15 ml of methanol (yellow color) and then 12.8 g (0.09 mole) of CH_3I (gradual decolorization) [4]. The mixture was refluxed for 1 h and then let stand overnight. After removal of the solvent the product was extracted with ether and distilled. We obtained 1.7 g of (I). Found: C 46.82; H 9.77%. $C_6H_{17}OPS$. Calculated: C 46.64; H 9.45%.

p-Tolyl Ester of Diisopropylthiolphosphinic Acid (II). Using method a, from 1.8 g of diisopropylphosphine, 2.86 g of p-toluenesulfonyl chloride, and 1.2 g of pyridine in 40 ml of ether (the mixture warms up to reflux) we obtained 1.9 g of (II), which was identified by the NMR spectrum (see Table 1).

Methyl Ester of tert-Butylbenzylthiolphosphinic Acid (III). Using method a, from 0.7 g of tert-butylbenzylphosphine, 0.44 g of methanesulfonyl chloride, and 0.3 g of pyridine in 25 ml of ether we obtained 0.45 g of (III), which, after distillation, crystallizes when kept in the refrigerator and sublimes in vacuo at 55° (1 mm). Found: C 60.25; H 7.91%. $C_{12}H_{19}OPS$. Calculated: C 59.50; H 7.85%.

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CONCLUSIONS

The reaction of secondary phosphines with sulfonyl chlorides gives sulfenylphosphine oxides (esters of dialkylthiolphosphinic acids), and not sulfonylphosphines.

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