Chemistry

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Abstract

Full Text

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INTERACTION OF N,N-DIALKYLAMINOSULFENYL CHLORIDES WITH TRIALKYL PHOSPHITES

A NEW METHOD FOR THE PREPARATION OF DIALKYL *S*-DIALKYLAMINOTHIOPHOSPHATES

(Presented by Academician M. I. Kabachnik on 4 VI 1962)

The dialkyl *S*-dialkylaminothiophosphates (II) previously obtained by us are representatives of a new type of chemical compound containing an interesting grouping of covalently bound atoms: phosphorus, sulfur, and nitrogen.

The transformations of compounds (II) described so far (thermal decomposition, reaction with hydrogen chloride) confirm the correctness of the chemical structure proposed for them and indicate the potential possibility of their use in the synthesis of organic derivatives of phosphorus and sulfur.

Compounds (II) were first obtained by replacing chlorine in dialkyl *S*-chlorothiophosphates ([1]) (I) with an amino group:

$$\underset{\text{(I)}}{(\mathrm{RO})_2\mathrm{P(O)}-\mathrm{SCl}} + 2\mathrm{HNR}'_2 \rightarrow \underset{\text{(II)}}{(\mathrm{RO})_2\mathrm{P(O)}-\mathrm{SNR}'_2} + \mathrm{R}'_2\mathrm{NH}\cdot\mathrm{HCl}.$$

The method given above is inconvenient, despite all its simplicity. The presence of the amine hydrochloride formed as a result of the reaction considerably complicates purification of the amide. It is possible that the amine hydrochloride is not indifferent with respect to the amide. In this connection, we previously succeeded in obtaining only diethyl *S*-diethylaminothiophosphate in analytically pure form.

In studying the chemical properties of (II), we found that they do not interact under ordinary conditions with trialkyl phosphites (IV). This led us to the idea of using a reaction of the Arbuzov type for the synthesis of dialkyl *S*-dialkylaminothiophosphates (II). As the electrophilic reagent introducing the group $-\mathrm{SNR}'_2$, we used the readily available N,N-dialkylaminosulfenyl chlorides $\mathrm{R}'_2\mathrm{NSCl}$ (III). We established that the reaction of chlorides (III) with trialkyl phosphites proceeds spontaneously with a considerable thermal effect according to the scheme:

$$\underset{\text{(III)}}{R'_2NSCl} + P(OR)_3 \rightarrow \underset{\text{(IV)}}{\left[R'_2N - S - \overset{\oplus}{P}(OR)_3\, Cl^{\ominus}\right]} \rightarrow \underset{\text{(II)}}{(RO)_2P(O) - S - NR'_2} + RCl.$$

Isolation of compounds (II) presents no difficulties, since the only by-product of the reaction is a readily volatile alkyl chloride.

A typical experiment was carried out as follows. N,N-dialkylaminosulfenyl chloride (1 mole) was added dropwise to trialkyl phosphite (1 mole)

with intensive cooling and mechanical stirring. The temperature of the reaction mixture was maintained below 10°. The reaction product was purified by distillation in vacuo.

The dialkyl *S*-dialkylaminothiophosphates $(RO)_2P(O)SNR'_2$ obtained by us, their constants, and the results of analyses are given in Table 1.

Table 1

R	R′	b.p., °C/mm	n_D^{20}	Yield, %	C, % found	C, % calcd.	H, % found	H, % calcd.	P, % found	P, % calcd.
Et	Et	52–54/0.01	1.4665	74	40.08	39.8	8.3	8.3	13.02	12.8
Pr	Et	70–71/0.03	1.4644	57	45.03	44.58	8.96	8.98	11.62	11.5
Bu	Et	110–115/0.01*	1.4645	70	48.52	48.45	9.56	9.82	11.04	10.41

* Molecular distillation.

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Note: Figure translations are in progress. See original paper for figures.

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