through alumina to remove traces of molybdenum salts using pentane as the eluent. Gas-liquid chromatographic analysis showed that the total yield of isomeric tolylphenylmethanes was 0.29 g (88%).

#### CONCLUSIONS

The benzylation of aromatic compounds was carried out efficiently under mild conditions by the action of trimethylbenzylsilane in the presence of  $MoCl_5$ ,  $AlCl_3$ , or  $WCl_6$  with the formation of the corresponding diarylmethanes. The benzylation in the presence of  $MoCl_5$  conforms to behavior typical of electrophilic substitution.

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# NEW DATA ON THE REACTION OF TRIALKYL TRITHIOPHOSPHITES WITH ALKYL HALIDES

UDC 542.91:547.1'118

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The reaction of phosphonous derivatives of P(III) acid thioesters with alkyl halides studied by A. E. Arbuzov proceeds in accord with the classical scheme and leads to the predominant formation of phosphine sulfides [1]. However, we have shown that substitution of the alkylthio group by a halogen at the P(III) atom in trialkyl trithiophosphites is also possible upon the action of alkyl halide (the products of the Arbuzov reaction were not isolated in this case) [2]. A subsequent study of the reactivity of P(III) acid thioesters showed that the reaction in the case of phosphonite derivatives is accomplished both by the Arbuzov reaction and by substitution of the alkyl thio group and is complicated by a series of secondary processes [3].

Hence, it has become accepted that the reactivity of P(III) acid thioesters relative to alkyl halides varies depending on the environment of the phosphorus atom. In going from phosphonous to phosphite derivatives, there is a shift in the direction of the alkylation of the P-S bond from the phosphorus atom to the sulfide sulfur atom [3-5].



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-mnN		T, °C, reac-	Yield	Bp, °C (p,	20	<sup>31</sup> P NMR	IR sp V. CI	bectrum,		PMR s	pectrum, ô, pp	om, J Hz		Other prod-
ber	RHal	tion time	0/0	mm Hg)	$d_{u}$	spectrum, 6, ppm	P=S	psc	CH3P	$CH_{3}(Ph)CP$	CH <sub>2</sub> P	CH3CS	$CH_2S$	ucts, %
1*	MeI	20, 5 months	64	75 (0,02)	1,6054	78	640	515-535	2,15 d, 3 <i>J</i> =13,0		I	$^{1,36}_{3J_{ m HH}}$ $^{7,0}_{ m HH}$	$^{2,92}_{3J_{\rm HP}}$ d.t, $^{3J_{\rm HP}}$ 14,0	EtI, 80
7* 7	MeI	100, 5 h	55	89 (0,5)	1,6062	78	640	515-535	Spectrum &	analogous to the	preceding			
* ന	EtI	150, 4 h	78	87 (0,04)	1,5978	93	623	518540		$^{1,22}_{J_{HH}=7,0,}$	$^{2,77}_{\rm d,q}$ , $^{2,17}_{\rm HP}$ $^{2,14,6}_{\rm HP}$	$^{1,35}_{HH}$ t, $^{3}J_{HH}$ =7,3	$^{2,90}_{3J_{\rm HP}=14,6}$	Ett. 87 Ett. 83, Ft. 47
4 5 ** 5	BzBr BzCl	20, 6 months 175, 8 h	46 36	$\begin{array}{c} 144 \\ 150 \\ (0,07) \end{array}$	1,6315 1,6320	88 88 88	$632 \\ 632$	505535	I	7,30 br.s	$^{3,68}_{2J_{\rm HP}=13,0}$	$^{1,33 t}_{H\Pi} = 7,3$	2,92 d. <b>q</b> , <sup>3</sup> J <sub>HP</sub> =14,6	EtBr, 50
								505-535	Spectrum a	inalogous to the	preceding			
40.00	1 1	Maria I	10											

Thionephosphonates from the Reaction of Triethyl Trithiophosphite with Alkyl Halides TABLE 1.

C 47.83, H 6.16, P 11.23, S 34.78. C<sub>10</sub>H<sub>15</sub>PS<sub>3</sub>. Calculated, %: P 11.23, S 34.25. \*Kosolapoff and Meier [8]. \*\*Found, %: C 48.03, H 6.43,



However, we have recently shown that under mild conditions  $P(SEt)_3$  reacts with MeI to form products of the Arbuzov reaction [6]. In a continuation of these studies, we investigated the reaction of  $P(SEt)_3$  with MeI, EtI,  $PhCH_2Cl$ , and  $PhCH_2Br$  at different temperatures with 1:1 ratio of the starting reagents. The reactions with EtI and  $PhCH_2Cl$  were studied previously [2] and the corresponding sulfides and dithiohalophosphites were identified.

In addition, we have established that the major products are the corresponding thionephosphonates, which are the Arbuzov reaction products (see Table 1), virtually independently of the temperature

 ${\rm (EtS)_{3}P+RHal} \rightarrow {\rm (EtS)_{2}PR+EtHal}$ 

 $\mathbf{R} = \mathbf{Me}, \mathbf{Et}, \mathbf{Bz}; \mathbf{Hal} = \mathbf{I}, \mathbf{Br}, \mathbf{Cl}.$ 

The <sup>31</sup>P NMR spectra of the reaction mixtures indicate that the Arbuzov pathway holds for the alkyl iodides. This pathway accounts for more than 90% of the reaction (the conversion was determined relative to the relative intensity of the peak of the final phosphonate). Benzyl chloride and benzyl bromide are less reactive toward trithiophosphite but, under more vigorous conditions, they also lead, albeit in lower yields, to benzylphosphonate. In addition, trialkylsulfonium iodides are formed in the reaction of trithiophosphite with alkyl iodides. However, the yield of these products does not exceed 5%. The <sup>31</sup>P NMR spectra of the low-boiling fractions obtained from the reactions with the benzyl halides indicates trace amounts of a compound with  $\delta P$  160-190 ppm characteristic for P(III) nuclei with a phosphorus-halide bond. The formation of these compounds may be attributed to the direct substitution of an alkylthio group by halogen according to the scheme proposed in our previous work [2] and secondary reactions. Thus, a model reaction has shown that triethyl trithiophosphonate reacts with EtI under analogous conditions to give triethylsulfonium iodide.

#### EXPERIMENTAL

The <sup>31</sup>P NMR spectra were taken on a KGU-4 NMR spectrum at 10.2 MHz relative to 85% H<sub>3</sub>PO<sub>4</sub>. The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz for 25-30% solutions relative to TMS. The IR spectra were taken on a UR-20 spectrometer.

The reactions of  $P(SEt)_3$  with alkyl halides were carried out in sealed ampules. The conversion was determined by <sup>31</sup>P NMR spectroscopy. The products were isolated from the reaction mixtures by fractionation. The physical indices and spectral characteristics of the products isolated are given in Table 1.

<u>Reaction of Triethyl Trithiophosphonate with Ethyl Iodide.</u> A mixture of 8.7 g triethyl trithiophosphonate and 6.4 g ethyl iodide was heated in a sealed ampul for 4 h at 150°C. Crystals appeared upon maintenance of the reaction mixture for several days. The liquid portion was decanted off and the crystals were washed and recrystallized from ether to give 0.1 g (1%) triethylsulfonium iodide which decomposes at 143°C [9]. The IR spectrum of this sample was identical to that of the product obtained from the reaction of triethyl trithiophosphite with ethyl iodide. Fractionation of the liquid portion gave 7.2 g (83%) triethyl trithiophosphonate with bp 117°C (0.2 mm),  $n_D^{2^0}$  1.5983 and 4.7 g (74%) ethyl iodide with bp 70-72°C,  $n_D^{2^0}$  1.5150.

## CONCLUSIONS

The major pathway for the reaction of trialkyl trithiophosphites with alkyl halides is alkylation of the phosphorus atom with the formation of alkylthionephosphonates.

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<sup>35</sup>C1 NQR SPECTRUM OF WS<sub>2</sub>SeC1<sub>5</sub>

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UDC 543.422:541.67:541.49:546.78

In our previous studies, we investigated the NQR spectra of  $MoS_2SeCl_5$ ,  $MoS_2SeBr_5$ , and  $WS_2SeBr_5$  and showed that these compounds are complexes of metal thiohalides with selenium dihalides [1, 2]. In a continuation of this work, we studied the NQR spectrum of their chloride analog, tungsten thioselenium chloride,  $WS_2SeCl_5$  (TTC). The results obtained are given in Table 1. The spectrum for the analogous molybdenum compound is given for comparison.

The spectrum of TTC, similar to that for molybdenum thioselenium chloride, consists of two groups of lines: a high-frequency doublet and a low-frequency triplet. The high-frequency doublet is located closer to the frequencies of the chlorine atoms at selenium in the complexes of metal chlorides with selenium chloride (36-38 MHz) than at sulfur (41-43 MHz) in the analogous complexes with sulfur chlorides [3-5] and was assigned to the chlorine atoms at selenium. The slight splitting is the result of crystallographic inequivalence. The lowfrequency triplet is assigned to the chlorine atoms at tungsten and shifted toward higher values in comparison with the 35Cl NQR frequencies in tungsten chlorides and oxochlorides (9-15 MHz) [6]. According to x-ray diffraction structural analysis [7], the structure of tungsten thioselenium bromide (TTB) is insular and consists of centrosymmetric [WS<sub>2</sub>Br<sub>3</sub>(SeBr<sub>2</sub>)], dimers. The tungsten atoms are noncoordinated. Three crystallographically independent bromine atoms are bound to tungsten and two are bound to selenium. Two bromine atoms at tungsten are bridging atoms which link W and Se and one bromine atom is in a terminal position. TTC has analogous structure since the spectra of TTC and TTB are similar. We then understand the large splitting in the low-frequency component of the spectrum. The line at 21.182 MHz corresponds to the terminal chlorine atom, while the lines at 16.182 and 15.956 MHz correspond to the bridging atoms which link W and SE.

Comparison of the NQR spectra of all four tungsten and molybdenum thiohalides indicates that their structures are analogous and may be represented as  $[MS_2Hal_3(SeHal_2)]_2$  complexes (M = Mo, W; Hal = C1, Br) with sharply inequivalent halide atoms at the metal.

# EXPERIMENTAL

The NQR spectra were taken on a pulse spectrometer. A sample of tungsten thioselenium chloride was obtained by an exchange reaction from thioselenium bromide in selenium chloride.

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