ADDITION OF OO-DIETHYL HYDROGEN PHOSPHORODITHIOATE TO VINYL ARYL SULFIDES AND VINYL ESTERS

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The reation of OO-dialkyl hydrogen phosphorodithioates with unsaturated compounds has been described in a patent [1], but it was assumed without proof that the adducts formed were constructed in accordance with Markovnikov's rule. In one of the preceding investigations [2] it was shown that various OO-dialkyl hydrogen phosphorodithioates do in fact add to vinyl alkyl sulfides in accordance with Markovnikov's rule. Decomposition of the adducts with mercuric chloride in alcohol was used to prove their structure. Now we have used the same method to show that OO-diethyl hydrogen phosphorodithioates give normal products in accordance with Equation (1) not only with vinyl alkyl sulfides but also with vinyl aryl sulfides and vinyl alkyl and aryl ethers.

$$CH_{2} = CHXR + (C_{2}H_{5}O)_{2}P - SH \rightarrow (C_{2}H_{5}O)_{2}P - SCHXR$$

$$\downarrow \\ CH_{3} \qquad (1)$$

where X = S, O; $R = C_2H_5$, C_5H_5 .

In fact, the resulting compounds split quantitatively in accordance with Equations (2) and (3), and this fact was also used by us to determine their purity (table).

$$(C_{2}H_{5}O)_{2}P - SCHOR + HgCl_{2} + 2C_{2}H_{5}OH \rightarrow HCl + CH_{3}CH (OC_{2}H_{5})_{2} + (C_{2}H_{5}O)_{2}P - SHgCl + CH_{3}CH (OC_{2}H_{5})_{2} + (C_{2}H_{5}O)_{2}P - SHgCl + (C_{2}H_{5}O)_{2}P - S]_{2}Hg + HgCl_{2}$$

$$R = C_{2}H_{5}, C_{6}H_{5}.$$

$$(C_{2}H_{5}O)_{2}P - SCHSC_{6}H_{5} + 2HgCl_{2} + 2C_{2}H_{5}OH \rightarrow 2HCl + CH_{3}CH (OC_{2}H_{5})_{2} + CH_{3}$$

$$+ C_{6}H_{5}SHgCl + (C_{2}H_{5}O)_{2}P - SHgCl + CH_{3}CH (OC_{2}H_{5})_{2} + CH_{3}CH + CH_{3}CH (OC_{2}H_{5})_{2} + CH_{3}CH + CH_{3}CH + CH_{3}CH (OC_{2}H_{5})_{2} + CH_{3}CH + CH_{3}$$

uivalent •	ound calc.		6,11 117,5		7,02 258,2			8,4 306,2								
found ⁶	calc.		9,54 11		12,00	11,98		9,91	10,11	07.07	10,40	ort or				-
S, %	calc.	 1 00	29,87		24,99	24, 79		21,11	20,93	10 00	23.4	T 600		28,83	28,45	-
H, %	calc.		5,89		7,17	7,35		6,30	6,25	00 J	0,08 6 59	30.0		1		
found 70	calc.	10 77	44,31		37,05	37,17		$\frac{47,25}{5}$	47,01	22 14	<u>33 05</u>	20,000	-	J		-
MR found	calc.		89,87		67,04	68,67		83,56	83,54		l			ł		
d_4^{20}		1,1851		1,1284			1,1566		1010	1,1916		1,2996		-		
n_D^{20}		1,5751		1,4960			1,5450		6762	1,5342		1,5760		-		
ວ. "	.q.8 1m) (3H	011	(0,045)		50 - 52	(0,025)		9697	(170'0)		1			1		-
Yield, %		1 75		11 60			111 20		17 0.2	V 94		VI 86			-	
Name			thio)-ethyl phosphoro-	dithioate	00-diethyl S -α-ethoxy-	ethyl phosphorodithio-	ate	OO-diethyl S- α -phenoxy ⁺¹	ethyl phosphorodithio-	ate	00-diethyl S-α-ethylsul-	finylethyl phosphorodi-	thioate	00-diethyl S-α-phenyl-	sulfinylethyl phosphoro-	dithioate
Formula		S S	Cartevist Othe	ຽ	(C ₂ H ₆ O) ₂ Ṕ—SCHOC ₂ H ₆	ွင်မႇ	× 1	(C2H&O)2P-SCHOC,H5	ĊH,	× ×	(C2H2O)2P-SCHSOC2H5	ĊH,	80 11	(C2H,O)2P-SCH3SOC4H5	ĊH ,	

• Found by titration with NaOH after decomposition by HgCl₂ in alcohol in accordance with [2].

The results obtained emphasize the importance of the acidity of the addend, which determines the direction of addition to the double bond. Thus, it has recently been found [3] that thioacetic acid, which is a weaker acid than the OO dialkyl hydrogen phosphorodithioates, adds in accordance with Markovnikov's rule only to vinyl alkyl ethers, and always adds only anomalously to vinyl aryl ethers. Compounds (I)-(III) and the OO diethyl S- α -ethylthioethyl phosphorodithioate (IV) synthesized in accordance with Equation (2) and the sulfoxides (V) and (VI) obtained by the oxidation of (I) and (IV) have been investigated for acaricidal activity (by M. P. Shabanova, All-Union Institute for Plant Protection of the V. I. Lenin All-Union Academy of Agricultural Sciences) and for toxicity to warm-blooded animals (Yu. S. Kagan, Kiev Institute for Industrial Health and Occupational Diseases). Preliminary results show that preparation (I) has the most interesting properties, possessing in concentrations of 0.025-0.015% stable (for up to 20 days) acaricidal activity against the gossamer mite and a low toxicity with respect to warm-blooded animals (LD₅₀ = 65 mg/kg; LD₁₀₀ = 200 mg/kg)[•].

Preparation (IV), differing from (I) by the presence of an ethyl group on the sulfur atom in place of the phenyl group, did not possess systematic activity for the gossamer mite and, in addition, was almost twice as toxic for warm-blooded animals. Preparations (II) and (III) possessed no acaricidal activity whatever. The sulfinyl compounds (V) and (VI) possessed a high acaricidal activity but proved to be extremely toxic to warm-blooded animals. These results indicate the interest of further investigations of preparations of the type of OO-dialkyl S- α -arylthio-ethyl phosphorodithioates.

EXPERIMENTAL

The synthesis of preparations (I)-(IV) was carried out by adding OO-diethyl hydrogen phosphorodithioate to an excess of the vinyl sulfides and ethers at such a rate that the temperature of the reaction mixture did not exceed 60° (see table).

Decomposition with mercuric chloride. a) To 1 g of (II) was added 2.62 g of mercuric chloride in 11 ml of

ethanol. After 3 hours, filtration gave 1.62 g of a crystalline residue (calculated for $(C_2H_5O)_2$ P-SHgCl (VIII - 1.631 g). The residue was disproportionated by boiling with benzene for 1 hour, after which it had m.p. 121-123°.

An m.p. of 125° is given in the literature [2] for $[(C_2H_5O)_2P-S]_2$ Hg

By titration of an aliquot of the mother liquors with 0.1 N NaOH, 95.3% of the theoretical HCl was found, and after distillation from the residue of salts 100.5% of diethyl acetal was found by quantitative determination by the hydroxylamine method.

b) Under the same conditions, 1 g of (III) yielded 1.24 g of the salt (VII) (theoretical 1.371 g); found by titration: 100.7% of HCl and 98.86% of diethyl acetal.

c) Under analogous conditions, 1 g of (I) yielded 2.14 g of total mercury salts [in accordance with Equation (3) the theoretical amount should be 2.37 g]. By titration, 96% of HCl and 99.28% of diethyl acetal were found.

<u>Preparation of (V) and (VI)</u>. Oxidation of (I) and (IV) was carried out in acetone solution with an equivalent amount of $30\% H_2O_2$. The sulfinyl compounds were purified by removing the starting materials which had not reacted in a vacuum of 0.02-0.03 mm at 60° .

SUMMARY

1. Phenyl vinyl sulfide and vinyl alkyl and aryl ethers add OO-diethyl hydrogen phosphorodithioate in accordance with Markovnikov's rule.

2. OO-Diethyl S- α -phenylthioethyl phosphorodithioate possesses acaricidal activity, associated with considerably less toxicity to warm-blooded animals than the compound isomeric with it possessing a thio group in the β position.

[•] After we had synthesized the preparations listed above and sent them for trial, we became aware of a patent of Schrader on the synthesis of insecticidal preparations based on OO-diethyl hydrogen phosphorodithioates and vinyl aryl sulfides [4].

LITERATURE CITED

- 1. E. O. Hook and P. H. Moss, German Patent 833, 807, 1952; Chem. Zb. 1953, 2182.
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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.