bis(α-OXY-β,β,β-TRICHLOROETHYL)-PHOSPHONIC ACID ESTERS

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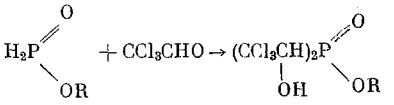
The reaction of hypophosphonic acid with chloral is described in the literature [1, 2]. The authors showed that, depending on the ratios of the reagents, the product formed is either α-oxy-β,β,β-trichloroethylphosphonous acid or bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid. The latter acid is used for preparing its own derivatives in which the OH group is replaced by other groups [3]. Such compounds are of interest as possessing potential biological activity. From this point of view the preparation of bis(α-oxy-β,β,β-trichloroethyl) phosphonic acid esters by the following reaction scheme seems to us to be of equal interest



where R is alkyl.

We did not isolate in the pure state the methyl- and ethylhypophosphites obtained by the reaction of the corresponding orthoformic acid esters with hypophosphorus acid because of their instability. In the reaction with chloralwe obtained a mixture of products consisting of the alkylhypophosphites of the corresponding ester and alcohol of formic acid.

The remaining alkylhypophosphites were prepared by the esterification of hypophosphorus acid with alcohols in the presence of $AlCl_3$ [5, 6]. Irrespective of the ratio of chloral and alkylhypophosphite taken in the reaction the products formed are the esters of bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid. The reaction is exothermic in the absence of catalysts. The products are white crystalline substances, insoluble in water, and having only low solubility in alcohol and acetone. The structures of the compounds obtained were confirmed by elemental and infrared spectrum analysis. The properties of the compounds synthesized are shown in Table 1. Preliminary tests on the methyl-, ethyl and butyl esters of bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid showed that they did not possess contact insecticidal properties.

EXPERIMENTAL

Preparation of bis(α-Oxy-β,β,β-trichloroethyl) phosphonic Acid Ester. A current of nitrogen was passed with stirring for 1.0-1.5 h through a mixture of 6.6 g hypophosphorus acid and 10.6 g methylortho formate. The mass obtained was added dropwise to a solution of 29.5 g chloral in petrol ether, the rate of addition being controlled so that the temperature of the reaction did not exceed 40-50°. After the reaction had finished a residue began to deposit which was filtered off after several h. Recrystallization from a mixture of ethyl alcohol and acetone (1:1) gave 22.5 g (60%) of bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid methyl ester, mp 180-181° Found %: P 8.19; Cl 56.68. $C_5H_7O_4PCl_6$. Calculated %: P 8.26; Cl 56.80.

bis(α-Oxy-β,β,β-trichloroethyl)phosphonic acid ethyl ester was prepared similarly.

Preparation of bis(α-Oxy-β,β,β-trichloroethyl)phosphonic Acid Butyl Ester. 12.2 g of butyl hypophosphite was added dropwise to a solution of 29.5 g chloral in petrol ether, the rate of addition being controlled so that the temperature of the reaction mixture did not exceed 50-60°. After the reaction had finished a residue was deposited which was filtered off after several h. Recrystallization from a mixture of ethyl alcohol and acetone or a mixture of ethyl alcohol and benzene gave 29.12 g

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TABLE 1 $ROP[CH(OH)CCl_3]_2$ (O)

R	mp, °C	Found, %		Empirical formula	Calculated, %		Yield, %
		P	Cl		P	Cl	
CH_3	180—181	8,19	56,68	$C_5H_7O_4PCl_6$	8,26	56,80	60
C_2H_5	177—178	7,91	—	$C_6H_9O_4PCl_6$	7,96	—	75
C_6H_7	175—176	8,02	52,80	$C_7H_{11}O_4PCl_6$	7,69	52,85	70
C_4H_9	173—174	7,30	51,60	$C_8H_{13}O_4PCl_6$	7,43	51,08	70
C_5H_{11}	170—171	7,04	48,80	$C_9H_{15}O_4PCl_6$	7,19	49,40	50
C_6H_{13}	166—167	7,31	47,35	$C_{10}H_{17}O_4PCl_6$	6,98	47,88	55
C_9H_{19}	152—153	6,19	43,58	$C_{13}H_{23}O_4PCl_6$	6,37	43,75	35

(70%) of bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid butyl ester, mp 173-174°. Found %: P 7.30; Cl 51.60. $C_8H_{12}PO_4Cl_6$. Calculated %: P 7.43; Cl 51.08.

The propyl, amyl, hexyl and nonyl esters of bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid were prepared similarly.

CONCLUSIONS

The reaction of hypophosphorus acid esters with chloral es studied. A series of esters of bis(α-oxy-β,β,β-trichloroethyl)phosphonic acid esters is obtained.

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