ESTERS OF 1-METHYL-1-HYDROXY-2-PENTACHLOROTHIO-PHENYLETHYLPHOSPHINIC ACID

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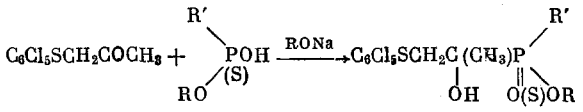
In a continuation of studies on the synthesis of new physiologically active organophosphorus derivatives of pentachlorophenol and pentachlorothiophenol [1-2] we synthesized esters of 1-methyl-1-hydroxy-2-pentachlorothiophenylphosphinic acid. To pentachlorothiophenylacetone, produced from acetone and pentachlorophenylsulfenyl chloride, we added dialkylphosphorous acids, esters of ethylphosphinic acids, and dialkylthiophosphorous acids in the presence of sodium alcoholate according to the reaction



R represents lower alkyls: R' is C_2H_5 or OR. The constants, yields, and results of the analysis are presented in Table 1. The pesticidal activity of these esters is being studied.

EXPERIMENTAL

Synthesis of Pentachlorothiophenylacetone. To 160 ml of abs. acetone, we added in portions 30 g of pentachlorophenylsulfenyl chloride. The mixture was heated while boiling the acetone until complete solution and a change of the color of the solution from orange to colorless. The solution was filtered in the hot state to free it of turbidity. Upon cooling, crystals of pentachlorothiophenylacetone, with m.p. 125-126°, precipitated in a yield of 22 g or 70% of the theoretical.

Synthesis of the Dimethyl Ester of 1-Methyl-1-hydroxy-2-pentachlorothiophenylethylphosphinic Acid. A 3.9 g portion of pentachlorothiophenylacetone was mixed with 5 g of methyl phosphorous acid (a large excess of the acid was used to dissolve the pentachlorothiophenylace-

TABLE 1

Formula	M.p., °C	Found %			Calculated %			Yield of recrystallized products, %
		P	Cl	S	P	Cl	S	
$C_6Cl_5SCH_2COCH_3$	125—126	—	52.81 53.09	8.81 9.01	—	52.43	9.16	70
$C_6Cl_5SCH_2C(CH_3)P(OCH_3)_2$ OH O	188—189	6.73 6.75	40.2 39.89	7.32	6.91	39.58	7.13	44
$C_6Cl_5SCH_2C(CH_3)P(OC_2H_5)_2$ OH O	200—201	6.31 6.32	37.48 37.45	6.92 6.85	6.50	37.25	6.71	50
$C_6Cl_5SCH_2C(CH_3)P(OC_3H_7\text{-}n)_2$ OH O	167—168	5.79 5.97	34.80 34.86	6.57	6.14	35.18	6.34	50
$C_6Cl_5SCH_2C(CH_3)P(C_2H_5)(OCH_3)$ OH O	155—158	6.71	39.75	—	6.94	39.75	—	23
$C_6Cl_5SCH_2C(CH_3)P(C_2H_5)(OC_2H_5)$ OH O	166—167	7.02	38.84 38.77	—	6.73	38.54	—	49
$C_6Cl_5SCH_2C(CH_3)P(C_2H_5)(OC_3H_7)$ OH O	149—151	6.79	37.31 37.23	—	6.53	37.41	—	35
$C_6Cl_5SCH_2C(CH_3)P(OC_2H_5)_2$ OH S	106—107	6.2 6.53	35.85	—	6.3	36.04	—	31
$C_6Cl_5SCH_2C(CH_3)P(OC_3H_7\text{-}i)_2$ OH S	98—99	5.5	34.3 34.4	11.92	5.95	34.1	12.3	19

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tone) and freshly prepared sodium methylate was added dropwise to the mixture until the spontaneous heating of the reaction mixture ceased. The mixture was heated for 4 h at 110-120°. After cooling the reaction product crystallized. The crystalline product, filtered to remove excess dimethylphosphorous acid and washed with ether, possessed m.p. 171-179°. Recrystallization from methanol yielded 2 g of the dimethyl ester of 1-methyl-1-hydroxy-2-pentachlorothiophenylethylphosphinic acid with m.p. 188-189°. Yield of the pure product 44% of the theoretical.

CONCLUSIONS

Eight new esters of 1-methyl-1-hydroxy-2-pentachlorothiophenylethylphosphinic acid was synthesized.

LITERATURE CITED

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2. D. Kh. Yarmukhanetova and I. V. Cheplanova, Izv. AN SSSR, Ser. Khim., 1966, 489.
