SYNTHESIS OF SOME MIXED ESTERS OF THIOPHOSPHORIC ACID

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An important position among the great number of organophosphorus insecticides is occupied by various sulfur-containing esters of phosphorus acids and, in particular, mixed esters of thiophosphoric acid. Some representatives of O,O-dialkyl S-1,2-dicarbalkoxyethyl thiophosphates have been described in the literature as extremely effective acaricides and insecticides [1]. To study the insecticide properties and physiological activity we synthesized some O,O-dialkyl S-carbalkoxymethylthiophosphates. A study of the insecticide properties of the esters we obtained showed that some of them have a high insecticidal activity (table). We have not yet studied the acaricide properties. The esters we obtained were also studied as antiglaucoma agents.

We prepared the esters of O,O-dialkyl S-carbalkoxymethylphosphinic acids according to the following scheme:

$$(RO)_2POH + Na \longrightarrow (RO)_2PONa$$

$$(RO)_2PONa + S \longrightarrow (RO)_2P(=S)ONa$$

$$(RO)_2PONa + HalCH_2R' \longrightarrow (RO)_2P(=O)SCH_2R'$$

where R = C_2H_5, i-C_3H_7, n-C_4H_9 and R' = $COOC_2H_5$, $COOCH_3$, CN.

To determine the structures of the compounds obtained more accurately, we plotted the Raman and infrared absorption spectra of the two following compounds:

$$(C_2H_5O)_2P(=O)SCH_2COOC_2H_5$$

$$(C_2H_5O)_2P(=O)SCH_2COOCH_3 .$$

In both cases there was an intense infrared absorption band of a P—O bond with a maximum at 1260 - 1266 cm^{-1}. At the same time, the Raman spectra showed no lines of appreciable intensity at 600 cm^{-1}, which would have been expected for a P = S bond. The triol structure demonstrated for the compounds obtained agrees with the conclusions of Kabachnik et al. [2] on esters of alkylthiophosphinic acids.

Formula	b.p., °C (P, mm Hg)	n_D^{20}	d_4^{20}	MR		P analysis		Yield %	Toxicity (granary weevil)	
				Calculated	Found	Calculated	Found		solution conc., %	mortality after 7 days, %
$(C_2H_5O)_2P(O)-SCH_2COOCH_3$	129 (3)	1,4645	1,2192	55,10	54,85	12,81	12,92 12,93	26,0	0,05 0, 1	100 100
$(C_2H_5O)_2P(O)-S-CH_2COOC_2H_5$	138 (3)	1,4622	1,1826	59,71	59,57	12,11	12,12 12,26	71,7	0,05 0, 1	95 100
$(C_2H_5O)_2P(O)-S-CH_2CH_2COOCH_3$	137 (3)	1,4640	1,1867	59,73	59,55	12,11	12,30 12,24	30,5	0,05 0, 1	0 0
$(i-C_3H_7O)_2P(O)-SCH_2COOC_2H_5$	134 (3)	1,4568	1,1203	68,95	69,05	10,92	11,08 10,93	66,0	0,05 0, 1	0 0
$(C_4H_9O)_2P(O)-SCH_2COOC_2H_5$	150, (2,5)	1,4642	1,0984	78,19	78,43	9,94	9,83 9,85	40,0	0,05 0, 1	2 12
$(C_2H_5O)_2P(O)-SCH_2CN$	132—135 (3)	1,4700	1,1970	49,16	48,71	14,83	15,10 15,09	24,0	0,01 0,05 0, 1	32 100 100/18 hr

EXPERIMENTAL

Synthesis of diethyl carbethoxymethyl thiophosphate. To the sodium diethyl phosphite obtained from 8.5 g of sodium and 50 g of diethyl phosphite in 250 ml of ligroin was added 11.6 g of sulfur. After the mixture had been heated for an hour, 60.5 g of bromoacetic ester was added dropwise to the precipitated salt. The reaction mixture was then heated for 2 hr, the precipitate removed by filtration, the ligroin evaporated, and the residue vacuum distilled. We obtained 60.7 g of diethyl carbethoxymethyl thiophosphate with the constants given in the table. By analogous syntheses we also prepared diethyl carbomethoxymethyl thiophosphate, diethyl β-carbomethoxyethyl thiophosphate, diisopropyl carbethoxymethyl thiophosphate, dibutyl carbethoxymethyl thiophosphate, and diethyl cyanomethyl thiophosphate, whose constants are given in the table.

SUMMARY

Six esters of O,O-dialkyl S-carbalkoxymethylphosphinic acids that have not been described in the literature were prepared and their structures demonstrated.

LITERATURE CITED

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