SOME ETHYLPHOSPHINIC AND -PHOSPHONIC ESTERS

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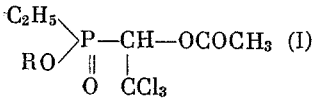
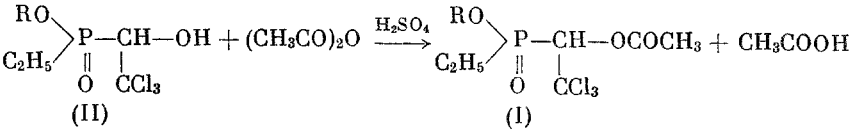
In our laboratory we have studied the reactions of dialkyl 2,2,2-trichloro-1-hydroxyethylphosphonates with carboxylic acid anhydrides. By this method we have prepared dialkyl 1-acetoxy-2,2,2-trichloroethylphosphonates and have shown that these can be used as insecticidal and medicinal preparations [1].

In this paper we describe the preparation of some (1-acetoxy-2,2,2-trichloroethyl)ethylphosphinic esters



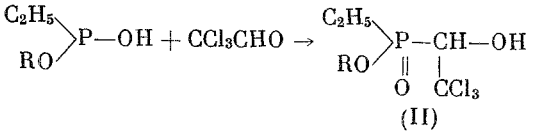
(I) by the reaction of acetic anhydride with ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinic esters (II). The reaction was catalyzed by a few drops of concentrated sulfuric acid



in which R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9.

The reaction gives low yields, for partial decomposition and resinification of the products occur in the distillations. Higher yields can be obtained by the use of a fairly large excess of acetic anhydride. The principal physicochemical constants and the analyses of the compounds are given in the table.

In the course of the work we also synthesized previously undescribed ethyl(2,2,2-trichloro-1-hydroxyethyl)-phosphinic esters by the reaction of alkyl hydrogen ethylphosphinites [2] with chloral [3] in accordance with the scheme:



in which R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9.

The esters (II) in which R = n-C_3H_7, i-C_4H_7, n-C_4H_9, i-C_4H_9 were not obtained in the pure state because reaction did not take only one course, but was more complicated. For further transformations we took the crude uncrystallized product. Preliminary tests on some of these compounds showed that the esters (II) have a toxicity which exceeds that of dialkyl 2,2,2-trichloro-1-hydroxyethylphosphonates. We also carried out the dehydrochlorination of one of the esters, namely, ethyl ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinate, by treatment with sodium ethoxide in ethanol or with an organic base. It was found that rearrangement occurred [4] and 2,2-dichlorovinyl ethyl ethylphosphonate (III) was obtained in low yield:

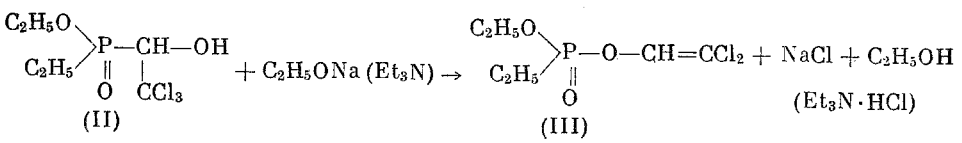
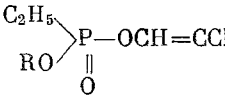


TABLE 1

Compound	B. p., °C (p, mm)	n_D^{20}	d_4^{20}	Found					Calculated					Yield, %
				C, %	H, %	P, %	Cl, %	*MR*	C, %	H, %	P, %	Cl, %	*MR*	
$(CH_3O)(C_2H_5)P(=O)-CH(CCl_3)-O-COCH_3$	91—92 ($6\cdot10^{-3}$)	1,4870	1,408	—	—	9,68; 9,80	35,70; 35,80	60,77	28,23	4,03	10,42	35,80	60,53	43
$(C_2H_5O)(C_2H_5)P(=O)-CH(CCl_3)-O-COCH_3$	93—94 (10^{-2})	1,4833	1,355	30,74; 30,82	4,69; 4,95	10,00; 9,60	33,90; 34,00	65,66	30,82	4,49	9,95	34,19	65,15	36
$(n\text{-}C_3H_7O)(C_2H_5)P(=O)-CH(CCl_3)-O-COCH_3$	108—112 (10^{-2})	1,4790	1,317	33,37; 33,42	5,28; 5,21	9,36; 9,17	32,00; 32,12	70,09	33,18	4,91	9,52	32,72	69,76	38
$(i\text{-}C_3H_7O)(C_2H_5)P(=O)-CH(CCl_3)-O-COCH_3$	103—104 (10^{-2})	1,4752	1,309	33,34; 33,34	5,30; 5,13	9,04; 9,40	31,80; 31,88	70,06	33,18	4,91	9,52	32,72	69,76	20
$(n\text{-}C_4H_9O)(C_2H_5)P(=O)-CH(CCl_3)-O-COCH_3$	121—123 (10^{-2})	1,4778	1,286	35,67; 35,38	5,75; 5,61	8,99; 8,87	31,05; 31,50	74,67	35,35	5,30	9,13	31,37	74,38	22
$(i\text{-}C_4H_9O)(C_2H_5)P(=O)-CH(CCl_3)-O-COCH_3$	121—123 (10^{-2})	1,4760	1,281	35,58; 35,34	5,58; 5,45	9,17; 9,06	31,05; 31,50	74,74	35,35	5,30	9,13	31,37	74,38	20

This ester, and also other esters of formula  have been described earlier [5, 6].

EXPERIMENTAL

Preparation of (1-Acetoxy-2,2,2-trichloroethyl)ethylphosphinic Esters (I). The ester (II) was introduced into a four-necked round-bottomed flask with a stirrer, and addition was made of 100% excess of acetic anhydride to which 3-4 drops of concentrated sulfuric acid had been added as catalyst. The reaction went with the liberation of a little heat, and after 20-30 min the crystalline ester went completely into solution. The reaction mixture was heated at 100° for 2-3 h. Reaction was then considered to be complete. Excess of acetic anhydride and the acetic acid formed in the reaction were distilled off at a residual pressure of 10-15 mm. The residue was vacuum-fractionated two or three times. The esters (I) obtained were clear thick liquids.

Methyl Ester (I, R=CH_3). This was prepared from 16 g of the methylester (II, R=CH_3), 12.7 g of acetic anhydride, and 3 drops of concentrated H_2SO_4 by heating the reaction mixture for 3 h at 100°. After two vacuum distillations we isolated 8 g (43%) of (I, R=CH_3); b. p. 91-92° ($6 \cdot 10^{-3}$ mm); n_D^{20} 1.4870; d_4^{20} 1.408.

Ethyl Ester (I, R=C_2H_5). This was prepared by the reaction of 15 g of the ethyl ester (II, R=C_2H_5) and 11.5 g of acetic anhydride in presence of 2 drops of concentrated H_2SO_4. After three vacuum distillations we isolated 6 g (36%) of (I, R=C_2H_5); b. p. 93-94° (0.01 mm); n_D^{20} 1.4833; d_4^{20} 1.355.

Propyl Ester (I, R=n-C_3H_7). This was prepared by the reaction of 30.4 g of the propyl ester (II, R=n-C_3H_7) and 21.5 g of acetic anhydride in presence of 3 drops of concentrated H_2SO_4. After three vacuum distillations we isolated 13 g (38%) of (I, R=n-C_3H_7); b. p. 108-112° (0.01 mm); n_D^{20} 1.4790; d_4^{20} 1.317.

Isopropyl Ester (I, R=i-C_3H_7). This was prepared by the reaction of 24.2 g of the isopropyl ester (II, R=i-C_3H_7) and 171.1 g of acetic anhydride in presence of 3-4 drops of concentrated H_2SO_4.

After two vacuum distillations we isolated 5 g (20%) of (I, R=i-C_3H_7); b. p. 103-104° (0.01 mm); n_D^{20} 1.4752; d_4^{20} 1.309.

Butyl Ester (I, R=n-C_4H_9). This was prepared by the reaction of 35.8 g of the butyl ester (II, R=n-C_4H_9) and 24.5 g of acetic anhydride in presence of 3 drops of concentrated H_2SO_4. After two vacuum distillations we isolated 9 g (22%) of (I, R=n-C_4H_9); b. p. 121-123° (0.01 mm); n_D^{20} 1.4778; d_4^{20} 1.286.

Isobutyl Ester (I, R=i-C_4H_9). This was prepared by the reaction of 27 g of the isobutyl ester (II, R=i-C_4H_9) and 18.5 g of acetic anhydride in presence of 4 drops of concentrated H_2SO_4. After two vacuum distillations we obtained 6 g (20%) of (I, R=i-C_4H_9); b. p. 121-123° (0.01 mm); n_D^{20} 1.4760; d_4^{20} 1.281.

Preparation of Ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinic Esters (II). One mole of the alkyl hydrogen ethylphosphonite was stirred in a round-bottomed flask, and 1 mole of chloral was added gradually. The reaction was exothermic. By control of the rate of the addition and by external cooling the reaction temperature was kept at about 50°. The mixture was then heated at 80° for 3 h. The hot clear thick liquid was transferred to a crystallizer. Recrystallization was from benzene or dibutyl ether. The purified products formed light white crystals.

(II, R=CH_3)—b. p. 125-128°. Found: C 23.22; 23.39; H 4.02; 3.83; P 12.26; 12.05; Cl 42.34; 42.18%. $C_5H_{10}O_3Cl_3P$. Calculated: C 23.48; H 3.91; P 12.13; Cl 41.69%.

(II, R=C_2H_5)—b. p. 142-145°. Found: C 26.6; 26.42; H 4.79; 4.71; P 10.97; 11.20; Cl 39.85; 40.20% $C_6H_{12}O_3Cl_3P$. Calculated: C 26.71; H 4.45; P 11.50; Cl 39.52%. We were unable to isolate the esters (II) in which R=n-C_3H_7, i-C_3H_7, n-C_4H_9 and i-C_4H_9 in a pure state.

Dehydrochlorination of Ethyl Ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinate (II, R=C_2H_5) with Sodium Ethoxide. A mixture of 12 g of (II, R=C_2H_5) and 15 ml of absolute alcohol was prepared in a round-bottomed flask with a stirrer. Sodium ethoxide solution (1.02 g of sodium in 15 ml of absolute ethanol) was added dropwise. The reaction was slightly exothermic, and after a few minutes a white turbidity appeared. The reaction mixture was heated at 80° for 2-3 h. The precipitate was separated by centrifugation (2.0 g), alcohol was distilled off at a residual pressure of 10-12 mm, and the residue was vacuum-distilled. After two distillations we isolated 2 g (19%) of (III); b. p. 70-75° (0.001 mm); n_D^{20} 1.4623; d_4^{20} 1.260. Found: MR 50.69. Calculated: MR 50.04.

Dehydrochlorination of Ethyl Ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinate (II, R=C_2H_5) with Triethylamine. A mixture of 45.8 g of (II, R=C_2H_5) and 150 ml of dry ether was prepared in a round-bottomed flask with a stirrer; the starting substance is insoluble in ether, but as triethylamine (17.2 g) was added the crystals dissolved. Triethylamine hydrochloride was filtered off, ether was removed at a residual pressure of 10-13 mm, and the residue was vacuum-distilled. After two distillations we isolated 5 g (12%) of (III); b. p. 69-70° (0.001 mm); n_D^{25} 1.4610; d_4^{25} 1.265. Found: P 13.75; 13.56%; MR 50.55. Calculated: P 13.30%; MR 50.04.

SUMMARY

1. By the reaction of ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinic esters with acetic anhydride in presence of a few drops of sulfuric acid (1-acetoxy-2,2,2-trichloroethyl)ethylphosphinic esters were obtained.

2. By the reaction of alkyl hydrogen ethylphosphonites with chloral ethyl(2,2,2-trichloro-1-hydroxyethyl)-phosphinic esters were obtained.

3. In the dehydrochlorination of ethyl(2,2,2-trichloro-1-hydroxyethyl)phosphinic esters rearrangement occurs with formation of alkyl 2,2-dichlorovinyl ethylphosphonates.

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