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Abstract

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On the Rearrangement of Methyldi-(diethylphosphon)-carbinol

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The American investigators Connel and Coover, having studied the reaction of acetophosphonic ester with diethylphosphorous acid in the presence of diethylamine, came to the conclusion that the product formed is methyldi-(diethylphosphon)-carbinol (I). In the IR spectrum of I, according to data in (^{1}), there was an absorption band of medium intensity corresponding to a hydroxyl group. In the IR spectrum of the product obtained in the reaction of isobutyrylphosphonic ester with diethylphosphorous acid, for which the structure of a diphosphoncarbinol was also assigned, the authors found only weak absorption bands of the hydroxyl group, which was explained by the presence of hydrogen bonding between the OH and P=O groups. Cade (^{2}), who studied analogous reactions between various ketophosphonic esters and dialkylphosphorous acids in the presence of sodium ethoxide, likewise considered that the products formed are diphosphoncarbinols.

In studying the reaction of vinyl acetate with diethylphosphorous acid, we isolated, along with the acetate of methyldiethylphosphoncarbinol (II), a high-boiling product which, according to our assumption and in accordance with the scheme given below, should be methyldi-(diethylphosphon)-carbinol (I) or its acetate (III). The data of elemental analysis of the high-boiling product corresponded to I, and its constants were identical with those reported for the carbinol by Connel and Coover and by Cade.

Fig. 1. IR absorption spectra of diethyl α-(diethylphosphonethyl) phosphate (IV)

Figure 1: Fig. 1. IR absorption spectra of diethyl α-(diethylphosphonethyl) phosphate (IV)

$$CH_2{=}CHOCOCH_3 + (C_2H_5O)_2POH \longrightarrow CH_3C(=O)P(OC_2H_5)_2 + CH_3CHO$$

$$CH_3C(=O)P(OC_2H_5)_2 \xrightarrow{(C_2H_5O)_2POH} CH_3C(OH)\,[P(=O)(OC_2H_5)_2]_2 \quad (I)$$

$$CH_3C(OH)\,[P(=O)(OC_2H_5)_2]_2 \xrightarrow{CH_2=CHOCOCH_3} CH_3C(OCOCH_3)\,[P(=O)(OC_2H_5)_2]_2 \quad (III)$$

$$CH_3CHO \xrightarrow{(C_2H_5O)_2POH} CH_3CH(OH)P(=O)(OC_2H_5)_2 \xrightarrow{CH_2=CHOCOCH_3} CH_3CH(OCOCH_3)P(=O)(OC_2H_5)_2$$

However, the properties of the product obtained did not correspond to structure I: in the IR spectrum there was no absorption characteristic of a hydroxyl group; a negative result was obtained in attempts to acetylate the product with acetyl chloride, ketene, and vinyl acetate. We repeated the experiments of the previous investigators. The products obtained in the reactions of acetophosphonic ester with diethylphosphorous acid in the presence of diethylamine and sodium ethoxide proved to be completely identical in constants to the high-boiling product from the reaction of diethylphosphorous acid with vinyl acetate.

Taking into consideration the data of a number of investigators (^{3}–^{5}) on the rearrangements of α-hydroxy-β-haloalkylphosphonic, α-hydroxy-α-cyanoalkylphosphonic, and α-hydroxy-α-acetoethylphosphonic esters into the corresponding phosphates, we assumed that in all the reactions described above, under the influence of temperature and catalysts, a rearrangement of methyldi-(di-

ethylphosphon)-carbinol (I) into diethyl α-(diethylphosphonethyl) phosphate (IV):

$$CH_3C(OH)[P(O)(OC_2H_5)_2]_2 \longrightarrow CH_3CH(OP(O)(OC_2H_5)_2)(P(O)(OC_2H_5)_2) \quad (IV)$$

The structure of IV was proved by us by means of transesterification reactions and counter-synthesis. On heating IV with ethyl alcohol in the presence

Fig. 1. I.R. absorption spectra of diethyl α-(diethylphosphonethyl) phosphate (IV):
1 –from the reaction of diethylphosphorous acid and acetophosphinic ester in the presence of diethylamine;

Fig. 2. IR absorption spectra: 1 — diethyl-α-(diethylphosphonoethyl)-phosphate (IV); 2 — methyldi-(diethylphosphon)-carbinol (I); 3 —(I) in CCl_4 solution, $C \approx 0.75$ wt.%, $d = 9.25$ mm

Figure 2: Fig. 2. IR absorption spectra: 1 —diethyl-α-(diethylphosphonoethyl)-phosphate (IV); 2 —methyldi-(diethylphosphon)-carbinol (I); 3 —(I) in CCl_4 solution, $C \approx 0.75$ wt.%, $d = 9.25$ mm

2 —from the counter-synthesis reaction;
3 —from the reaction of diethylphosphorous acid and acetophosphinic ester in the presence of sodium ethoxide;
4 —from the reaction of vinyl acetate and diethylphosphorous acid

of sodium ethoxide, triethyl phosphate was obtained. IV was synthesized from the acid chloride of the diethyl ester of phosphoric acid and the diethyl ester of α-hydroxyethylphosphinic acid:

$$(C_2H_5O)_2P(O)Cl + CH_3CH(OH)P(O)(OC_2H_5)_2 \longrightarrow CH_3CH(OP(O)(OC_2H_5)_2)(P(O)(OC_2H_5)_2)$$

The constants of the product of the counter-synthesis and its I.R. spectrum coincided with those for the products from the reactions of vinyl acetate and acetophosphinic ester with diethylphosphorous acid (Fig. 1 and Table 1).

It seemed of interest to determine the conditions under which the above-described rearrangement process I into IV takes place. For this purpose we decided to carry out the reaction of acetophosphinous ester with diethylphosphorous acid under mild conditions, in the presence of a small amount of diethylamine and at a temperature not exceeding 40-50°. Diethylamine and the unreacted starting materials were removed by gradual and cautious heating of the reaction mixture in vacuo. The process was stopped when the temperature had been brought to 110-120°. The product formed proved to be methyldi-(diethylphosphon)-carbinol. The constants of I and IV are presented in Table 1.

The data of elemental analysis and molecular refraction corresponded to I. In the IR spectrum of this compound there is an intense broad band in the region 3300–3250 cm^{-1}, which may be assigned to absorption of the associated hydroxyl group. When the IR spectrum was recorded in a solution of carbon tetrachloride, a narrow absorption band of medium intensity at 3570 cm^{-1} appeared, characteristic of a free hydroxyl group (Fig. 2).

Fig. 2. IR absorption spectra: 1 —diethyl-α-(diethylphosphonoethyl)-phosphate (IV); 2 —methyldi-(diethylphosphon)-carbinol (I); 3 —(I) in CCl_4 solution, $C \approx 0.75$ wt.%, $d = 9.25$ mm.

When I is heated in a sealed ampoule at 135–140° for several hours, its isomerization into IV occurs. In the presence of diethylamine the isomerization process is accelerated. The rate of isomerization was determined from the change in the refractive index of I. The experimental results are presented in Fig. 3. After the experiment had been completed, the IR spectrum of the product was recorded. It lacked the absorption band characteristic of the hydroxyl group that was present in I. Thus, we have shown that methyldi-(diethylphosphon)-carbinol, formed as the initial product in the interaction of diethylphosphorous acid with vinyl acetate or acetophosphinous ester, isomerizes in the course of the reactions, and especially during distillation, into diethyl-α-(diethylphosphonoethyl)-phosphate.

Experimental Part

Reaction of diethylphosphorous acid with diethyl ester of acetophosphinous acid

To a mixture of 4.1 g of diethylphosphorous acid and 5.4 g of diethyl ester of acetophosphinous acid, several drops of diethylamine were added. The reaction mixture was cooled with cold water and left to stand for several hours at room temperature. The unreacted starting substances were removed by heating the mixture in vacuo at a temperature not exceeding 120°. The methyldi-(diethylphosphon)-carbinol (I) obtained in this way, in an amount of 8 g, is a rather viscous, slightly yellow-colored liquid. n_D^{20} 1.4510, d_4^{20} 1.1870, MR_D 72.16, calculated 71.64.

Found, %: P 19.65; 19.69
$C_{10}H_{24}O_7P_2$. Calculated, %: P 19.49.

Table 1

Compound	Method of preparation	B.p. in °C, pressure in mm Hg	n_D^{20}	d_4^{20}
$CH_3C[P(OC_2H_5)_2]_2$ ‖ ‖HO O(I)	Reaction of diethylphosphorous acid with acetophosphinous ester in the presence of diethylamine at 40–50°	–	1.4510	1.1870
$CH_3CH\,(OP(O)(OC_2H_5)_2)\,(P(O)(OC_2H_5)_2)$(IV)	Isomerization of methyldi-(diethylphosphon)-carbinol (I)	151–152 at 1 mm	1.4310	1.1542*
$CH_3CH\,(OP(O)(OC_2H_5)_2)\,(P(O)(OC_2H_5)_2)$(IV)	Reaction of diethylphosphorous acid with acetophosphinous ester in the presence of sodium ethylate	149–150 at 1 mm	1.4308	1.1535**
$CH_3CH\,(OP(O)(OC_2H_5)_2)\,(P(O)(OC_2H_5)_2)$(IV)	Reaction of diethylphosphorous acid with vinyl acetate	152–153 at 1 mm	1.4310	1.1538

Compound	Method of preparation	B.p. in °C, pressure in mm Hg	n_D^{20}	d_4^{20}
$CH_3CH(OP(O)(OC_2H_5)_2)(P(O)(OC_2H_5)_2)$ (IV)	Reaction of diethyl phosphorochloridate with α-oxyethylphosphinous ester	152-153 at 1.5 mm	1.4307	1.1540

* Data of McConnell and Coover. B.p. 140-150° at 0.7 mm, n_D^{20} 1.4311 (^{1}).

** Data of Cade. B.p. 125° at 0.06 mm, n_D^{20} 1.4350, d_4^{20} 1.1540 (^{2}).

Isomerization of methyldi-(diethylphosphon)-carbinol. 8 g of methyldi-(diethylphosphon)-carbinol were heated in a sealed ampoule at 135-140° for 5 h. As a result of distillation of the reaction mixture, 6.8 g of diethyl α-(diethylphosphonoethyl) phosphate were obtained. B.p. 151-152° at 1 mm, n_D^{20} 1.4310, d_4^{20} 1.1542, MR_D 71.30, calcd. 71.23.

Found, %: P 19.39; 19.26
$C_{10}H_{24}O_7P_2$. Calculated, %: P 19.49.

Fig. 3. Rate of isomerization of methyldi-(diethylphosphon)-carbinol (I) into diethyl α-(diethylphosphonoethyl) phosphate (IV): 1 –at 135-137° in the presence of diethylamine; 2 –at 140-145°; 3 –at 135-137°.

Reaction of diethyl α-oxyethylphosphinous ester with diethyl phosphorochloridate. To a mixture of 17 g of diethyl α-oxyethylphosphinous acid ester, 10 g of triethylamine, and 200 ml of dry ether, with stirring, 17 g of diethyl phosphorochloridate were added. The mixture was heated for three hours on a water bath. 7 g of diethyl α-(diethylphosphonoethyl) phosphate were obtained. B.p. 152-153° at 1.5 mm. n_D^{20} 1.4307, d_4^{20} 1.1540, MR_D 71.33, calcd. 71.23.

Found, %: P 19.50; 19.70
$P_{10}H_{24}O_7P_2$. Calculated, %: P 19.49.

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Note: Figure translations are in progress. See original paper for figures.