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Abstract

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ON THE INTERACTION OF SODIUM DIETHYLPHOSPHITE WITH 1,2-DIBROMOCYCLOHEXANE AND 1,2-DIBROMOETHANE*

The literature contains data indicating that the reaction of sodium diethylphosphite with 1,2-dibromo derivatives leads to removal of bromine and formation of unsaturated compounds. Thus, Nilen (1) described the formation of ethylene under the action of sodium diethylphosphite on dibromoethane. One of us, jointly with B. P. Lugovkin (2), described the preparation of styrene from dibromostyrene; together with N. P. Bogonosova, the preparation of tetramethylethylene from the corresponding dibromide (3), and of phenanthrene from dibromophenanthrene (4). The composition of the phosphorus-containing products in these reactions was not studied in detail. The presence of diethylphosphorous acid and of a subphosphoric ester was indicated (2). It seemed of interest to us to determine what phosphorus derivatives are formed in the interaction of sodium diethylphosphite with 1,2-dibromo derivatives. As an example, 1,2-dibromocyclohexane was taken. The reaction proceeds with formation of cyclohexene and phosphorus-containing products. Distillation of the latter made it possible to isolate the following compounds:

1. Diethylphosphorous acid (b.p. 69° (11 mm); n_D^{20} 1.4110; d_0^{20} 1.0873).
2. A fraction with b.p. 61-61.5° (2.5 mm); n_D^{20} 1.4850; d_0^{20} 1.4669, which proved to be a mixture of dibromocyclohexane (60%) with triethyl phosphate (40%).
3. Tetraethyl pyrophosphite (b.p. 75.5-76° (2 mm); n_D^{20} 1.4350; d_0^{20} 1.0566). A mixed sample with a complex with CuI, prepared from tetraethyl pyrophosphite**, gave no depression.
4. Tetraethyl ester of subphosphoric acid (b.p. 109-112° (3 mm), n_D^{20} 1.4310; d_0^{20} 1.1225); according to its IR spectrum (Fig. 1,b) it is identical with the analogous ester obtained by the action of bromine on sodium diethylphosphite (5).
5. A fraction with b.p. 131-134° (2 mm) (see Table 1). The latter fraction might have been tetraethyl pyrophosphate. However, its constants differed somewhat from those of pyrophosphate.

Thus, the organophosphorus compounds obtained in the interaction of dibromocyclohexane with sodium diethylphosphite proved to be the same as in the case of the interaction of sodium diethylphosphite with bromine (^{5}).

The IR spectrum of fraction 5*** (Fig. 2,a) resembles the IR spectrum of tetraethyl pyrophosphate (^{6}), prepared according to Toy (^{7}). However, in the region of $\nu(P = O)$ the spectra differ. In the spectrum of fraction 5 there is an intense broad band $\nu(P = O)$ at 1260 with a shoulder at 1300 cm^{-1}, whereas in pyrophosphate the band at 1300 cm^{-1} is symmetrical. It may be assumed that fraction 5 is a mixture containing pyrophosphate.

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* In connection with the appearance of a short communication by Ya. Mikhalskii (^{12}) on the preparation of an isomer of a subphosphoric ester with a P—P bond, we consider it necessary to publish the results of some of our investigations, in which the formation of an isomer of a subphosphoric ester with a P—P bond was also established.

** Obtained by the action of the acid chloride of diethylphosphorous acid on sodium diethylphosphite.

*** Owing to the small quantities, the Raman spectrum was not recorded.

Table 1

$(C_2H_5O)_2PONa + A$

A	B.p., °C	P, mm	d_0^{20}	n_D^{20}	Found P, %
1,2-dibromocyclohexane	131—133	2	1.1603	1.4360	22.22; 22.20
$BrCH_2CH_2Br$	141—142	3	1.1665	1.4288	22.08; 22.28
Br_2	1st fr. 135—136	2	1.1747	1.4283	22.21; 22.60
Br_2	2nd fr. 138—140	3	1.1811	1.4295	22.51; 22.53
$(C_2H_5O)_2P(O)Cl$	1st fr. 102—103	$8 \cdot 10^{-2}$	1.1656	1.4350	23.02; 23.01
$(C_2H_5O)_2P(O)Cl$	2nd fr. 141—141.5	3	1.1727	1.4333	—
SO_2Cl_2	103—103.5	$4 \cdot 10^{-2}$	1.1920	1.4275	21.39; 21.39; 21.47

The second substance could have been the isomerization product of the subphosphoric ester

$$(C_2H_5O)_2P(=O)-O-P(=O)(OC_2H_5)(C_2H_5) \quad (I),$$

which, in boiling point, is close to pyrophosphate (^{5}). However, the IR spectrum of I (Fig. 2,b) has, in the region of $\nu(P=O)$, a band at 1298 cm^{-1} with a shoulder at 1275 cm^{-1}, and thus the band at 1260 cm^{-1} in the spectrum of fraction 5 cannot belong to isomer I.

We repeated Nylén' s experiments (^{1}) and investigated the phosphorus-containing reaction products in greater detail.

The following products were isolated: 1) ethylene, 2) unreacted dibromoethane, 3) diethylphosphorous acid (b.p. 39.5–40° (1 mm); n_D^{20} 1.4080; d_0^{20} 1.0728); 4) triethyl phosphate (b.p. 60–61° (1 mm); n_D^{20} 1.4075; d_0^{20} 1.0697); 5) tetraethyl pyrophosphite (b.p. 71–72° (1 mm); n_D^{20} 1.4310; d_0^{20} 1.0576; compound with CuJ, m.p. 117–118°); 6) tetraethyl ester of subphosphoric acid (b.p. 104–105° (2 mm); n_D^{20} 1.4270; d_0^{20} 1.1243); 7) a fraction with b.p. 141–142° (3 mm), close in constants (see Table 1) and IR spectrum to fraction 5 in the experiment with dibromocyclohexane (Fig. 2a); 8) ethyl ester of diphosphonethane (b.p. 159–160° (2 mm); n_D^{20} 1.4410; d_0^{20} 1.1353). The formation of small amounts of diphosphonethane ester has also been reported by other investigators (^{8}).

The IR spectrum of fraction 7 in the region of $\nu(P=O)$ had a band with maxima at 1260 and 1297 cm^{-1} of equal intensity.

As can be seen, in the reaction of sodium diethyl phosphite with dibromoethane, the same phosphorus-containing products are formed as in the reaction of sodium diethyl phosphite with bromine (^{5}).

To determine the homogeneity of the pyrophosphate fraction in the reaction of sodium diethyl phosphite with bromine, we repeated this experiment under the conditions described in (^{5}), but in an atmosphere of nitrogen, and obtained entirely analogous results.

The high-boiling fractions corresponding to tetraethyl pyrophosphate were separated into two fractions with boiling points: 1) 135–136° (2 mm) and 2) 138–140° (3 mm) (see Table 1).

According to the IR spectrum, the isolated fractions are not pure pyrophosphate. In the region of $\nu(P'=O)$, in addition to the band at 1300 cm^{-1}, there is absorption at 1260 cm^{-1} in the form of a shoulder, the intensity of which in the spectrum of fraction 2 is somewhat lower.

The second component of the pyrophosphate fraction could have been an isomer of the subphosphoric ester with a P—P bond,

$$(C_2H_5O)_2P(=O)-P(=O)(OC_2H_5)_2 \quad (II),$$

Fig. 1. IR absorption spectra: a—tetraethyl pyrophosphite; b—tetraethyl ester of hypophosphorous acid

Figure 1: Fig. 1. IR absorption spectra: a—tetraethyl pyrophosphite; b—tetraethyl ester of hypophosphorous acid

Fig. 2. IR absorption spectra: a—fraction with b.p. 131-134° (2 mm) from the experiment with dibromocyclohexane; b—isomerization product of the tetraethyl ester of hypophosphorous acid

Figure 2: Fig. 2. IR absorption spectra: a—fraction with b.p. 131-134° (2 mm) from the experiment with dibromocyclohexane; b—isomerization product of the tetraethyl ester of hypophosphorous acid

obtained

By Baudler' s method (^{9}), by the action of diazoethane on hypophosphorous acid, or in a mixture with pyrophosphate by the action of sodium on the acid chloride of diethylphosphorous acid. According to Baudler (^{9}), for isomer (II) with a P—P bond, the characteristic lines in the IR spectrum are 245 (P—P) and 1256 cm^{-1} (P=O).

Fig. 1. IR absorption spectra: *a*—tetraethyl pyrophosphite; *b*—tetraethyl ester of hypophosphorous acid

Fig. 2. IR absorption spectra: *a*—fraction with b.p. 131-134° (2 mm) from the experiment with dibromocyclohexane; *b*—isomerization product of the tetraethyl ester of hypophosphorous acid

We repeated Baudler' s experiment on the action of sodium on the acid chloride of diethylphosphorous acid and obtained two fractions: fraction 1, 109-110° ($3 \cdot 10^{-2}$ mm); n_D^{20} 1.4275; d_0^{20} 1.1720 (P 22.77; 22.71%); fraction 2, 110-114° ($3 \cdot 10^{-2}$ mm); n_D^{20} 1.4255; d_0^{20} 1.1771.

The IR and Raman spectra, the constants, and the analytical data of fraction 1 and fraction I, isolated in the experiment involving the action of bromine on diethyl phosphite sodium salt, proved to be identical. The Raman spectra contain the lines P—P 246 (2) and P=O 1260 (2) cm^{-1} of isomer (II), and lines indicating the presence of pyrophosphate (236 (1), 280 (1), 695 (3), 817 (3), 1290 (4) cm^{-1}, etc.). The IR spectra in the region $\nu(\mathrm{P}=\mathrm{O})$ have a band at 1300 cm^{-1}, corresponding to pyrophosphate (^{6}), and a shoulder at 1260 cm^{-1}, coinciding in frequency with the $\nu(\mathrm{P}=\mathrm{O})$ line in the Raman spectrum of isomer II (^{9}).

Fig. 3. Separation of a mixture with b.p. 141-142° (3 mm) on Al_2O_3, solvent —ether-methanol (50:1 by volume).

Thus, the second component of the tetraethyl pyrophosphate fraction from the reactions of dibromocyclohexane, dibromoethane, and bromine with diethyl

Fig. 3. Separation of a mixture with b.p. 141-142° (3 mm) on Al_2O_3, solvent—ether-methanol (50:1 by volume)

Figure 3: Fig. 3. Separation of a mixture with b.p. 141-142° (3 mm) on Al_2O_3, solvent—ether-methanol (50:1 by volume)

phosphite sodium salt is a substance to which Baudler assigns the structure of isomeric subphosphoric ester II with a P—P bond. They cannot be separated by distillation because of the closeness of their boiling points. The components can be qualitatively separated by thin-layer chromatography on aluminum oxide (Fig. 3).

In order to obtain isomer II in pure form, we repeated the experiment of J. Michalski on the action of sulfuryl chloride on diethyl phosphite sodium salt ([10]), where, as J. Michalski believes, pure isomer II is obtained. On repeating the experiment, contrary to J. Michalski, we obtained pyrophosphate. Isomer II was not formed in the reaction. In addition to analytical data (see Table 1), the pyrophosphate was identified by IR and Raman spectra. In the Raman spectrum there are no lines at 245 (P—P) and 1256 (P=O), 775 and 1018 cm^{-1}, characteristic of isomer II, and all the lines of pyrophosphate are present ([11]). The IR spectrum of the product fully coincides with the IR spectrum of pyrophosphate ([6]) and has no absorption at 1260 cm^{-1}.

On repeating J. Michalski' s experiment ([12]) on the action of diethyl phosphite sodium salt on diethyl phosphorochloridate, two fractions were isolated (see Table 1). The IR spectrum of fraction 1 fully coincided with the spectrum of the product obtained with dibromocyclohexane (Fig. 2,a). Its Raman spectrum contains the pyrophosphate lines only with zero intensity and coincides with the Raman spectrum given by Baudler for isomer II ([9]).

Thus, with the exception of the reaction of diethyl phosphite sodium salt with sulfuryl chloride, where, according to our data, tetraethyl pyrophosphate is formed, in all other cases the pyrophosphate fractions represented mixtures of tetraethyl pyrophosphate with the isomer of tetraethyl subphosphoric ester to which a structure with a P—P bond (II) is assigned.

A comparison of the constants of the pyrophosphate fractions obtained in different reactions is given in Table 1.

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