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Fig. 1

Figure 1: Fig. 1

Abstract

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REACTION OF PHOSPHONITRILE CHLORIDE TRIMER WITH AROMATIC DIHYDROXY COMPOUNDS

(Presented by Academician I. V. Tananaev, 27 IV 1964)

It is known that the trimer of phosphonitrile chloride (^{1}) reacts with dihydric phenols with liberation of HCl and formation of polymeric products in high-boiling polar solvents at temperatures above 190°, or in ordinary organic solvents in the presence of pyridine or quinoline.

The present investigation was undertaken in order to study certain regularities of the reaction of the phosphonitrile chloride trimer with resorcinol and hydroquinone in a molar ratio of 1:1. In the interaction of the indicated compounds in the presence of theoretical amounts of pyridine (quinoline) in *m*-xylene or nitrobenzene, the amount of evolved HCl was determined by nonaqueous potentiometric titration of tertiary amines in samples of the reaction mixture, carried out with 0.005-0.01 N HCl solution in chloroform. The reaction in nitrobenzene at temperatures above 200° was carried out in a stream of nitrogen, and the hydrogen chloride was absorbed by 0.1 N alkali solution.

Fig. 1. Degree of completion of the reaction of phosphonitrile chloride trimer with resorcinol (*1-3*) and hydroquinone (*5-7*) and of the reaction of monophenoxytriphosphonitrile pentachloride with hydroquinone (*4*). Solvents—nitrobenzene (*1-3*) and *m*-xylene (*4-7*); catalysts—pyridine (*1, 4, 5*) and quinoline (*2, 3, 6, 7*); reaction temperatures 110° (*1, 3, 5, 7*) and 130° (*2, 6*); trimer concentration PhNX—0.3 M/l.

The nature of the solvent and of the tertiary amine, as well as the temperature of the process, have a considerable influence on the degree of completion of the reaction (Fig. 1).

The reaction products obtained in nitrobenzene are a mixture of low-molecular polymer homologs (Table 1), soluble in most organic solvents; on the basis of their composition and IR spectra (Fig. 2, *1*), it may be concluded that they are built up of alternating trimeric phosphonitrile rings and oxyaromatic radicals. The reaction in *m*-xylene in the presence of pyridine and quinoline leads to the formation of two fractions of the final product—soluble and insoluble. From a comparison of their composition and IR spectra (Fig. 2, *2, 3*) it follows that the insoluble fraction is the product of substitution of more than 2 chlorine atoms in the trimeric rings by oxyaromatic radicals, whereas the soluble fraction is a low-molecular substance with a predominant content of phosphonitrile rings; its yield does not exceed 25%, and in this case it is usually possible to isolate up to 20% of unreacted···

Table 1

Yield and composition of the products of the reaction of phosphonitrile chloride trimer with resorcinol and hydroquinone without catalyst at 200° (Nos. 6, 7), in the presence of pyridine at 110° (Nos. 1, 4, 5) and quinoline at 130° (Nos. 2, 3). Solvents: *m*-xylene (1-3) and nitrobenzene (4-7); concentration of phosphonitrile chloride trimer (mol/l): 0.3 (Nos. 1-5), 0.55 (No. 6), and 0.93 (No. 7)

Nos. of experiment	Dioxy compound	Yield	P	C	Cl	mol. wt.
1	Resorcinol	9.1[1]	21.80	17.18	43.97	805
1	Resorcinol	74.0[2]	18.45	23.13	15.21	–
2	Hydroquinone	23.8[1]	22.90	18.26	40.44	831
2	Hydroquinone	60.15[2]	12.90	47.57	6.14	–
3	Insoluble product (experiment No. 2)[3]	–	17.85	36.11	24.69	–
4	Resorcinol	95.0	20.11	22.13	35.97	644
5	Hydroquinone	93.8	20.25	18.01	38.68	793
6	Resorcinol	94.2	22.00	20.45	38.24	685
7	Hydroquinone	92.9	21.8	22.51	36.66	758

[1] Soluble fraction. [2] Insoluble fraction. [3] Interaction with an equal amount by weight of phosphonitrile chloride trimer.

of the reacting phosphonitrile chloride trimer. The disturbance of the equimolecularity of the reacting substances is apparently due to the fact that, under these conditions, replacement of the first chlorine atom in the trimeric phosphonitrile ring by an oxyaromatic radical increases the mobility of the remaining ones, as

Fig. 2

Figure 2: Fig. 2

a result of which they react primarily with the hydroxyl groups of dihydric phenols. After exhaustion of the dioxy compound and formation of intermediate products containing phenolic OH groups with a considerable degree of substitution, these products interact with unreacted trimer or with the soluble fraction (experiment No. 3, Table 1). The increase in the mobility of the chlorine atoms in monoaryloxy-substituted trimeric rings is confirmed by the fact that the interaction of hydroquinone with monophenoxytriphosphonitrile pentachloride (m.p. 40-41°) proceeds at a higher rate (curve 4, Fig. 1) than with PNC trimer under the same conditions; in this case the product formed in predominant yield is one in which not more than two chlorine atoms in monophenoxytriphosphonitrile pentachloride have been substituted.

In nitrobenzene medium this effect of the substituent on the mobility of the remaining chlorine atoms is evidently masked by a stronger polarization effect of the P—Cl bond, which leads to the formation of comparatively homogeneous products.

Fig. 2. IR transmission spectra of the reaction products (Table 1). 1 —No. 6, 2 —No. 1[1], 3 —No. 2[2]. The spectra were recorded from a film of the substance on KBr. Characteristic absorption bands (5): 500-600 cm^{-1} (P—Cl), 980-1020 and 1130-1170 cm^{-1} (P—O—C-aryl); 1210-1250 cm^{-1} (P=N bond of the substituted trimeric ring) and 3400-3600 cm^{-1} (phenolic OH groups).

A kinetic study of the interaction of phosphonitrile chloride trimer with resorcinol and hydroquinone in nitrobenzene medium under various conditions (Table 2) was carried out up to 50% completion of the reaction, when interaction of the initial substances takes place predominantly. In the presence of pyridi-

in the presence of quinoline the process proceeds as a second-order reaction (a linear dependence of the reciprocal concentration of the PNC trimer on the duration of the process); in the absence of a catalyst the order of the reaction was determined from the time of its half-completion (2).

Table 2

Results of a kinetic study of the reaction of phosphonitrile chloride trimer with resorcinol and hydroquinone in nitrobenzene in the presence of quinoline (Nos. 1, 2) and without catalyst (Nos. 3, 4)

No.	Dioxy compound	Reaction temperature, °C	Reaction order	K_{av}, mol · s	Activation energy, cal/mol
1	Resorcinol	110	2	5.98	6,050
1	Resorcinol	130	2	9.32	6,050

No.	Dioxy compound	Reaction temperature, °C	Reaction order	K_{av}, mol · s	Activation energy, cal/mol
1	Resorcinol	200	2	26.22	6,050
2	Hydroquinone	110	2	2.14	10,450
2	Hydroquinone	130	2	4.97	10,450
2	Hydroquinone	200	2	30.50	10,450
3	Resorcinol	200	1.55	–	–
4	Hydroquinone	209	1.30	–	–

The fractional order in this case indicates that the nucleophilic substitution of the first chlorine atom in phosphonitrile chloride trimer proceeds by a mechanism intermediate between S_N1 and S_N2. Under these conditions the monomolecular mechanism is associated with heterolysis of the P—Cl bond in the phosphonitrile chloride trimer and formation of a phosphonitronium ion. The possibility of this process is confirmed by studies of the thermal polymerization of phosphonitrile chloride trimer (^{3}) and by investigation of the electrical conductivity of its solutions (^{4}).

In view of the low molecular weight of the reaction products obtained in nitrobenzene medium, and the possible formation of a large number of isomeric compounds, we used liquid adsorption chromatography for their separation. Freshly prepared products (experiments Nos. 4–7, Table 1) were subjected to chromatographic separation. Silica gel of grades 2K and KSK was used as the adsorbent, introduced into the column by the wet method. The fractions were eluted with mixtures of petroleum ether and benzene, with benzene, and with mixtures of benzene and acetone of various compositions and, after removal of the solvents in vacuo, were analyzed. The number of fractions ranged from 15 to 30; most of them were viscous liquids or low-melting solids. It was found that the molecular weight of the eluates increased as the polarity of the solvents increased. The coincidence of the elemental composition and molecular weights of the fractions with those calculated for the structures shown in Table 3 makes it possible to assign to a given fraction the corresponding empirical formula.

Table 3

Results of chromatographic separation of the reaction products of phosphonitrile chloride trimer with resorcinol and hydroquinone

No.	Structures	Content of structures in the reaction products (Nos. 4–7 of Table 1), % –No. 4	Content of structures in the reaction products (Nos. 4–7 of Table 1), % –No. 5	Content of structures in the reaction products (Nos. 4–7 of Table 1), % –No. 6	Content of structures in the reaction products (Nos. 4–7 of Table 1), % –No. 7
1	–	0	0	8	10
2	– –	31	30	43	7
3	– – –	36	41	25	52
4	– – – – –	0	4	9	10
5	– – – – –	13	0	0	4
6	– – – – –	7	3	0	0
7	– – – – –	2	10	0	0

Note. –residue of the trimeric phosphonitrile ring; ––residue of the dioxy compound. The structures are given without taking into account possible geometrical isomers.

Between the principal fractions, fractions of intermediate composition and molecular weight were isolated,

which contain a mixture of two substances of different structure: the content of the first in the initial mixture is coming to an end, while the second is only beginning to be eluted.

As follows from the data of Table 3, the products of the interaction of phosphonitrile chloride trimer with resorcinol or hydroquinone contain predominantly dimeric (two phosphonitrile rings) structures (Nos. 1-3). After isolation of the dimeric compounds, tetrameric compounds and substances of more complex structure are eluted in small amounts. It should be noted that we were unable to isolate fractions containing appreciable amounts of trimeric or pentameric compounds.

Upon repeated chromatography of the first fraction of product No. 6 (Table 3), a previously undescribed compound was isolated: 1,3-bis-(pentachlorotriphosphonitriloxy)benzene–a white crystalline substance with m.p. 71-72°, of the following composition:

Found, %: C 10.01; H 0.59; Cl 48.10; P 25.29; N 11.55
Calculated, %: C 9.83; H 0.55; Cl 48.50; P 25.40; N 11.47

By repeated chromatography of the remaining fractions of this product, it has so far not been possible to isolate other individual compounds, owing to the large number of possible isomeric forms for structures Nos. 2–7 of Table 3.

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