CHEMISTRY

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1960

SovietRxiv

Abstract

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CHEMISTRY

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RADIATION METHOD FOR THE SYNTHESIS OF CERTAIN DERIVATIVES OF PHOSPHONITRILE CHLORIDE

Among inorganic polymeric compounds possessing plastic properties, phosphonitrile chloride $(PNCl_2)_n$ ($^{1-8}$) is of greatest interest. However, the practical application of this relatively heat-resistant polymer is hindered by its rather easy hydrolyzability. The introduction of certain organic substituents (for example, alkoxy radicals) into the phosphonitrile chloride molecule leads to a considerable increase in its stability with respect to hydrolysis (^{9,10}). But to obtain such derivatives, prolonged heating of a mixture of reagents is usually necessary. At the same time their yields, as a rule, are low. For example (^{9}), *n*-butyl phosphonitrile ether $[PN(OC_4H_9)_2]_x$ is formed only after heating at 117° for 13 hours a mixture of phosphonitrile chloride, *n*-butyl alcohol, and sodium or potassium butylate.*

At present, the action of penetrating radiation is finding ever wider use in the synthesis of organic compounds (^{11}) and in the preparation of inorganic products (^{12}). We investigated the possibility of synthesizing butyl phosphonitrile ether by irradiating, with a high-energy electron beam, a mixture of phosphonitrile chloride tetramer and *n*-butyl alcohol at room temperature.

The tri- and tetramer of phosphonitrile chloride were synthesized by the procedure of (^{13}). Butyl alcohol was purified beforehand and absolutized. The radiation source was a 1.0–1.2 MeV electron accelerator consisting of a vertical sectioned tube for direct acceleration and a cascade valve-capacitor voltage multiplier (^{14}). The solutions were irradiated in glass cells with a thin glass membrane. The dose-rate value was monitored by measuring the electron current in the solution, which was carried out with the aid of a molybdenum probe sealed into the cell. In experiments with *n*-butyl alcohol, for cooling the solution and uniformly stirring it, air saturated with vapors of *n*-butanol was passed through the cell. The course of the reaction was monitored by the change in the viscosity of the solution with the aid of an Ostwald viscometer, and also by determining the chlorine content in the compounds formed. It was established that, under the action of a stream of fast electrons on solutions of phosphonitrile chloride tetramer in *n*-butyl alcohol, substitution of both chlorine atoms in the phosphonitrile chloride molecule by butoxy radicals occurs.

Below is a description of one of the typical experiments for isolating butyl phosphonitrile ether. Eighty ml of a 5% solution of phosphonitrile chloride tetramer in absolute *n*-butyl alcohol was irradiated for 6 hours with electrons of energy 0.6 MeV at a current strength in the solution of $3\,\mu$A. The integral dose was $1.5 \cdot 10^{22}$ eV/ml. During irradiation, air was passed through the solution. In the course of the experiment the temperature did not exceed 30°. After irradiation, the *n*-butanol was distilled off in vacuo with heating—on a water bath. A viscous brown liquid with an unpleasant odor was found in the residue. Its analysis corresponded to the phosphonitrile ester of *n*-butyl alcohol:

$[PN(OC_4H_9)_2]_x$.	Found, %:	C 50.10; H 9.04
	Calculated, %:	C 50.26; H 9.42

The yield of the product was 45%, i.e., almost twice as high as by the method of (9).

Table 1

Change in viscosity and chlorine content in a 5% solution of tetrameric phosphonitrile chloride in *n*-butanol as a function of the integral electron-irradiation dose (0.6 MeV)

Irradiation time, min	Integral irradiation dose, eV/ml	Solution viscosity, centipoises	Chlorine content,* %	Irradiation time, min	Integral irradiation dose, eV/ml	Solution viscosity, centipoises	Chlorine content,* %
0	0	3.243	100	10	$8.0 \cdot 10^{20}$	3.274	22.8
2	$1.6 \cdot 10^{20}$	3.126	24.7	12	$9.6 \cdot 10^{20}$	3.232	16.2
4	$3.2 \cdot 10^{20}$	3.329	23.2	14	$1.1 \cdot 10^{21}$	3.357	14.5
6	$4.8 \cdot 10^{20}$	3.417	27.8	20	$1.6 \cdot 10^{21}$	3.362	13.8
8	$6.4 \cdot 10^{20}$	3.550	29.2				

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* The author of ([9]) does not give the yield of the reaction product. We reproduced the procedure described by him. It turned out that the yield is only 28%.

Fig. 1. Change in viscosity of a 5% solution of tetrameric phosphonitrile chloride in *n*-butyl alcohol as a function of the integral irradiation dose

Figure 1: Fig. 1. Change in viscosity of a 5% solution of tetrameric phosphonitrile chloride in *n*-butyl alcohol as a function of the integral irradiation dose

* In the unirradiated solution, the chlorine content was taken as equal to 100%.

Table 1 gives the results of measuring the viscosity of irradiated 5% solutions of the tetramer in *n*-butyl alcohol and of determining the chlorine content in the products obtained. Mean values of 2–4 measurements are given. The error in determining the viscosity did not exceed 1%.

Figure 1 shows the characteristic change in viscosity of a 5% butanolic solution of the tetramer as a function of the integral irradiation dose. It may be concluded that the process of radiolytic interaction of phosphonitrile chloride with *n*-butyl alcohol is complex in character. The sharp decrease in chlorine content and the decrease in viscosity at the initial moment of irradiation are apparently due to the occurrence of a chain substitution reaction. In this case, the dissolved substance is probably acted upon chiefly by hydrogen atoms arising during radiolysis of *n*-butyl alcohol (for example, according to the scheme $CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CHOH + H$). As a result of interaction with atomic hydrogen, the tetramer ring is cleaved, radicals of the monomer and dimer are formed, and chlorine atoms are eliminated in the form of HCl

Fig. 1. Change in viscosity of a 5% solution of tetrameric phosphonitrile chloride in *n*-butyl alcohol as a function of the integral irradiation dose

$$4H + (PNCl_2)_4 \rightarrow 2(PNCl)_2 + 4HCl \tag{1}$$

or

$$4H + (PNCl_2)_4 \rightarrow 4PNCl + 4HCl, \tag{1a}$$

$$H + PNCl \rightarrow PN + HCl, \tag{2}$$

$$PNCl + C_4H_9OH \rightarrow PN(OC_4H_9)_2 + HCl, \tag{3}$$

$$PNOC_4H_9 + C_4H_9OH \rightarrow PN(OC_4H_9)_2 + H, \tag{4}$$

$$PN + 2C_4H_9OH \rightarrow PN(OC_4H_9)_2 + 2H. \tag{5}$$

The hydrogen atoms obtained by reactions (4) and (5) again react with the tetramer, etc.

However, upon further irradiation, owing to the high concentration of the hydrogen chloride being formed, along with cyclization the reverse reaction between HCl and the butoxy derivatives is also possible. This is indicated by the results of chlorine analyses (Table 1). Therefore a maximum appears on the curve in Fig. 1. The second minimum, apparently, is due to suppression of the reverse reaction. The increase in the viscosity of the solution at high values of the integral irradiation dose is probably explained by cyclization of the butoxy-substituted compound with subsequent formation of polymeric chain molecules.

The radiation method for obtaining butyl phosphonitrilic ether has a number of advantages in comparison with the usual methods of its synthesis: higher yield, ease of isolation from the reaction mixture, and a low reaction temperature.

The influence of ionizing radiation on a 2% solution of the phosphonitrile chloride trimer in absolute dioxane was also studied. Upon irradiation with electrons of energy 0.8 MeV, the viscosity of the dioxane solution at first increased considerably; then the formation of a white flocculent precipitate was observed. Prolonged standing (for 3 months) of the initial solution also led to an analogous result. After removal of dioxane by distillation in vacuo, the residue was analyzed (Table 2).

Table 2

Analysis of compounds obtained from the dioxane solution of the phosphonitrile chloride trimer

Experiment No.	Concentration of trimer in dioxane, %	Experimental conditions: integral irradiation dose, eV/ml	Experimental conditions: reaction duration	Results of analyses, %: C	Results of analyses, %: H
1	3	–	3 months	26.71	4.52
2	2	$1.6 \cdot 10^{22}$	2 h	26.82	4.34
Calculated for $(PNClC_4H_8O_2)_x$	Calculated for $(PNClC_4H_8O_2)_x$	Calculated for $(PNClC_4H_8O_2)_x$	Calculated for $(PNClC_4H_8O_2)_x$	28.48	4.75

According to the analyses, the substance formed in dioxane has the composition $(PNClC_4H_8O_2)_x$, i.e., it is the product of substitution of one chlorine atom of phosphonitrile chloride by a dioxane molecule. This compound is characterized by considerable resistance to hydrolysis: it does not decompose even on boiling with alcoholic alkali. The structure of the compound obtained is subject to further study.

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Received
16 I 1960

CITED LITERATURE

1. H. N. Stokes, *J. Am. Chem. Soc.*, **17**, 276 (1895); **18**, 629, 780 (1896); **19**, 782 (1897).
2. P. Reynaud, *C. R.*, **194**, 2054 (1932).
3. O. Schmitz-Du Mont, H. Kükens, *Zs. anorg. u. allgem. Chem.*, **238**, 189 (1938).
4. O. Schmitz-Du Mont, A. Braschos, *Zs. anorg. u. allgem. Chem.*, **243**, 113 (1939).
5. K. H. Meyer, W. Lotmar, G. W. Pankow, *Helv. chim. Acta*, **19**, 930 (1936).
6. L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).
7. C. J. Brown, *J. Polym. Sci.*, **5**, 465 (1950).
8. F. Patat, *Angew. Chem.*, **65**, 173 (1953).
9. D. Lipkin, Pat. USA 2192921, 1940.
10. T. Goldschmidt, B. Dischon, *J. Polym. Sci.*, **3**, 481 (1948).
11. L. V. Abramova, N. I. Shevardina, K. A. Kocheshkov, *DAN*, **123**, 681 (1958).
12. A. A. Balandin, V. I. Spitsyn, L. I. Barsova, V. I. Duzhenkov, *ZhFKh*, **33**, 736 (1959).
13. R. Schenk, G. Römer, *Ber.*, **57**, 1343 (1924).
14. P. Ya. Glazunov, G. B. Radzievskii, Collection "The Effect of Ionizing Radiations on Inorganic and Organic Systems," Publishing House of the USSR Academy of Sciences, 1958, p. 395.

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