PERFLUORODIISOCYANATES

I. L. Knunyants, M. P. Krasuskaya, and D. P. Del'tsova

UDC 542.91 + 541.452 + 546.16

By the reaction of the hydrazides of perfluorodicarboxylic acids that we have described previously [1] with nitrous acid and the interaction of the dichlorides of the perfluorodicarboxylic acids with sodium azide, with the subsequent Curtius rearrangement of the azides formed we have synthesized perfluoropolymethylene diisocyanates of the general formula $OCN(CF_2)_nNCO$, where n = 3, 4, 8

$$\left.\begin{matrix} H_2NHNCO(CF_2)_nCONHNH_2 \xrightarrow{HNO_2} \\ ClCO(CF_2)_nCOCl \xrightarrow[NaN_3]{} \end{matrix}\right\} \rightarrow [N_3CO(CF_2)_nCON_3] \xrightarrow[-N_2]{\Delta} O{=}C{=}N(CF_2)_nN{=}C{=}O$$

The known perfluoroalkyl monoisocyanates R_fNCO have been obtained, mainly, by the reactions of acid chlorides with sodium azide and subsequent rearrangement [2, 3]. The perfluoropolymethylene diisocyanates are colorless liquids with a sharp smell that are sensitive to atmospheric moisture; they react vigorously with alcohols, giving the corresponding perfluoropolymethylene diurethanes

$$OCN(CF_2)_nNCO \xrightarrow[0-5^\circ]{ROH} ROCONH(CF_2)_nNHCOOR$$

$n = 3, 4, 8$; $R = C_2H_5$; $C_6H_5CH_2$

EXPERIMENTAL

Production of Perfluorodiisocyanates From Dihydrazides of Perfluorodicarboxylic Acids. A solution of 0.01 mole of the dihydrazide of a perfluorodicarboxylic acid in 0.04 mole of concentrated HCl and 10-20 ml of water was mixed with 30 ml of m-xylene; the mixture was cooled to 0-5° and stirred, and a solution of 0.04 mole of $NaNO_2$ in 5 ml of water was added in drops at such a rate that the temperature of the reaction mixture did not exceed 10°. Stirring was continued for a further 2 h with cooling, then the xylene layer was separated off, washed with $NaHCO_3$ solution and with water, and dried over $MgSO_4$ and then with metallic sodium. The dried solution of the azide in xylene was placed in a flask with a reflux condenser and a thermometer with measuring the temperature within the liquid. It was slowly heated in an atmosphere of nitrogen; at ~90° the azide began to decompose with the evolution of nitrogen. Heating was continued, the nitrogen liberated being collected. After the evolution of nitrogen had ceased, the perfluorodiisocyanate formed was distilled. It was purified by redistillation in a column in a current of dry nitrogen. The following compounds were obtained: 1) hexafluorotrimethylene 1,3-diisocyanate ($OCN(CF_2)_3NCO$ with b.p. 84-85°, n_D^{20} 1.3302, d_4^{20} 1.5330, yield 37%. Found %: C 25.53; F 48.72; N 11.67; MR 31.16. $C_5F_6O_2N_2$. Calculated %: C 25.64; F 48.71; N 11.96; MR 31.50; and 2) octafluorotetramethylene diisocyanate $OCN(CF_2)_4NCO$ with b.p. 105-106°, n_D^{20} 1.3412, d_4^{20} 1.544, yield 34%. Found %: C 25.51; F 53.15; N 10.09. $C_6F_8O_2N_2$. Calculated %: C 25.35; F 53.52; N 9.85.

In view of the low solubility of the dihydrazide of perfluorosebacic acid in xylene, hexadecafluorooctamethylene diisocyanate was not obtained by this method.

Preparation of Perfluorodiisocyanates From Chlorides of Perfluorodicarboxylic Acids. With stirring and cooling, a solution of 0.01 mole of the dichloride of perfluoroglutaric or perfluoroadipic acid in 10 ml of xylene was added in drops to a solution of 0.03 mole of activated NaN_3 in a mixture of 5 ml of water and 20 ml of m-xylene. The mixture was stirred for 2 h with ice cooling, and the xylene layer was separated off and dried over $MgSO_4$ and then with Na. The resulting solution of azide in xylene was heated in an atmosphere of nitrogen at 90-130°, the decomposition of the azide being carried out under the conditions described above. This gave hexafluorotrimethylene diisocyanate with b.p. 84-85°, yield 72% of theoretical, and octafluorotetramethylene diisocyanate with 105-106°, yield 78% of theoretical. An emulsion of 5.2 g of the chloride of perfluorosebacic acid in 10 ml of diphenyl ether was

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1110-1111, June, 1966. Original article submitted December 10, 1965.

added in small portions to a suspension of 1.3 g of activated NaN_3 in 20 ml of dry diphenyl ether at ~30°, and then the mixture was stirred with heating in the boiling water bath for 4-5 h. After this, the temperature was slowly raised to 259° (the boiling point of the diphenyl ether) and the nitrogen liberated by the decomposition of the azide was collected. When the evolution of nitrogen was complete, the resulting diisocyanate was distilled in vacuum. This gave 1.6 g of hexadecafluorooctamethylene diisocyanate $OCN(CF_2)_8 \cdot NCO$ with b.p. 105° (220 mm), n_D^{20} 1.3258, yield 32%. Found %: C 25.21; F 63.46; N 5.38. $C_{10}F_{16}O_2N_2$. Calculated %: C 24.79; F 62.81; N 5.78.

Preparation of Perfluoropolymethylene Diurethanes. In a current of nitrogen, and with cooling, 0.002 mole of alcohol was added to a solution of 0.001 mole of the perfluorodiisocyanate in 2-3 ml of dry ether. After the elimination of the ether in vacuum, the diurethane was obtained as a residue with a yield of 85-90%. It was recrystallized from benzene. In this way were obtained: 1) hexafluorotrimethylene dibenzylurethane with m.p. 112-114°. Found %: C 50.80; H 3.62; F 25.25; N 6.18. $C_{19}H_{16}F_6N_2O_4$. Calculated %: C 50.66; H 3.55; F 25.33; N 6.22. 2) Octafluorotetramethylene diethylurethane with m.p. 131-133°. Found %: C 32.09; H 3.26; F 40.60; N 7.37. $C_{10}H_{12}F_8N_2O_4$. Calculated %: C 31.91; H 3.19; F 40.42; N 7.44; and 3) hexadecafluorooctamethylene dibenzylurethane with m.p. 132-134°. Found %: C 40.82; H 2.12; F 43.03; N 3.96. $C_{24}H_{16}F_{16}N_2O_4$. Calculated %: C 41.14; H 2.28; F 43.42; N 4.00.

CONCLUSIONS

1. Perfluorodiisocyanates $OCN(CF_2)_nNCO$ (n = 3, 4, 8) have been obtained by the reaction of hydrazides of perfluorodicarboxylic acids with nitrous acid or that of chlorides of perfluorodicarboxylic acids with sodium azide and subsequent rearrangement of the azides of the acids so formed under the conditions of the Curtius reaction.

2. The reaction of the perfluorodiisocyanates with alcohols has given perfluoropolymethylene diurethanes.

LITERATURE CITED

1. N. P. Krasuskaya, D. P. Del'tsova, and I. L. Knunyants, Izv. AN SSSR, Ser. khim., 1965, 2039.
2. A. Ahlbrecht and D. Husted, U.S. Patent 2,617,817 (1952).
3. M. Sander, Monatsh. Chem. 95, No. 2, 608 (1964).
