Chemistry

Academician A. N. NESMEYANOV, Corresponding Member of the USSR Academy of Sciences R. Kh. FREIDLINA

1958

SovietRxiv

Abstract

Full Text

Chemistry

Academician A. N. NESMEYANOV, Corresponding Member of the USSR Academy of Sciences R. Kh. FREIDLINA
and A. B. BELYAVSKII

TELOMERIZATION OF ETHYLENE WITH TETRACHLOROETHYLENE

Chloroolefins that are incapable of polymerization can enter into telomerization reactions with olefins. In this process the chloroolefins play the role of reaction-chain transfer agents and supply terminal groups to the telomer molecules. Among reactions of this type, the telomerization of ethylene with tetrachloroethylene is of great interest as a route to the synthesis of reactive tetrachloroalkenes containing an even number of carbon atoms in the molecule (scheme (1)).

$$\mathrm{CCl_2 = CCl_2 + nCH_2 = CH_2 \xrightarrow{initiator} Cl(CH_2CH_2)_{nCCl} = CCl_2}. \qquad (1)$$

It may be assumed that the tetrachloroalkenes obtained in this way will make it possible to synthesize a variety of polyfunctional compounds of the even series, just as various bi- and polyfunctional compounds of the odd series are synthesized from $\alpha, \alpha, \alpha, \omega$-tetrachloroalkanes obtained by telomerization of ethylene with carbon tetrachloride (for a summary of these reactions, see ([1])). It should be noted that compounds containing the $\mathrm{CCl_2 = CCl}$ group were previously difficult to obtain; even their preparation from compounds containing the $\mathrm{CH = CCl_2}$ group is a multistage process, for example according to scheme (2):

$$\mathrm{RCH_2CCl_3 \to RCH = CCl_2 \to RCHCl\,CCl_3 \to RCCl = CCl_2}. \qquad (2)$$

The telomerization reaction of ethylene with tetrachloroethylene should lead to the synthesis of compounds containing the trichlorovinyl group in a single step. This reaction is mentioned in a patent ([2]). The reaction was carried out in the presence of benzoyl peroxide at 115° and 95 atm. From the mixture of products only tetrachlorohexene, boiling over a wide temperature range, was isolated.

We carried out the reaction of ethylene with tetrachloroethylene under pressures from 50 to 200 atm, in the presence of water and without water; benzoyl peroxide, tert-butyl peroxide, azo-bis-isobutyric acid dinitrile, and azoaminobenzene were tested as initiators. In all cases, carrying out the reaction in the presence of water gave a greater conversion of tetrachloroethylene. The best of the initiators tested proved to be peroxides.

The study showed that tetrachloroethylene is a less reactive reaction-chain transfer agent than, for example, carbon tetrachloride or chloroform. Thus, the conversion of tetrachloroethylene in the best experiments amounted to only 20% under conditions of repeated addition of initiator during the reaction. The inertness of tetrachloroethylene is also indicated by the fact that, when the pressure is increased, the content of higher tetrachloroalkenes in the reaction-product mixture rises rapidly. Fractionation of the reaction-product mixture showed that the lower $\alpha, \alpha, \beta, \omega$-tetrachloroalkenes ($n = 1, 2$) are readily isolated in individual form. The higher fractions contain by-products of the reaction, from which it is difficult to free them. Despite

despite the indicated difficulties, we succeeded in obtaining tetrachloroalkenes containing 4, 6, and 8 carbon atoms in the molecule and in studying some of their chemical transformations.

By the interaction of tetrachloroalkenes ($n = 2, 3$) with diethylamine, diethylamino derivatives of the structure $(C_2H_5)_2N(CH_2CH_2)_nCCl = CCl_2$ were obtained, which proves the presence of only one chloromethyl group in the molecule.

When metallic sodium was allowed to act on the bases obtained, acetylene derivatives of the structure $(C_2H_5)_2N(CH_2CH_2)_nC \equiv CH$ were isolated, which proves the presence of a trichlorovinyl group (cf. with ([3])).

In contrast to the higher tetrachloroalkenes, 1,1,2,4-tetrachlorobutene-1, on interaction with diethylamine, is dehydrochlorinated with formation of 1,1,2-trichlorobutadiene-1,3.

Experimental Part

Telomerization reaction of tetrachloroethylene with ethylene. A rocking autoclave of stainless steel, capacity 2700 ml, was charged with 1000 ml of tetrachloroethylene (1620 g), 500 ml of water, and ethylene was introduced to a pressure of 50 atm. The mixture was heated to a temperature of 140°. At this temperature and pressure, every hour and a half 20 ml of a solution of tert-butyl peroxide in tetrachloroethylene was added. In all, over 15 h, 12 g of peroxide in 200 ml of tetrachloroethylene was added. The products of two experiments were combined; in all, 4185 g of mixture was obtained. For fractionation, 2400 g of the mixture was taken.

After distillation of 1782 g of tetrachloroethylene, a residue of 618 g was obtained, which was fractionated in vacuo. The following were obtained: fraction I, 35–65°/22 mm, 108 g; fraction II, 60–90°/10 mm, 95 g; fraction III, 90–115°/10 mm, 144 g; fraction IV, 96–110°/2 mm, 50 g; fraction V, 111–130°/2 mm, 27 g; fraction VI, residue, 173 g.

After secondary distillation on a column, from fractions II, III, IV there were isolated, respectively:

a) **1,1,2,4-Tetrachlorobutene-1** (77 g). B.p. 66°/9 mm, n_D^{20} 1.5140, d_4^{20} 1.4708. Found MR 39.69. For $C_4H_4Cl_4$, MR calculated 39.67.

Found %: C 24.93; 24.98; H 2.17; 1.98
Calculated %: C 24.77; H 2.08

b) **1,1,2,6-Tetrachlorohexene-1** (130 g). B.p. 103–104°/8.5 mm, n_D^{20} 1.5090, d_4^{20} 1.3551. Found MR 48.92. For $C_6H_8Cl_4$, MR calculated 48.91.

Found %: C 32.67; 32.68; H 3.77; 3.79
Calculated %: C 32.47; H 3.63

Literature data (2): b.p. 99–103°/10 mm, n_D^{25} 1.5060, d^{25} 1.3456.

c) **1,1,2,8-Tetrachlorooctene-1** (27 g). B.p. 111–112°/2 mm, n_D^{20} 1.5060, d_4^{20} 1.2206. Found MR 58.26. For $C_8H_{12}Cl_4$, MR calculated 58.63.

Found %: C 39.34; 39.40; H 4.68; 4.69
Calculated %: C 38.43; H 4.83

The intermediate fractions and the residue were not investigated.

1,1,2-Trichlorobutadiene-1,3. A solution of 90 g (0.46 mole) of 1,1,2,4-tetrachlorobutene-1 in 67 g (0.92 mole) of diethylamine was placed in three glass ampoules. The ampoules were heated to 22–25° and held at this temperature for 48 h. The precipitated hydrochloride was separated off, the solution was washed with a weak solution of acid, dried over sodium sulfate, and distilled. Obt–

obtained 51 g (70.5% of theory) of 1,1,2-trichlorobutadiene-1,3, b.p. 75°/80 mm, n_D^{20} 1.5355, d_4^{20} 1.3733. Found MR 35.72. For $C_4H_3Cl_3F_2$ calculated MR 34.34.

Found, %:	C 30.61; 30.25;	H 2.15; 1.97
Calculated, %:	C 30.51;	H 1.92

1,1,2-Trichlorobutadiene-1,3 polymerizes readily.

1,1,2-Trichloro-6-diethylaminohexene-1. Into a stainless-steel autoclave were charged 44 g (0.2 mole) of 1,1,2,6-tetrachlorohexene-1, 30 g (0.4 mole) of diethylamine, and 50 ml of methyl alcohol. The mixture was heated at 95-105° for 6 h and worked up in the usual manner. The base was dried over Na_2SO_4 and distilled. There were obtained 43.2 g of 1,1,2-trichloro-6-diethylaminohexene-1, b.p. 128.5°/9 mm, n_D^{20} 1.4860, d_4^{20} 1.1175. Found: MR 66.45. For $C_{10}H_{18}Cl_3NF$ calculated MR 66.45.

Found, %:	C 46.33; 46.42;	H 7.88; 7.13
Calculated, %:	C 46.44;	H 7.02

Hydrochloride, m.p. 187° (from alcohol)

Found, %:	C 40.77; 40.79;	H 6.63; 6.67
Calculated, %:	C 40.69;	H 6.49

1,1,2-Trichloro-8-diethylaminooctene-1. Into a stainless-steel autoclave were charged 95 g of the tetrachlorooctene fraction, b.p. 110–114°/2 mm, 60 g (0.76 mole) of diethylamine, and 50 ml of methyl alcohol. The mixture was heated at 95–105° for 6 h. After the usual workup, the basic products were separated from the neutral ones. The neutral products (15 g) were not investigated. On distillation of the basic products, 28 g of 1,1,2-trichloro-8-diethylaminooctene-1 were obtained, b.p. 147°/5 mm, n_D^{20} 1.4855; d_4^{20} 1.0835. Found MR 75.90. For $C_{12}H_{22}NCl_3F$ calculated MR 75.69.

Found, %:	C 50.46; 50.56;	H 7.82; 7.81
Calculated, %:	C 50.27;	H 7.73

Hydrochloride, m.p. 116° (from acetone)

Found, %:	C 44.83; 44.72;	H 7.19; 7.19
Calculated, %:	C 44.59;	H 7.17

6-Diethylaminohexene-1. Into a three-necked flask were charged 7.84 g (0.34 mole) of finely divided metallic sodium and 30 ml of ether; with stirring, a small quantity of 1,1,2-trichloro-6-diethylaminohexene-1 in ether solution was added. After 2–3 min the reaction began spontaneously, and then the remaining solution of 1,1,2-trichloro-6-diethylaminohexene-1, a total of 21 g (0.085 mole) in 25 ml of ether, was added dropwise. The thickened mass was stirred for 4 h. After 15 h the mixture was treated with methyl alcohol and water. The organic layer was extracted with ether, dried over Na_2SO_4, and distilled. There were isolated 8.3 g of 6-diethylaminohexene-1, b.p. 73°/12 mm, n_D^{20} 1.4450, d_4^{20} 0.8120. Found MR 50.24. For $C_{10}H_{19}NF$ calculated MR 50.31.

Found, %:	C 77.83; 77.99;	H 12.54; 12.47
Calculated, %:	C 78.35;	H 12.48

Hydrochloride, m.p. 120.5–121° (from acetone):

Found, %:	C 63.04; 62.82;	H 10.60; 10.70
Calculated, %:	C 63.30;	H 10.62

8-Diethylaminooctyne-1. Obtained from 40 g of 1,1,2-trichloro-8-diethylaminohexene-1 by treatment with metallic sodium in ethereal solution, as described in the preceding experiment. There were obtained 15.5 g of 8-diethylamino-

octine-1, b.p. 96°/10 mm, n_D^{20} 1.4478, d_4^{20} 0.8146. Found MR 59.50. For $C_{12}H_{23}NF$ calculated MR 59.54.

Found, %: C 79.14; 79.42; H 12.77; 12.90
Calculated, %: C 79.48; H 12.80

Hydrochloride, m.p. 81° (from acetone)

Found, %: C 66.28; 66.36; H 11.17; 11.12
Calculated, %: C 66.17; H 11.10

Received
5 VII 1958

References Cited

1. A. N. Nesmeyanov, R. Kh. Freidlina, L. I. Zakharkin, *Usp. khim.*, **26**, 655 (1956).

2. English Patent 589055; *Chem. Abstr.*, **42**, 583 (1948). L. I. Zakharkin, *Izv. AN SSSR, OKhN*, **1955**, 1009.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.