TELOMERIZATION OF ACRYLONITRILE WITH N, N-DICHLORO-p-CHLOROBENZENE SULFAMIDE

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In the preceding work we studied the addition and telomerization of allyl chloride and acrylonitrile with N, N-dichloro-p-chlorobenzenesulfamide in the presence of dicyclohexylperoxydicarbonate [1]. This reaction can be described by the scheme: $p-ClC_6H_4SO_2NCl_2 + CH_2 = CHX _initiator$ $p-ClC_6H_4SO_2NCl(CH_2 - CHX)_n$ ·Cl, where X = CH₂Cl, CN. Compounds with n = 1, 2 were isolated, side formation of the corresponding amides occurred, and a compound having the structure: $p-ClC_6H_4SO_2N(CH_2CHCH_2Cl)_2$ was obtained in the

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case of allyl chloride. It was proposed that these reactions have radical character.

This work studies the telomerization of acrylonitrile with N, N-dichloro-p-chlorobenzenesulfamide in greater detail. With the purpose of obtaining higher telomers we investigated the effect of the (monomer) :(telogen) ratio on the yield of telomer fractions. The reaction was carried out in a carbon tetrachloride medium in the presence of dicyclohexylperoxydicarbonate (5 moles %) at a monomer – telogen ratio (in moles) of 2:1.4; 4:1; 6:1; and 10:1 (Table 1). The reaction products were isolated as the amides $[p-ClC_6H_4$ ·SO₂NH(CH₂CHCN)_nCl], for which the reaction mixture was treated with sodium bisulfite.

It is seen from Table 1 that with increasing acrylonitrile to N, N-dichloro-p-chlorobenzenesulfamide ratio the yield of lower telomers decreases and the yield of higher telomer fractions increases. α -Chloro- β -(p-chlorobenzenesulfamido)propionitrile (I, n = 1) and α -chloro- γ -cyano- δ -(p-chlorobenzenesulfamido)valeronitrile (II, n = 2) were isolated from the reaction mixture of experiment 1 (see Table 1). The syrupy fraction, evidently containing telomers with n = 3-5, was not examined more closely. A fraction was also obtained in experiment 1, which from molecular weight and elemental composition resembles a telomer with n = 6. Fractions close to telomers having n (average) = 7 and 9 were obtained in experiment 2 (see Table 1) and a fraction of telomers with n (average) = 14 was obtained in experiment 4. The enumerated telomer fractions are pale yellow, crystalline materials with increasing melting point. Telomers having n = 6, 7, 9 are soluble in alcohol, acetone, and tetrahydrofuran (THF), and poorly soluble in CCl₄, CHCl₃, benzene, and petroleum ether. Infrared spectra of the isolated telomers show the presence of NH groups in the studied compounds, which confirms their affiliation with the class of N-monoalkylarylsulfamides.

The molecular weight of telomers having n = 1, 2, 6 was determined by the transient equilibrium method of Archibald [2]. The application of this method to the determination of the molecular weight of low molecular weight compounds was shown in [3].

Experi-	CH ₂ CHC N	Yield of telomer fractions, $\%$ of theor. , calculated on the dichloroamide			
ment No.	$Cl_2NSO_2C_6H_4Cl-p, M*$	n = 1	n == 2	n = 3-5	$n \ge 6$
1 2 3 4	2 4 6 10	20-24	12—15 8—10 —	8-12 35-40 18-23 11-15	10-16 21-27 45-52 57-62

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• In all experiments 0.05 mole of N,N-dichloro-p-chlorobenzenesulfamide was used.

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EXPERIMENTAL

<u>Telomerization of Acrylonitrile with N, N-Dichloro-p-chlorobenzenesulfamide</u>. The reaction mixture consisting of 13 g of dichloroamide, 5.3 g of acrylonitrile, 1.43 g of dicyclohexylperoxydicarbonate, and 30 ml of CCl_4 was heated with stirring in a stream of N_2 to 60-65°C. This temperature was maintained for 1.5 h, in which time the reaction terminated. After cooling the reaction mixture to room temperature, the precipitate was separated from the liquid portion by decantation. The residue remaining in the flask was washed at 60°C and stirred with 20 ml of CCl_4 . The liquid portion of the reaction mixture and the CCl_4 used for washing were combined (extract A). The precipitate was washed at 60°C with stirring with an additional two 20 ml portions of CHCl₃ and the chloroform extracts were combined (extract B). Extracts A and B and the remaining solid residue (C) were treated with an aqueous solution of NaHSO₃ with heating on a water bath for 30 min. The aqueous layer was separated and the lower layer was washed with warm water and dried over CaCl₂. The solid residue (C) after NaHSO₃ treatment was washed with water and dried.

Isolation of Telomers with n = 1, 2, and 6. From the CCl_4 solution after treatment with NaHSO₃ and distillation of approximately half of the CCl_4 , cooling precipitated a solid from which was obtained 2.8 g of α -chloro- β -(p-chlorobenzenesulfamido)propionitrile (I), identical with that isolated earlier [1]. Found: mol. wt. 285.4. $C_9H_8Cl_2N_2O_2S$. Calculated: mol.wt. 279.

Further distillation of CCl₄ from the filtrate after separation of (I) yielded 2.5 g of α -chloro- γ -cyano- δ -(p-chlorobenzenesulfamido)propionitrile (II), mp 68°C (from CCl₄). Found: C 43.4; H 3.4; Cl 21.1; N 12.4%; mol.wt. 340. C₁₂H₁₁Cl₂N₃O₂S. Calculated: C 43.3; H 3.3; Cl 21.4; N 12.6%; mol.wt. 332. ν_{max} 3300 (NH); 1330, 1165 (SO₂NH) cm⁻¹.

From extract B after treatment with bisulfite and distillation of $CHCl_3$ was obtained 4 g of a syrupy material having the following elemental composition: C 50.1; H 3.8; N 16.5; Cl 17.3 and evidently being a mixture of amides having n = 3, 4, 5.

The major portion of precipitate (C) (2.7 g), treated with NaHSO₃, dissolved upon boiling in 30 ml of ethanol. After cooling the alcoholic extract and partial distillation of the alcohol was obtained 1.9 g of material, mp 135-140°C (dec., C₂H₅OH). Found: C 52.7; H 4.3; Cl 12.6; N 18.3; mol.wt. 553. C₂₄H₂₃Cl₂ \cdot N₇O₂S. Calculated: C 52.8; H 4.2; Cl 13.0; N 18.0%; mol. wt. 554 (n = 6). ν_{max} 3275 (NH); 1330, 1165 (SO₂NH) cm⁻¹. The residue which was insoluble in alcohol was not investigated further.

Isolation of Telomers with n (average) = 7 and 9. The fraction having the telomer composition with n = 7 was isolated from the reaction mixture (experiment 2, see Table 1). After treatment of the CCl₄ extract with sodium bisulfite was obtained 1.6 g of (II) (n = 2). From the chloroform extract was obtained 8.7 g of a syrupy material which was not identified.

From the solid residue, which was insoluble in CCl_4 and $CHCl_3$, after treatment with NaHSO₃ was obtained 8.1 g of material. A portion of it dissolved upon boiling with alcohol (60 ml). After separation of the insoluble portion, cooling of the filtrate yielded 2.8 g of material, mp 150–158 °C (dec.). Found: C 53.8; H 4.6; Cl 11.7; N 18.4%. $C_{27}H_{26}Cl_2N_8O_2S$. Calculated: C 54.2; H 4.4; Cl 11.9; N 18.7% (n = 7). ν_{max} 3280 (NH), 1340, 1165 (SO₂NH) cm⁻¹.

The portion of the material which was insoluble in alcohol was treated with acetone. Addition of petroleum ether to the acetone solution precipitated 2.5 g of a solid, mp 190-200°C (dec.). Found: C 56.0; H 4.5; Cl 10.9; N 20.4%. C₃₃H₃₂Cl₂N₁₀O₂S. (n = 9). Calculated: C 56.2; H 4.6; Cl 10.1; N 19.9%. ν_{max} 3270 (NH); 1340, 1165 (SO₂NH) cm⁻¹. The material which was insoluble in acetone was not identified (0.9 g).

Isolation of the Telomer with n (average) = 14. Treatment of the reaction mixture (experiment 4, see Table 1) similarly to that presented in the preceding experiments yielded 29 g of a solid product, the major portion of which was insoluble in alcohol and acetone and had mp 205-215°C (dec.). Its elemental composition corresponded approximately to a telomer having n = 14. Found: C 59.2; H 4.9; Cl 7.0; N 21.4%. $C_{48}H_{47}Cl_2N_{15}O_2$ (n = 14). Calculated: C 59.6; H 4.9; Cl 7.3; N 21.7. ν_{max} 3275 (NH), 1350, 1170 (SO₂NH) cm⁻¹.

Infrared spectra were recorded on a UR-10 spectrophotometer using KBr (concentration 0.5%). Molecular weight determined from gradient sedimentation curves obtained on a MOM-120 ultracentrifuge at 20°C in tetrahydrofuran at C = 0.01 g/ml.

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CONCLUSIONS

1. Telomerization of acrylonitrile with N, N-dichloro-p-chlorobenzenesulfamide in the presence of dicyclohexylperoxydicarbonate was studied.

2. Telomers having n = 1, 2, and 6, and telomer fractions with n (average) = 7, 9, and 14 were isolated.

LITERATURE CITED

- 1. R. Kh. Freidlina, N. A. Rybakova, G. K. Semin, and É. A. Kravchenko, Dokl. Akad. Nauk SSSR, <u>176</u>, 352 (1967).
- 2. W. Archibald, J. Phys. Colloid. Chem., 51, 1205 (1947).
- 3. G. I. Timofeeva and V. N. Babin, Dokl. Akad. Nauk SSSR, 182, 1102 (1968).