# IONIC TELOMERIZATION OF STYRENE WITH N,N-DICHLORO-p-CHLOROBENZENESULFONAMIDE

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The addition of N,N-dihaloaryl(alkyl)sulfonamides (dihaloamides) to unsaturated compounds has been intensely studied in recent years [1-8]. Interest in this reaction is associated with the wide availability of the dihaloamides, the ease with which they enter into the indicated reaction, and the possibilities of using the adducts for various syntheses, for example, the synthesis of aziridines. We were the first to run the radical telomerization of acrylonitrile [1, 9] and allyl chloride [1] with N,N-dichloro-p-chlorobenzenesulfonamide. It was shown by us on a number of examples that the addition of dichloroamides to unsaturated compounds can be easily accomplished by both the radical and the ionic mechanism [10], in view of which a comparative study of radical and ionic telomerization on the same systems is of great interest.

In the present paper was accomplished the ionic telomerization of styrene with N, N-dichloro-p-chlorobenzenesulfonamide. It was shown by us [10] that the ionic addition of N,N-dichloro-p-chlorobenzenesulfonamide to styrene (in the air, without an initiator) leads to the formation of an adduct that has the structure of (I). Under radical addition conditions (in nitrogen, without an initiator) an adduct is formed that has the structure of (II):

The structure of adducts (I) and (II) was proved by the IR and NMR spectra.

It should be mentioned that the possibility of the ionic and radical addition of N,N-dichlorosulfonamide to unsaturated compounds was shown recently by the example of the addition of N,N-dichloroethanesulfonamide to 1-dodecene [8].

The ionic telomerization of styrene with N,N-dichloro-p-chlorobenzenesulfonamides was run in methylene chloride medium, in the presence of  $SnCl_4$ , at a monomer-telomer ratio (in moles) of 4:1.

| Number  | Telomer homo-<br>logs n | Yield, in % when<br>based on starting<br>dichloroamide | Bp, °C                                      | IR spectrum, fre-<br>quency, cm <sup>-</sup><br>characteristic<br>for NH group | Found, %  |  |   |   | Calc.,%   |  |   |
|---|-------------------------|--|---|--|---|--|---|---|---|--|---|
|   |                         |  |   |  | σ   | н  | CI  | Empirical formula   | с   | н  | CI  |
| 1<br>2<br>3<br>4<br>5<br>6<br>7                   | 1<br>3<br>5<br>6<br>14  | 38<br>13<br>4<br>2<br>10<br>4<br>3                     | 179<br>170<br>162<br>148<br>70<br>74<br>120 | 3250<br>Nöne<br>3250<br>None<br>3240<br>None                                   | 50,78<br>56,45<br>66,96<br>71,26<br>73,89<br>76,40<br>82,72 | 3,96<br>4,02<br>5,37<br>5,39<br>5,90<br>6,25<br>7,04 | 21,39<br>22,40<br>13,01<br>13,21<br>11,93<br>8,46<br>5,92 | C <sub>10</sub> H <sub>10</sub> Cl <sub>0</sub> NO <sub>2</sub> S<br>C <sub>22</sub> H <sub>40</sub> Cl <sub>0</sub> NO <sub>2</sub> S<br>C <sub>40</sub> H <sub>40</sub> Cl <sub>0</sub> NO <sub>4</sub> S<br>C <sub>40</sub> H <sub>40</sub> Cl <sub>0</sub> NO <sub>4</sub> S<br>C <sub>40</sub> H <sub>40</sub> Cl <sub>0</sub> NO <sub>4</sub> S<br>C <sub>40</sub> H <sub>40</sub> Cl <sub>0</sub> NO <sub>5</sub> S<br>C <sub>41</sub> H <sub>50</sub> Cl <sub>2</sub> NO <sub>2</sub> S<br>C <sub>108</sub> H <sub>10</sub> Cl <sub>0</sub> NO <sub>2</sub> S | 50,91<br>56,35<br>66,91<br>70,72<br>73,26<br>76,24<br>82,49 | 3,93<br>4,27<br>5,39<br>5,64<br>5,88<br>6,24<br>6,76 | 21,42<br>22,73<br>13,20<br>13,64<br>12,04<br>8,35<br>6,20 |
| *Compounds 1 and 2 years response 11 and from CC1 |                         |  |   |  |   |  |   |   |   |  |   |

TABLE 1

\* Compounds 1 and 2 were recrystallized from  $CCl_4$ —petroleum ether, and compounds 4-7 were recrystallized from  $C_2H_5OH-C_6H_{6*}$ 

<sup>†</sup>The molecular weight was determined cryoscopically in benzene. For n = 6: found 854, calc. 886; for n = 14: found 1689, calc. 1719.

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Telomers, containing 1, 2, 3, 5, 6, and 14 units of the monomer in the molecule (Table 1), were isolated after treating the reaction mixture with sodium bisulfite. Assignment of the telomerization products as being N-disubstituted (III) and N-trisubstituted arylsulfonamides (IV) was made on the basis of the IR spectra and the analysis data (see Table 1):

# $\begin{array}{c} \text{HNCH} (\text{C}_{6}\text{H}_{5}) \text{ CH}_{2} (\text{CHCH}_{2})_{n-1} \text{Cl} \\ \downarrow & \downarrow \\ \text{SO}_{2}\text{C}_{6}\text{H}_{4}\text{Cl}_{-p} & \text{C}_{6}\text{H}_{5} & (\text{III}) \\ & \text{CH} (\text{C}_{6}\text{H}_{5}) \text{CH}_{2} [\text{CH} (\text{C}_{6}\text{H}_{5}) \text{CH}_{2}]_{m} \text{Cl} \\ p\text{-ClH}_{4}\text{C}_{6}\text{O}_{2}\text{SN} & (\text{IV}) \\ & \text{CH} (\text{C}_{6}\text{H}_{5}) \text{CH}_{2} [\text{CH} (\text{C}_{6}\text{H}_{5}) \text{CH}_{2}]_{n-m-2} \text{Cl} \end{array}$

Frequencies characteristic for the  $SO_2N$  group (1340, 1150 cm<sup>-1</sup>) were present in the IR spectra of all of the isolated compounds. The trisubstituted amides (IV) failed to show in the IR spectra the frequencies characteristic for the NH group. On the basis of the data obtained in studying the telomer homolog with n = 1, it may be assumed that the first styrene fragment adds to the nitrogen atom in harmony with the Markovnikov rule. The orientation of the addition of subsequent fragments requires further study.

The radical telomerization of styrene with an N,N-dichloroarylsulfonamide, accomplished without the addition of an initiator, in a nitrogen atmosphere, leads to the formation of telomers with a different structure.

## EXPERIMENTAL

<u>Telomerization of Styrene with N,N-Dichloro-p-chlorobenzenesulfonamide</u>. To a mixture of 6.5 g of the dichlorosulfonamide, 1 ml of a 10% solution of  $SnCl_4$  in  $CH_2Cl_2$ , and 20 ml of  $CH_2Cl_2$ , cooled to  $-20^\circ$ , was added 10.4 g of styrene, devoid of polymer. The reaction mixture warmed up rapidly to 43-45° due to exothermic reaction. After exothermic reaction had ceased, the mixture was held at the same temperature for 1 h. The next day the reaction mixture was treated with aqueous NaHSO<sub>3</sub> solution, with heating up to  $60-70^\circ$ .

The general scheme for separating the reaction mixture consisted in the fact that, after treatment with NaHSO<sub>3</sub>, the less soluble lower telomerization products (n = 1, 2, 3) deposited in the precipitate. They were washed with hot water to separate the p-chlorobenzenesulfonamide and were separated by fractional crystallization from CCl<sub>4</sub>. The fractional crystallization was followed by TLC on Al<sub>2</sub>O<sub>3</sub>, using a CHCl<sub>3</sub> –heptane-ethanol mixture (3:7:1) as the solvent. The organic layer was dried over CaCl<sub>2</sub>, filtered, and the filtrate was treated with alcohol to fractionally precipitate the chlorinated polystyrene (1.8 g) and higher telomer homologs with  $n \ge 5$ . We were able to isolate the telomers with n = 6, both those containing and not containing the NH group. These compounds are not separated in the above-mentioned TLC system and have a close solubility. However, in the different experiments one of these substances was formed in predominant amount, which made it possible to separate them. The yield of the obtained compounds, when based on the starting N,N-dichloro-p-chlorobenzenesulfonamide, the melting points, and the microanalysis results are given in Table 1. All of the obtained compounds represented white crystalline substances.

### CONCLUSIONS

The ionic telomerization of styrene with N,N-dichloro-p-chlorobenzenesulfonamide was accomplished in methylene chloride medium in the presence of  $SnCl_4$ . Telomers with the following composition were isolated: a) p-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH(C<sub>8</sub>H<sub>8</sub>)<sub>n</sub>Cl, n = 1, 3, 6 and

> b) p-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N,  $(C_8H_8)_m$  Cl ( $C_8H_8$ )<sub>m</sub> Cl ( $C_8H_8$ )<sub>n-m</sub> Cl

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