### TELOMERIZATION OF ETHYLENE WITH

## PHENYLDIAZONIUM CHLORIDE

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The Meerwein reaction continues to be the subject of many investigations (see, for example, [1]). We proposed a new approach to studying this reaction [2], and specifically it was shown that when aryldiazonium chlorides are reacted with excess acrylonitrile under the conditions of the Meerwein reaction there occurs, together with the formation of many of the usual accompanying products, telomerization according to the scheme:

 $\begin{array}{c} \operatorname{ArN_2Cl} + \operatorname{CH_2=CHCN} \xrightarrow{\operatorname{CuCl_2}} \operatorname{Ar} \left[\operatorname{CH_2CH} (\operatorname{CN})\right]_n \operatorname{Cl} \\ \operatorname{Ar=C_6H_5}, \ p-\operatorname{NO_2C_6H_4}; \ n=1, \ 2 \end{array}$ 

This process is of theoretical interest, since in it is absent the usual step of chain transfer via reaction of the growing radical  $(\operatorname{ArCH}_2\operatorname{CHCN})_n$  with the telogen  $(\operatorname{ArN}_2\operatorname{Cl})$  [2]. As is known [3], the yields of the chloroacrylation products for nucleophilic unsaturated compounds is lower than for electrophilic compounds, even in the reactions with aryldiazonium salts that contain electron-acceptor substituents, which, apparently, is associated with the absence of the usual step of chain transfer. It is specifically this step in radical addition [4] and telomerization [5] that is most sensitive to polar effects (a high reaction rate of radicals and substrates with an unlike polar effect). The yield of the chloroarylation products apparently depends to a large degree on the relative reaction rates of the radicals  $\operatorname{Ar}(\operatorname{CH}_2\operatorname{CHX})_n$  with copper salts [2] and of the reactions competing with it. From this standpoint it is of interest to study the reaction of ethylene with aryldiazonium chlorides, which is the subject of the present paper. In addition, this reaction with ethylene is also interesting for the reason that the obtained telomers have a simpler structure, do not contain asymmetric carbon atoms, and can be studied by the GLC method.

The reaction of ethylene with phenyldiazonium chloride in the presence of  $CuCl_2$  and  $CH_3CO_2Na$  in aqueous acetone medium proceeds in a complex manner, but we were able to show that, the same as in the case of acrylonitrile, telomerization takes place according to the scheme:

$$C_6H_5N_2Cl + n (CH_2 = CH_2) \rightarrow C_6H_5(CH_2CH_2)_n Cl$$

$$n = 1,2$$

The telomers were identified by GLC employing authentic specimens [6, 7]. In addition, from  $\beta$ chloroethylbenzene and  $\omega$ -chlorobutylbenzene, both from those isolated from the reaction mixture and from the authentic specimens, were obtained the picrates of the isothiuronium derivatives, which failed to show a depression of the mixed melting points. The yields of all of the products were determined by GLC using benzyl chloride as the standard (Table 1).

As can be seen from Table 1, under the selected conditions the main reaction product is chlorobenzene (Sandmeyer reaction). The total yield of telomers was only 7-10%. The obtaining of telomer homologs, biphenyl (dimerization product of the phenyl radical) and chlorobiphenyls (arylation products of chlorobenzene) indicates the formation of free phenyl radicals in the reaction mixture. The total yield of telomers, with n = 1 and 2, is much smaller than in the case of acrylonitrile (for acrylonitrile the total yield is approximately 35% of theory). This is found to be in agreement with the data given in [3], where it is

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TABLE 1

ang pang ang pang pang pang pang pang pa	Yields, * in % of theory, when based on charged aniline				
Experimental conditions	C₅H₂Cl	C₀H₅ (CH₂)₂Cl	C <sub>8</sub> H5 (CH2)4Cl	$\mathrm{C_5H_5}-\mathrm{C_6H_5}$	$ClC_{6}H_{4}C_{6}H_{5}$ (o-, m- and p-)
In the presence of CH <sub>3</sub> COONa Without CH <sub>3</sub> COONa	14 12	7 10	0,7 0,5		1,5 3

\* The calibration was made for  $\beta$ -chloroethylbenzene, and the correction was insignificant.

indicated that poorer yields of the chloroarylation products are obtained for nucleophilic unsaturated compounds.

### EXPERIMENTAL

The telomerization of ethylene with phenyldiazonium chloride was run in a rotated, 1-liter stainless steel autoclave. Into the autoclave was charged a solution of phenyldiazonium chloride (obtained from 29 g of aniline), 7.5 g of CuCl<sub>2</sub> and 40 g of CH<sub>3</sub>COONa in 20 ml of H<sub>2</sub>O and 250 ml of acetone. The ethylene pressure was 65-70 atm and the temperature was 40°. After 3 h the reaction mixture was diluted with water and extracted with ether. The ether extract was washed several times with water, then with Na<sub>2</sub>CO<sub>3</sub> solution, again with water, and dried over CaCl<sub>2</sub>. After distilling off the ether the residue was clarified by passage though a small layer of Al<sub>2</sub>O<sub>3</sub>, then eluted with hexane, and the hexane was distilled off. The obtained mixture was chromatographed on a 2-meter column, with an inside diameter of 0.4 cm, using Celite-545 as the solid phase, 10% fluorinated silicone as the stationary phase, a column temperature of 171°, helium as the carrier gas, and detection by the heat conductivity.

The reaction mixture, obtained from several experiments, was vacuum-distilled through a column. The obtained fractions of telomers, with n = 1 and 2, were identified via the picrates from the isothiuronium salts. In addition, we isolated biphenyl with mp 69-70° and p-chlorobiphenyl with mp 74-76° (the isolated products failed to depress the mixed melting points with the authentic samples. Found: C 76.54; H 4.93; Cl 17.72%.  $C_{12}H_9Cl$ . Calculated: C 76.39; H 4.80; Cl 18.79%). We isolated o-chlorobiphenyl, which was identified by GLC employing an authentic specimen (found: C 76.32; H 5.25%).

From  $\omega$ -chlorobutylbenzene was obtained the  $\omega$ -phenylbutylisothiuronium picrate, mp 137-138° (from alcohol). The mixed melting point with an authentic specimen was not depressed. The identity of the picrates was also established by the method of TLC on Al<sub>2</sub>O<sub>3</sub> (system: acetone – hexane). Found: C 46.19; H 4.35; S 7.29%. C<sub>17</sub>H<sub>19</sub>O<sub>7</sub>N<sub>5</sub>S. Calculated: C 46.67; H 4.35; S 7.32%.

We also obtained  $\beta$ -phenylethylisothiuronium picrate, mp 135-136° (from alcohol). The mixed melting point with an authentic specimen was not depressed, while the mixed melting point with  $\omega$ -phenylbutyliso-thiuronium picrate was distinctly depressed. Found: C 43.76; H 3.62; S 7.83%. C<sub>15</sub>H<sub>15</sub>O<sub>7</sub>N<sub>5</sub>S. Calculated: C 43.76; H 3.67; S 7.82%.

#### CONCLUSIONS

A study was made of the reaction of ethylene with phenyldiazonium chloride under the conditions of the Meerwein reaction. Telomers having the structure  $C_6H_5(CH_2CH_2)_nCl$ , where n = 1 or 2, were identified, and also biphenyl, and the p- and o-chlorobiphenyls.

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