ORGANIC AND BIOLOGICAL CHEMISTRY

ADDITION OF α-HALO ETHERS TO UNSATURATED COMPOUNDS

COMMUNICATION 2. ADDITION OF ALLYL CHLOROMETHYL AND 1-CHLOROETHYL ETHYL ETHERS

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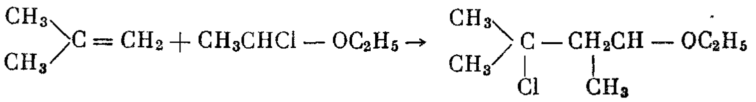
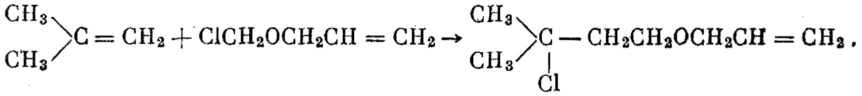
This work forms a continuation of our study of the addition of α-halo ethers to unsaturated compounds. As unsaturated compounds we have taken isobutene and styrene, and as halo ethers—allyl chloromethyl and 1-chloroethyl ethyl ethers. Allyl chloromethyl ether was prepared in the usual way by the chloromethylation of allyl alcohol; the constants of the product agreed with those given in the literature [1]. 1-Chloroethyl ethyl ether was synthesized by Shostakovskii's method [2]. After excess of hydrogen chloride had been driven off, the 1-chloroethyl ethyl ether was taken for reaction without purification by distillation. Its constants also agreed with data in the literature [2]. In the addition of these two ethers to isobutene we obtained two γ-chloro ethers:

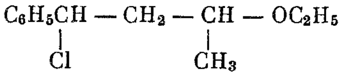


$$(CH_3)_2C=CH_2 + CH_3CHCl-OC_2H_5 \rightarrow (CH_3)_2\underset{Cl}{C}-CH_2\underset{CH_3}{CH}-OC_2H_5 \quad \text{(I)}$$

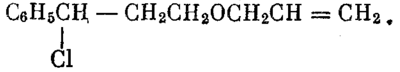


$$(CH_3)_2C=CH_2 + ClCH_2OCH_2CH=CH_2 \rightarrow (CH_3)_2\underset{Cl}{C}-CH_2CH_2OCH_2CH=CH_2, \quad \text{(II)}$$

As a result of the reaction of these α-halo ethers with styrene we obtained, respectively

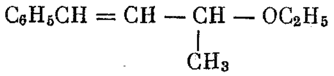


$$C_6H_5\underset{Cl}{CH}-CH_2-\underset{CH_3}{CH}-OC_2H_5 \quad \text{(III)}$$



$$C_6H_5\underset{Cl}{CH}-CH_2CH_2OCH_2CH=CH_2, \quad \text{(IV)}$$

The structures of the γ-chloro ethers (III) and (IV) were confirmed by their conversion into the unsaturated compounds:

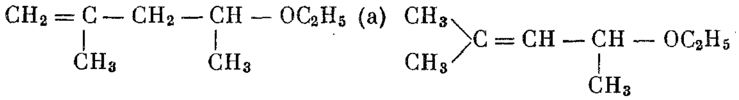


$$C_6H_5CH=CH-\underset{CH_3}{CH}-OC_2H_5 \quad \text{(V)}$$

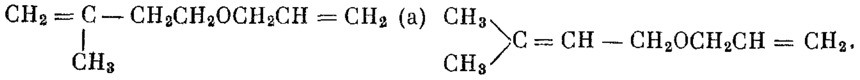
$$C_6H_5CH=CH-CH_2OCH_2CH=CH_2, \quad \text{(VI)}$$

In the infrared spectrum of (VI) an intense peak at 968 cm^{-1} points to the presence of C=C, a trans-substituted double bond. The corresponding ν C=C is at 1672 cm^{-1}, i.e., at the usual position for unconjugated trans-substituted double bonds.

In the dehydrochlorination of 3-chloro-1,3-dimethylbutyl ethyl ether (I) and of allyl 3-chloro-3-methylbutyl ether (II) in each case a mixture of two isomers is evidently obtained:



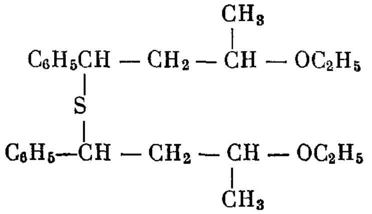
$$CH_2=\underset{CH_3}{C}-CH_2-\underset{CH_3}{CH}-OC_2H_5 \text{ (a) } (CH_3)_2C=CH-\underset{CH_3}{CH}-OC_2H_5 \quad \text{(VII)}$$



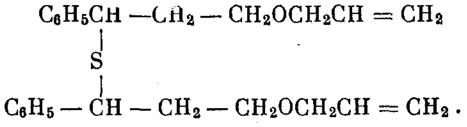
$$CH_2=\underset{CH_3}{C}-CH_2CH_2OCH_2CH=CH_2 \text{ (a) } (CH_3)_2C=CH-CH_2OCH_2CH=CH_2. \quad \text{(VIII)}$$

For (VIII) we determined the infrared spectrum. In the double bond region there were two absorption maxima of appreciable intensity at 1657 and 1683 cm^{-1}, of which the first was the larger. In the region of the characteristic out-of-plane deformation vibrations of $=C-H$ bonds there was a peak at 889 cm^{-1}, which belonged to the $CH_2{=}C\begin{smallmatrix}R_1\\R_2\end{smallmatrix}$ grouping, which confirms the formation of the compound (VIIIa). The second band, 1683 cm^{-1} indicates the presence of the compound (VIIIb).

By the reaction of 3-chloro-1-methyl-3-phenylpropyl ethyl ether and of allyl 3-chloro-3-phenylpropyl ether with sodium sulfide we obtained the corresponding sulfides:



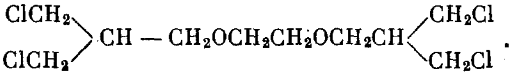
$$\begin{array}{l} C_6H_5CH-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-OC_2H_5 \\ \quad | \\ \quad S \\ \quad | \\ C_6H_5-CH-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-OC_2H_5 \end{array} \qquad (IX)$$



$$\begin{array}{l} C_6H_5CH-CH_2-CH_2OCH_2CH=CH_2 \\ \quad | \\ \quad S \\ \quad | \\ C_6H_5-CH-CH_2-CH_2OCH_2CH=CH_2\,. \end{array} \qquad (X)$$

Attempts to bring about the addition of 1-chloroethyl ethyl ether and of allyl chloromethyl ether to allyl chloride and to allyl acetate were not successful. When heated with these unsaturated compounds in presence of zinc chloride, the first chloro ether decomposed with formation of HCl and ethyl vinyl ether, which rapidly polymerized in presence of $ZnCl_2$. In the addition of the second α-chloro ether to allyl chloride and to allyl acetate much resin was produced, and we were unable to isolate the desired compounds.

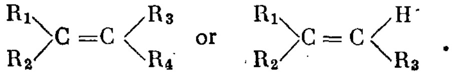
Apart from the above reactions we carried out also the addition of 1,2-bischloromethoxyethane to allyl chloride, styrene, and isobutene. 1,2-Bischloromethoxyethane was prepared by the method given by Lichtenberger [3]. By the addition of 1,2-bischloromethoxyethane to allyl chloride we obtained the compound



$$\begin{smallmatrix}ClCH_2\\ClCH_2\end{smallmatrix}\!\!>CH-CH_2OCH_2CH_2OCH_2CH<\!\!\begin{smallmatrix}CH_2Cl\\CH_2Cl\end{smallmatrix}\,. \qquad (XI)$$

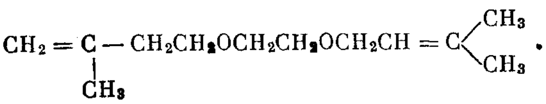
The direction of the addition of α-chloro ethers to allyl chloride was determined in work by Pishnamazzade and Gasanova [4]. We were unable to isolate the products of the addition of this dichloro ether to styrene and to isobutene in the pure state, because partial elimination of hydrogen chloride from the reaction products occurred during distillation. The product of the addition of 1,2-bischloromethoxyethane to styrene was dehydrochlorinated with solid potassium hydroxide, and we obtained the product $C_6H_5CH{=}CH{-}CH_2OCH_2CH_2OCH_2CH{=}CHC_6H_5$ (XII).

By the reaction of the product of the addition of 1,2-bischloromethoxyethane to isobutene with solid potassium hydroxide we obtained a product that did not contain chlorine. The infrared spectrum of this product was determined. It contained a characteristic band at 890 cm^{-1} due to the out-of-plane deformation vibrations of $=C-H$ bonds and a peak at 1652 cm^{-1}, which confirms the presence of a $CH_2{=}C\begin{smallmatrix}R_1\\R_2\end{smallmatrix}$ structure. A band at 1682 cm^{-1} may be assigned to



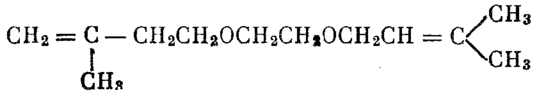
$$\begin{smallmatrix}R_1\\R_2\end{smallmatrix}\!\!>C=C<\!\!\begin{smallmatrix}R_3\\R_4\end{smallmatrix} \quad \text{or} \quad \begin{smallmatrix}R_1\\R_2\end{smallmatrix}\!\!>C=C<\!\!\begin{smallmatrix}H\\R_3\end{smallmatrix}\,.$$

The doublet at 1352, 1378 cm^{-1} confirms the presence of two methyl groups on one carbon atom. On the basis of these data we may consider the formula of the product to be



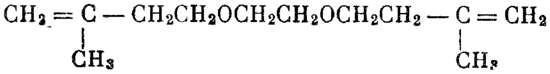
$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2CH_2OCH_2CH_2OCH_2CH=C<\!\!\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\,.$$

though on the basis of the same infrared data it may be supposed that the product is a mixture of the following isomers:



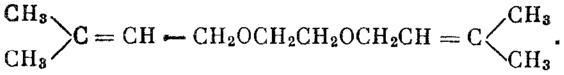
$$\underset{\displaystyle CH_3}{CH_2=\overset{}{C}}-CH_2CH_2OCH_2CH_2OCH_2CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$$

(a)



$$\underset{\displaystyle CH_3}{CH_2=C}-CH_2CH_2OCH_2CH_2OCH_2CH_2-\underset{\displaystyle CH_3}{C}=CH_2$$

(b)



$$\begin{matrix}CH_3\\CH_3\end{matrix}C=CH-CH_2OCH_2CH_2OCH_2CH=C\begin{matrix}CH_3\\CH_3\end{matrix}.$$

(c)

The peak at 1652 cm^{-1} is more intense than the peak at 1682 cm^{-1}. This gives us grounds to suppose that, if a mixture of products is obtained, then the most probable mixture is one of (a) and (b).

EXPERIMENTAL

Preparation of 3-Chloro-1,3-Dimethylbutyl Ethyl Ether. A mixture of 44 g of 1-chloroethyl ethyl ether and 2 g of mercuric chloride was prepared in a dark-colored bottle immersed in a cooling mixture at −18°. In the course of two hours 23 g of isobutene was passed into the bottle. The bottle was then tightly stoppered and left in the cooling mixture for 6-8 h; it was then left at room temperature for 2.5 days. At the end of the reaction the contents of the bottle were diluted with 100 ml of ether, and the ethereal solution was washed three times with water and dried with sodium sulfate. Ether was driven off, and the residue was vacuum-distilled. In the first fractionation from an Arbuzov flask we collected 43.3 g of a fraction boiling at 40-70° (10 mm). In refractionation from a flask with a Widmer column we obtained 34.7 g of the product of the addition of 1-chloroethyl ethyl ether to isobutene with the following constants: b.p. 42-44° (10 mm); d_4^{20} 0.9100; n_D^{20} 1.4218; Yield 52%. Found: Cl 22%; MR 45.94. $C_8H_{17}OCl$. Calculated: Cl 21.56%; MR 45.65.

Preparation of Allyl 3-Chloro-3-Methylbutyl Ether. This ether was prepared analogously from 51 g of allyl chloromethyl ether and 27 g of isobutene in presence of 2 g of mercuric chloride in 45% yield (35 g); b.p. 60-63° (10 mm); d_4^{20} 0.9461; n_D^{20} 1.4395. Found: Cl 21.8%; MR 45.96. C_8H_5OCl. Calculated: Cl 21.80%; MR 45.19.

Dehydrochlorination of 3-Chloro-1,3-Dimethylbutyl Ethyl Ether. As a result of three distillations of 11.2 g of 3-chloro-1,3-dimethylbutyl ethyl ether over solid potassium hydroxide (8 g each time) we obtained 5 g of dehydrochlorination product with the following constants: b.p. 110°; d_4^{20} 0.7967; n_D^{20} 1.4140; yield 57.4%. Found: C 74.96; 74.82; H 12.56; 12.77%; MR 40.21. $C_8H_{16}O$. Calculated: C 74.94; H 12.58%; MR 40.32.

The dehydrochlorination of allyl 3-chloro-3-methylbutyl ether was carried out analogously. A chlorine-free unsaturated compound was obtained; b.p. 140-143°; d_4^{20} 0.8221; n_D^{20} 1.4330; yield 71.4%. Found: C 76.25; 76.17; H 11.26; 11.30%; MR 39.85. $C_8H_{14}O$. Calculated: C 76.13%; H 11.18%; MR 39.89.

Preparation of 3-Chloro-1-Methyl-3-Phenylpropyl Ethyl Ether. A mixture of 36 g of 1-chloroethyl ethyl ether, 34.5 g of styrene, and 2 g of mercuric chloride was prepared in a snow-cooled dark-colored bottle. Thirty minutes after mixing the cooling bath was removed, and the bottle was left at room temperature for three days. At the end of the reaction the mixture was diluted with ether, and the solution was washed three times with water and dried with sodium sulfate. In the first fractionation we collected 41.5 g of a fraction of b.p. 85-89° (1 mm). Refractionation gave 40 g (56.7%) of a substance having: b.p. 87° (1 mm); d_4^{20} 1.0268; n_D^{20} 1.5002. Found: Cl 15.85%; MR 60.94. $C_{12}H_{17}OCl$. Calculated: Cl 16.66%; MR 60.25.

Allyl 3-Chloro-3-Phenylpropyl Ether was prepared analogously in 41.5% yield; b.p. 93-94° ($4\cdot10^{-2}$ mm); d_4^{20} 1.0587; n_D^{20} 1.5180. Found: Cl 17.10%; MR 60.38. $C_{12}H_{15}OCl$. Calculated: Cl 16.82%; MR 60.06.

Preparation of Dehydrochlorination Products. 11 g of 3-chloro-1-methyl-3-phenylpropyl ethery ether was heated under reflux with 9 g of solid potassium hydroxide for seven hours at 140°. Without any preliminary treatment the contents of the flask were fractionated. A fraction of b.p. 90-110° (8 mm) was refractionated from a flask with a Widmer column. We obtained 3 g (33%) of dehydrochlorination product: b.p. 100° (8 mm); d_4^{20} 0.9428; n_D^{20} 1.5184. Found: C 81.58; H 9.25%; MR 56.66. $C_{12}H_{16}O$. Calculated: C 81.77; H 9.15%; MR 55.19.

On heating 15.8 g of allyl 3-chloro-3-phenylpropyl ether with 8.5 g of potassium hydroxide dissolved in 50 ml of ethanol at 80-90° for eight hours we obtained 8 g (61%) of a chlorine-free ether: b.p. 136-138° (12 mm); d_4^{20} 0.9701; n_D^{20} 1.5314. Found: C 81.43; H 8.50%; MR 55.60. $C_{12}H_{14}O$. Calculated: C 82.77; H 8.10%; MR 54.72.

Preparation of Sulfides. A mixture of 20 ml of ethanol, 10 ml of water, and 9 g of $Na_2S \cdot 9H_2O$ was prepared in a round-bottomed flask fitted with reflux condenser. The mixture was brought to the boil, and 12.6 g of 3-chloro-1-methyl-3-phenylpropyl ethyl ether was added dropwise through the condenser, after which the mixture was heated for two hours at 80°. Alcohol was driven off, the mixture was diluted with water, and the organic layer was extracted with ether. The ethereal solution was dried with sodium sulfate and ether was driven off at the water pump. After the first fractionation we obtained 5 g of a substance of b.p. 105-135° (12 mm). After the second fractionation we obtained 4 g (35%) of the sulfide; b.p. 121-123° (12 mm); d_4^{20} 0.9765; n_D^{20} 1.5004. Found: C 74.25; H 9.05%; MR 116.49. $C_{24}H_{34}O_2S$. Calculated: C 74.57; H 8.87%; MR 117.11.

In an analogous way from 10.5 g of allyl 3-chloro-3-phenylpropyl ether we obtained 3 g (31.5%) of sulfide; b.p. 139-142° (1 mm); d_4^{20} 1.0492; n_D^{20} 1.5500. Found: C 75.54; 75.55; H 7.89; 7.82%; MR 116.13. $C_{24}H_{30}O_2S$. Calculated: C 75.35; H 7.91%; MR 116.18.

Addition of 1,2-Bischloromethoxyethane to Unsaturated Compounds

Addition to Allyl Chloride. A mixture of 24.8 g of 1,2-bischloromethoxyethane, 1 g of zinc chloride, and 0.5 ml of nitrobenzene was prepared in a round-bottomed flask fitted with reflux condenser. The flask was cooled with snow and salt to −18°. 23.8 g of allyl chloride was added dropwise through the condenser, and the reaction mixture was left overnight. On the next day the contents of the flask were heated at 50-60° in an oil bath for three hours. The treatment of the reaction mixture was carried out by the usual method (extraction with ether, washing, and drying). In the first fractionation we collected a fraction of b.p. 110-143° (1 mm) (6 g). Refractionation gave 4 g (8.2%) of a substance having: b.p. 153-155° (2 mm); d_4^{20} 1.2485; n_D^{20} 1.4841. Found: Cl 45.13; 45.63%; MR 71.50. $C_{10}H_{18}O_2Cl_4$. Calculated: Cl 45.45%; MR 71.13.

Addition of 1,2-Bischloromethoxyethane to Styrene, and Preparation of the Completely Dehydrochlorinated Product. For the experiment we took 70 g of styrene, 53.2 g of 1,2-bischloromethoxyethane, and 3 g of mercuric chloride. The mixture of the reactants was kept at room temperature for six days. It was then washed with water, and the organic layer was extracted with ether. The ethereal solution was dried with sodium sulfate. Ether was driven off at the water pump, and then excess of styrene was distilled of at 2 mm at a temperature of 50-60° in the bath. The residue amounted to 93.5 g and had: d_4^{20} 1.1370; n_D^{20} 1.5550; found Cl 15.72%. A mixture of 93 g of this undistilled product, 50 g of potassium hydroxide, and 100 ml of ethanol was introduced into a round-bottomed flask fitted with reflux condenser. The mixture was heated for eight hours with reflux of alcohol. Alcohol was driven off, the contents of the flask were diluted with water, the organic layer was extracted with ether, and the ether extract was dried. Ether was driven off, and the residue was heated up to 160° at a residual pressure of 3 mm. The weight of the residue after the heating was 45 g; d_4^{20} 1.0756; n_D^{20} 1.5792. Found: C 81.56; 81.34; H 7.57; 7.69%; MR 90.83. $C_{20}H_{22}O_2$. Calculated: C 81.59; H 7.54%; MR 89.71.

When the residue was heated above 160° at 3 mm the liquid thickened and partial decomposition occurred. The yield of undistilled product was 60%.

Addition of 1,2-Bischloromethoxyethane to Isobutene, and Preparation of Completely Dehydrochlorinated Product. The addition of the dichloro ether to isobutene was carried out by the procedure used in the preparation of 3-chloro-1,3-dimethylbutyl ethyl ether. We took 75 g of the dichloro ether, 55 g of isobutene, and 2.5 g of mercuric chloride. In the first fractionation we collected 40 g of a fraction of b.p. 90-110° (10 mm). Refractionation gave 34.6 g of a substance having: b.p. 115-120° (14 mm); d_4^{20} 1.0973; n_D^{20} 1.4538; found Cl 15.37; 15.22%. The 34.6 g of this product of the addition of 1,2-bischloromethoxyethane to isobutene, which was already partially dehydrochlorinated during the distillation, was distilled over potassium hydroxide three times. The third distillate did not contain chlorine. Distillation from a flask fitted with a Widmer column gave 6 g of completely dehydrochlorinated product; b.p. 104-106° (10 mm); d_4^{20} 0.8859; n_D^{20} 1.4508. Found: C 72.52; 72.54; H 11.30; 11.46%; MR 60.25. $C_{12}H_{22}O_2$. Calculated: C 72.67; H 11.18%; MR 59.96.

SUMMARY

1. The addition of 1-chloroethyl ethyl and allyl chloromethyl ethers to styrene and to isobutene was studied.

2. From the resulting 3-chloro-1-methyl-3-phenylpropyl ethyl and allyl 3-chloro-3-phenylpropyl ethers two sulfides were synthesized.

3. From these γ-chloro ethers, and also from 3-chloro-1,3-dimethylbutyl ethyl and allyl 3-chloro-3-methylbutyl ethers, unsaturated compounds were prepared by dehydrochlorination.

4. The addition of 1,2-bischloromethoxyethane to styrene, isobutene, and allyl chloride was carried out.

LITERATURE CITED

1. C. D. Hurd, Chem. Abstracts, 53, 2091 (1959).
2. M. F. Shostakovskii, Vinyl Ethers [in Russian], Izd. AN SSSR, pp. 108-109, 131 (1952).
3. J. Lichtenberger and L. Martin, Bull. Soc. Chim. France, 1945, 114.
4. B. F. Pishnamazzade and Sh. D. Gasanova, Azerb. khim. zh., 1960, No. 1, 35.