ACTION OF SULFURIC AND NITRIC ACIDS ON POLYCELOROALKANES AND POLYCHLOROALKENES

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The reaction of α , α , α , ω -tetrachloroalkanes with H_2SO_4 and HNO_3 was studied in detail in [1]. Compounds with the dichloromethyl group (RCH₂CHCl₂) are inert toward these acids [2]. The reaction of poly-chloroalkanes, containing the RCH₂CCl₂CH₂ grouping, and of polychloroalkenes with the RCH₂CCl = CH grouping (where R = CH₂Cl, CHCl₂), and of related compounds, with the indicated acids has received little study.

From the examples described in the literature [3-7] it follows that the hydrolysis of a dichloromethyl group in the allylic position, and of the chlorovinyl group, goes more easily than does the hydrolysis of the CCl_3 group, and the reaction does not involve the other halogen-containing groupings (CCl_3 , $CCl = CCl_2$, $(CH_2)_4$ Br) present in the molecule.

In the present paper we studied the action of H_2SO_4 and HNO_3 on $ClCH_2CH_2-CCl_2-(CH_2-CH_2)_n Cl(n=1,2)$ $CHCl_2-CH_2-CCl_2(CH_2)_4Cl$, $CH_3CCl=CH-CH_2Cl$, $ClCH_2CH_2CCl=CH(CH_2)_mCl(m=1,3)$, $CHCl_2CH_2CCl=CH \cdot (CH_2)_3Cl$.* The main difference between the studied compounds and those enumerated above is the presence of either CH_2Cl or $CHCl_2$ groupings in the β -position to the hydrolyzed group. Some of the obtained data are given in Table 1.

The hydrolysis of the investigated polychloroalkanes with conc. H_2SO_4 is accompanied by marked tarring and dehydrochlorination. A wide variation in the hydrolysis conditions (concentration of acid, temperature, time) failed to lead to yields of the ketones that were greater than those given in Table 1 for compounds (I) and (II). When a dichloromethyl group is present in the β -position to the dichloromethylene group, for example, in $CHCl_2-CH_2-CCl_2(CH_2)_4Cl$, the reaction with 92% H_2SO_4 solution fails to go at 65°C, while oxidation, with the formation of acids containing a smaller number of carbon atoms in the chain, occurs under more drastic conditions. All of the ω -chlorocarbocyclic acids that can be expected from the oxidation are formed when anhydrous HNO₃ acts on polychloroalkanes (I) and (II), and also the products of a more profound decomposition, for example CH_2O , which was identified as the 2,4-dinitrophenylhydrazone.

As can be seen from Table 1, the hydrolysis of polychloroalkenes (III)-(V) under the studied conditions goes more easily and in some cases gives better yields of the ketones. However, either a partial or a complete dehydrochlorination of the formed β -chlorethyl ketones also occurs under these conditions. Thus, the hydrolysis of compound (III) with H₂SO₄, similar to compound (I), gives divinyl ketone, which was isolated as the 2, 4-dinitrophenylhydrazone. Mixtures of the corresponding β -chlorethyl and vinyl ketones are formed in the other studied examples, namely (IV) and (V). A high yield of δ -chlorobutyl vinyl ketone was obtained from compound (IV) by the additional dehydrochlorination of the hydrolysis products with sodium acetate. We were unable to isolate the ketone with a β -chlorethyl group when (V) was hydrolyzed with H₂SO₄ which is evidently associated with the presence of the CH₃ group in series with the carbonyl group. Under the investigated conditions we were unable to obtain the corresponding ketones from the compounds that contain either the CHCl₂-CH₂-CCl₂ or the CHCl₂-CH₂-CCl=CH groupings.

The structure of the previously unknown δ -chlorobutyl vinyl ketone was confirmed by the NMR method. The NMR spectrum contains the ClCH₂ fragment (δ 3.50 ppm); the signal of the methylene group, found in series with the carbonyl group (2.60 ppm), and the signal from the other two methylene groups, with the center of the multiplet at 1.75 ppm. The signals of the vinyl portion of the spectrum are in good agreement with the data for propyl vinyl ketone [11], but they are shifted downfield by 0.3 ppm, which is evidently associated with the presence of chlorine in the δ -position.

* See [4,8-10] for the synthesis of polychloroalkanes and polychloralkenes with the indicated structure.

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	Reaction		Yield, in
	conditions		theory
$\mathrm{Cl}(\mathrm{CH}_2)_2\mathrm{CCl}_2(\mathrm{CH}_2)_2\mathrm{Cl}(\mathrm{I})$	92% H ₂ SO ₄ ,	$(CH_2=CH)_2C=N-NHC_6H_3$. $\cdot (NO_2)_2$	29
$Cl(CH_2)_2CCl_2(CH_2)_4Cl(II)$	$\begin{array}{c} 65^{\circ}, 6 \text{ h} \\ 92\% \\ \text{H}_2\text{SO}_4, \end{array}$	CH ₂ =CHCO(CH ₂) ₄ Cl	40
ClCH ₂ CH=CCl(CH ₂) ₂ Cl(III)	$50^{\circ}, 4^{\circ}$ h 92% $H_2SO_4,$	$(CH_2=CH)_2C=N-NHC_6H_3$. · $(NO_2)_2$	30
$Cl(CH_2)_2CCl=CH(CH_2)_3Cl(IV)$	$30^{\circ}, 2 h$ 92% $H_2SO_4,$	CH ₂ =CHCO(CH ₂) ₄ Cl	70
ClCH ₂ CH=CClCH ₃ (V)	30° , 1 h 92%- H_2SO_4 ,	$ClCH_2CH_2COCH_3$ $CH_2=CHCOCH_3$	40 11
$\mathbf{CHCl_2CH_2CCl_2(CH_2)_4Cl(VI)}$	$25^{\circ}, 40 \text{ h}$ 98% $H_2SO_4,$	$\begin{array}{c} \mathrm{CHCl}_{2}\mathrm{CO}_{2}\mathrm{H}\\ \mathrm{Cl}(\mathrm{CH}_{2})_{4}\mathrm{CO}_{2}\mathrm{H} \end{array}$	17 *
(I)	65°, 6 n 100% HNO ₃ ,	$Cl(CH_2)_n CO_2H$ n = 1, 2	39 *
(11)	50°, 6 h 100% HNO ₃ , 50° 6 h	$Cl(CH_2)_n CO_2 CH_3$ n = 1-4	51 *
	100,04 1		1

TABLE 1. Action of Acids on Polychloro Hydrocarbons

*The yields are based on the sum of the acids or esters.

A simulation was made of the spectrum on the basis of the parameters; $\delta_A = -4.25$, $\delta_B = +19.29$, $\delta_C = -12.4$ Hz (the chemical shifts are given relative to the center of the ABC multiplet, $\nu = 388.6$ Hz = 6.47 ppm). JAB = 1.15, J_{AC} = 17.5, J_{BC} = 10.7 Hz. The calculated spectrum is in satisfactory agreement with the experimental spectrum.

EXPERIMENTAL METHOD

The NMR spectra were obtained on a Hitachi–Perkin–Elmer R-20 instrument (60 MHz) for 30% solutions of the compound in CCl₄, relative to TMS. The GLC analysis of the ketones was run on an instrument equipped with a flame-ionization detector, a 1 m \times 0.2 cm column, while the stationary phase was 8% SE-30 deposited on Chromosorb W (80-100 mesh), and nitrogen was used as the carrier gas. The GLC analysis of the methyl esters of the ω -Cl-carboxylic acids was run on an instrument equipped with a detector based on the heat conductivity, a 1 m \times 0.3 cm column, 6% SE-301 or 6% polyethylene glycol deposited on Chromosorb W (60-80 mesh) as the stationary phase, and helium as the carrier gas.

<u>Action of H_2SO_4 on Polychloro Hydrocarbons</u>. 1,3,3,5-Tetrachloropentane (I). A stirred mixture of 10.5 g of (I) and 40 ml of 92% H_2SO_4 solution was heated at 65°C until the evolution of HCl was quantitative (6 h), after which it was poured over ice and steam-distilled. From the distillate we obtained 3.9 g of the 2,4-dinitrophenylhydrazone of divinyl ketone, mp 162° (from alcohol); cf. [4].

<u>1,3,5-Trichloro-2-pentene (III)</u>. After a similar treatment, from a mixture of 10.6 g of (III) and 20 ml of 92% H₂SO₄ solution at 30° for 2 h we obtained 3.7 g of the 2,4-dinitrophenylhydrazone of divinyl ketone, with mp 162°, and 1.3 g of the starting trichloropentene.

<u>1,3,3,7-Tetrachloroheptane (II)</u>. A mixture of 40 g of (II) and 200 ml of 92% H₂SO₄ solution was heated at 50° for 4 h, and then it was poured over ice and extracted with ether. After distilling off the solvent, the residue was treated with CH₃COONa in methanol as described in [12]. We obtained 10.1 g of δ -chlorobutyl vinyl ketone, bp 68° (2 mm); n_D²⁰ 1.4672; d₄²⁰ 1.0418. Found, %: C 57.22; H 7.58; Cl 24.16; MR 39.06. C₁₇H₁₁CClO. Calculated, %: C 57.34; H 7.56; Cl 24.18; MR 38.94.

<u>1,3,7-Trichloro-2-heptene</u> (IV). After a similar treatment, from a mixture of 10 g of (IV) and 20 ml of 92% H₂SO₄ solution at 30° for 1 h we obtained 5.1 g of δ -chlorobutyl vinyl ketone.

<u>1,3-Dichloro-2-butene (V)</u>. A mixture of 12.5 g of (V) and 30 ml of 92% H₂SO₄ solution was stirred at 25° for 40 min, and then it was poured over ice and extracted with ether. After a double distillation in the presence of hydroquinone we isolated 0.8 g of methyl vinyl ketone, bp 80°; n_D²⁰ 1.4090; d₄²⁰ 0.8609; cf. [13] and 4.14 g of methyl β -chloroethyl ketone, bp 66° (42 mm); n_D²⁰ 1.4370; d₄²⁰ 1.0953; cf [14]. The NMR spectrum of methyl β -chloroethyl ketone consists of the singlet of δ_{CH} at 2.18 ppm, and the triplets of δ_{CH_2} at 2.90 and δ_{CH_2Cl} at 3.71 ppm. The integral intensities correspond to the assumed assignments.

Action of HNO₃ on 1,3,3,7-Tetrachloroheptane II. To 10 g of (II) was gradually added 30 ml of HNO₃ solution (d 1.52) at 50° and the mixture was allowed to stand for 6 h. The HNO₃ was distilled in vacuo (water jet pump), and the residue was vacuum-distilled. We collected the fraction with bp 92-135° (7 mm) (7.6 g), to which was added an ether solution of CH_2N_2 . After distilling off the solvent, the residue (7.1 g), based on the GLC data, represented a mixture of the methyl esters of ω -chloroacetic (3%), ω -chloropropionic (18%), ω -chlorobutyric (15%), and ω -chlorovaleric (15%) acids.

CONCLUSIONS

1. A study was made of the action of conc. H_2SO_4 on polychloro hydrocarbons that contain the groupings $RCH_2CCl_2CH_2$ -and $RCH_2CCl=CH$ -(where $R = CH_2Cl$, $CHCl_2$). Ketones were obtained from the compounds where $R = CH_2Cl$.

2. The hydrolysis is accompanied by the dehydrochlorination of the β -chloroethyl group to give the corresponding vinyl ketones.

3. Under the studied conditions the hydrolysis of the chlorovinyl group goes more easily than that of the dichloromethylene group.

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