DEHYDROCHLORINATION OF POLYCHLOROALKANES THAT CONTAIN THE CH₃CCl₂CH₂CHCl GROUP

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In continuation of studying the dehydrochlorination of polychloroalkanes of variable structure [1, 2], in the present paper we studied the catalytic and alkaline dehydrochlorination of compounds of type CH_3 - CCl_2CH_2CHClX [X = H (I), Cl (II), CH₃ (III)]. Compounds (I)-(III) differ from those previously studied by us in that one of the substituents attached to the CCl_2 group is the CH_3 group. Of the compounds of this type the catalytic dehydrochlorination of 2,2-dichloro-6-bromohexane was described previously [3]. The reaction proceeds in the presence of FeCl₃ at 40-60° and leads to the chlorobromohexene in 80% yield; the direction of the dehydrochlorination was not established.

It was found that the catalytic and alkaline dehydrochlorination of compounds (I)-(III) leads to the formation of different products, and that the course of the dehydrochlorination is affected by the nature of the X substituent.

Previously it was mentioned that the presence of one and, even more so, of two chlorine atoms in the β -position to the CCl₂ group hinders the dehydrochlorination when Friedel-Crafts catalysts are used [1]. This fact also found confirmation when studying the catalytic dehydrochlorination of compounds (I)-(III), which proceeds at a higher temperature and with a lower yield of the dehydrochlorination product when compared with 2,2-dichloro-6-bromohexane (Table 1). In all cases the yield of the dehydrochlorination products does not exceed 30%, despite the high conversion of the starting compounds.

On the example of (II) it was shown that the best dehydrochlorination catalyst for these compounds is a mixture of $ZnCl_2$ and $FeCl_3$ in a ratio of ~6:1. In the presence of $ZnCl_2$ alone the reaction time increases 2 to 3 times, in the presence of $FeCl_3$ the yield of the product drops to 10%, while in the presence of $AlCl_3$ alone the reaction mass is converted completely to a tar.

The catalytic dehydrochlorination of compounds (I)-(III) proceeds by the following scheme



A mixture of 2,4-dichloro-2-butene and 2,4-dichloro-1-butene (IV) is obtained as the result of the dehydrochlorination of (I), i.e., the reaction proceeds along both directions a and b. The catalytic dehydrochlorination of (II) gave 2,4,4-trichloro-1-butene (V), while the dehydrochlorination of (III) gave 2,4-dichloro-1-pentene (VI) (see Table 1). Despite the fact that the reaction with (III) proceeds at a lower temperature, the yield of the dehydrochlorination product is not improved.

On the basis of the obtained data it may be formally concluded that in the case of (II) and (III) the dehydrochlorination proceeds via the chlorine of the CCl_2 group and the hydrogen of the CH_3 group, i.e., along direction *a*. However, it is not excluded that the catalytic dehydrochlorination of (II) and (III), the same as that of (I), proceeds along directions, but the products, formed according to direction b, are converted to a tar under the synthesis conditions. Actually, it was shown by a special experiment that 2,4,4-trichloro-2-butene, which should be formed by direction b in the dehydrochlorination of (II), is con-

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TABLE 1

Starting compound	Reaction compound	Catalyst	T., °C	Yield, %	Conver- sion,%
(11)	CH ₂ =CClCH ₂ CHCl ₂ (V)	ZnGl2* FeCl3 AlCl3 ZnCl2 + FeCl3	160—170 160—170 160—170 160—170	$\begin{array}{c} 25\\ 10\\ \overline{27}\end{array}$	80 100 100 76
(I)	$ \left\{ \begin{array}{ll} CH_2 = CClCH_2CH_2Cl & (IV) & 60\% \\ CH_3CCl = CHCH_2Cl & 40\% \end{array} \right. $	The same	140150	27	80
(III)	CH ₂ =CClCH ₂ CHClCH ₃ (VI)	57	110-120	26	75

* Reaction time 5 h; in the other cases it was 1.5-2h.

TABLE 2

			Reaction conditions			
compound	Reaction products	vield,	T, °C	moles of KOH/mole of starting compoun		
(I)	CH ₃ CCl ₂ CH=CH ₂ CH ₃ CCl=CHCH ₂ Cl CH ₃ CCl=CHCH ₂ Cl ₂ CH ₂ OCH ₃	23 20 8	0—5	1		
(11)	CH ₃ CCl ₂ CH=CHCl (VII) 35% CH ₃ CCl=CHCHCl ₂ (VIII) 65%	87	510	1		
(111)	$\begin{array}{c} CH_{3}CCI=CHCHClCH_{3} (IX)\\ CH_{3}CCI=CHCHCH_{3} (X)\\ & \\ OCH_{2}CH_{2}OCH_{3}\end{array}$	23 3	10-20	1		
(III)	(IX) (X)	11 32	20	3		

converted completely to a tar when heated at 130° for 20 min in the presence of catalytic amounts of a $ZnCl_2 + FeCl_3$ mixture. As a result, the catalytic dehydrochlorination of compounds (I)-(III) is accomplished via the chlorine of the CCl_2 group in the direction of both the methyl and, apparently, the methylene groups.

The data on the alkaline dehydrochlorination of (II) and (III) under the influence of KOH in methyl cellosolve are given in Table 2. For comparison we have also given in Table 2 the data on the dehydro-chlorination of (I), which were reported by us previously [2].



The dehydrochlorination of (II, X = Cl), the same as that of (I), proceeds with an involvement of the hydrogen of the CH₂ group and the chlorine of both of the chlorine-containing groups, and leads to the formation of a mixture of 1,3,3-trichloro-1-bute e (VII) and 1,1,3-trichloro-2-butene (VIII) in a respective ratio of 35:65 (GLC). If it is taken into account that the yield of the mixed isomers is close to quantitative, while compound (VIII) is formed in an amount that is approximately twice that of (VII), then it may be concluded that dehydrochlorination toward the CCl₂ group is accomplished to a greater degree than toward the CHCl₂ group.

A mixture of (VII) and (VIII) when heated with catalytic amounts of $ZnCl_2$ at 80° for 10 min is converted to (VIII), i.e., (VII) under the influence of $ZnCl_2$ undergoes allylic anionotropic rearrangement, the same as occurred in the case of 3,3,3-trichloro-1-propene [5].

The alkaline dehydrochlorination of (III) gives a complex mixture of products. However, 2,4-dichloro-2-pentene (IX) was isolated in the reaction with an equimolar ratio of the reactants; under the conditions of excess alkali, (III): KOH = 1:3, the main reaction product is 2-chloro-4-(β -methoxyethoxy)-2pentene (X). In addition, based on the NMR data, the fraction from which (IX) was isolated also contains CH₃CCl₂CH = CHCH₃ (characteristic signal of the CH₃CH group). Based on the NMR spectrum, the lowboiling fraction (two substances according to GLC) represents a mixture of the dienes CH₃CCl = CHCH = CH₂ and CH₂ = CClCH = CHCH₃. These products were not isolated in the pure state. As a result, the

TABLE 3

	1	δ, ppm from HMDS				J, Hz		
Compound	Sol-						_	_
	vent '	H _A	H_B	-CHCl-	-CH3CHCI	J_{AB}	JAX	JBX
$CH_{3}CCl_{2}CH_{2}CHClCH_{3}^{*}$ (111) $CH_{2}==CClCH_{2}CHClCH_{3}$ (V1)	$\begin{bmatrix} \mathrm{CCl}_4 \\ \mathrm{C}_6\mathrm{H}_6 \\ \mathrm{CCl}_4 \\ \mathrm{C}_6\mathrm{H}_6 \end{bmatrix}$	$2,65 \\ 2,19 \\ 2,60 \\ 2,27$	$2,65 \\ 2,37 \\ 2,60 \\ 2,39$	$\begin{array}{r} 4,28 \\ 4,06 \\ 4,18 \\ 3,96 \end{array}$	1,58 1,25 1,46 1,13	-15,6 -14,5	$6,7 \\ 7,3$	4,0 7,5

* $\delta_{CH_3CCl_2} = 2.05$ ppm in CCl₄, and $\delta_{CH_3CCl_2} = 1.90$ ppm in C₆H₆.

TABLE	:4
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		δ, ppm from HMDS							
Compound	Solvent	Hı	H2	=CCICH ₂	$\begin{array}{c} -\mathrm{CH_2Cl} \mathrm{Or} \\ -\mathrm{CHCl_2} \end{array}$				
H_{1}	CCl4	5,30	5,30	2,65	3,56				
H_2 CH ₂ CH ₂ CH ₂ Cl	C_6D_6	4,88	5,04	2,25	3,29				
$CH_2 = CClCH_2CHCl_2$ (V)	$\begin{array}{c} { m CCl}_4 \\ { m C_6D_6} \end{array}$	$5,37 \\ 4,90$	$5,37 \\ 5,08$	$3,12 \\ 2,74$	5,94 5,69				
$CH_2 = CClCH_2CHClCH_3 * (VI)$	$\begin{array}{c} \mathrm{CCl}_4 \\ \mathrm{C}_6\mathrm{D}_6 \end{array}$	$5,21 \\ 4,78$	$5,21 \\ 4,95$		-				

* See Table 3 for the chemical shifts of the other protons.

alkaline dehydrochlorination of (III) proceeds via the chlorine of both the CCl_2 and CHCl groups, in which connection the formed monoenes undergo further dehydrochlorination to dienes, while, in addition, in (IX) the allylic chlorine atom is replaced by an alkoxy group to give (X).

The structure of all of the obtained compounds was confirmed by the NMR method. As a rule, the NMR spectra represent the sum of the spectra of the fragments (1, 2, 7) known to us, for which reason we will discuss in detail only the characteristic traits of these spectra. The molecules $CH_3CCl_2CH_2CHClCH_3$ (III) and $CH_2 = CClCH_2CHClCH_3$ (VI) contain an asymmetric center, but the nonequivalence of the methylene protons is manifested only in C_6H_6 (Table 3).

The presence of the $CH_2 = CCl$ group is common for compounds (IV), (V), and (VI). It was found that in CCl_4 the H_1 and H_2 protons have equal shielding (a singlet in the spectrum), but in C_6H_6 they are non-equivalent (Table 4).

Compounds (VIII), (IX), and (X) belong to the type of compounds that were discussed in detail previously [6]. The spectral traits were ascertained for the Z- and E-isomers, of which only the chemical shift of the -CH = protons and the vicinal constant $J_{(=CH-CHCL-)}$ are characteristic in the given series of compounds (Table 5). Based on the data of the NMR spectra, (VIII) is found to be approximately 90% in the Z-form, for (IX) the Z: E ratio is ~70:30, while in compound (X) the E-isomer predominates somewhat.

The structure of $CH_3CCl_2CH = CHCl$ (VII) was proved by the NMR spectrum, which was obtained for a mixture of (VII) and (VIII). The NMR spectrum of (VIII) is given in Table 5. The NMR spectrum of (VII) consists of the known fragment of the CH_3CCl_2 and CHCl = CH group (AB system, $J_{AB} = 13.2$ Hz; $\delta_A = 6.60$; $\delta_B = 6.32$ ppm). Noticeable contamination with the second geometric isomer is absent. By analogy with [2, 6] it is possible to assume that (VII) is found mainly in the E-form.

EXPERIMENTAL METHOD

The GLC analysis was run on an instrument equipped with a flame-ionization detector and a 1 m \times 3 mm column packed with 8% SE-30 deposited on Chromosorb W. Nitrogen was used as the carrier gas.

The NMR spectra were obtained on a Hitachi-Perkin-Elmer R-20 instrument of 60 MHz, for 30% solutions of the compounds in CCl_4 , C_6D_6 , or C_6H_6 , at 34°.

<u>2,2,4-Trichloropentane (III)</u>. As described in [7], (III) was obtained in 37% yield from 1,1,1-trichloroethane and propylene using a trichloroethane-propylene mole ratio of 1:1. The constants and analysis of (III), and also of the other newly obtained compounds, are given in Table 6.

TABLE 5

			δ, pj				
Compound	Sol- vent	Configu- ration	CH₃CCl−	CH₃CH	–ĊH	=CH-	JCHCH
CH ₃ CCl=CHCHCl ₂ (VIII)	Z	CCl ₄	$2,11 \cdot 1 = 1$	_	$^{6,47}_{6,38}$	5,76	9,0
	E	$\begin{array}{c} C_6 D_6 \\ CCl_4 \\ C_6 D_6 \end{array} *$	2,11 1,50	-	6,22	6,03	9,8
CH ₃ CCl=CHCHClCH ₃ (IX)	Z	CCl ₄ CeDe	1,50 1,23	2,06	$4,76 \\ 4,84$	$5,48 \\ 5,32$	9,3
	E	CCl ₄ C ₆ H ₆	1,52 1,13	2,07 1,64	$4,58 \\ 4,30$	$5,76 \\ 5,61$	10,0
CH ₃ CCl==CHCHCH ₃ (X)	Z	CCl ₄ CeDa	2,06 1.74	1,12	$4,23 \\ 4,26$	5,36 5,17	8,0
OCH2CH2OCH3	E	CCl ₄ C ₆ D ₆	$\begin{array}{c}2,04\\1,76\end{array}$	1,14 0,99	$\begin{vmatrix} 4,04\\ 3,79 \end{vmatrix}$	$5,44 \\ 5,42$	9,0

* The assignment is made difficult in view of the fact that the E-form is present in small amount (~10%) in C_6D_6 .

Compound	Bp, °C (p, mm	n_D^{20}	d_4^{20}	MR found	found calculated			
	of Hg)			calculated	C	н	CI	
CH ₃ CCl ₂ CH ₂ CHClCH ₃ [8]	65(26)	1,4621	1,2041	$\frac{40,07}{39,89}$	$\frac{34,42}{34,22}$	$\frac{5,11}{5,19}$	$\frac{60,29}{60,59}$	
CH ₂ =CClCH ₂ CHCl ₂	74(98)	1,4800	1,3070	$\frac{34,53}{34,80}$	$\frac{30,34}{30,13}$	$\tfrac{3,25}{3,16}$	$\frac{66,70}{66,71}$	
CH2=CClCH2CHClCH3	75(100)	1,4563	1,0945	$\frac{34,58}{34,55}$	$\frac{43,33}{43,19}$	$\frac{5,73}{5,82}$	$\frac{50,71}{50,99}$	
CH ₃ CCl=CHCHCl ₂	83(93)	1,4861	1,2953	$\frac{35,26}{34,81}$	$\frac{30,32}{30,13}$	$\frac{3,17}{3,16}$	$\frac{66,00}{66,71}$	
CH3CCl=CHCHClCH3	79(97)	1,4641	1,0908	$\frac{35,08}{34,55}$	$\frac{43,39}{43,19}$	$\frac{5,81}{5,82}$	$\frac{50,38}{50,99}$	
CH3CCl=CHCHCH3	83(15)	1,4473	1,0108	$\frac{46,83}{47,25}$	$\frac{53,37}{53,77}$	$\frac{8,52}{8,46}$	$\frac{20,00}{19.85}$	
OCH2CH2OCH3	ļ				,	,	,	

TABLE 6

Catalytic Dehydrochlorination

<u>1,1,3,3-Tetrachlorobutane (II)</u>. To 58.8 g of (II) at 100° was added 0.2 g of a mixture of $ZnCl_2 + FeCl_3$ and the reaction products were distilled off slowly (the temperature of the reaction mixture was 160-170°). The distillation was accompanied by the evolution of HCl. The distillate at 130-135° was collected, which was distilled through a column. We obtained 11.9 g of (IV) and 14.1 g of (II).

1,3,3-Trichlorobutane (I). The dehydrochlorination of (I) was run in a similar manner at $140-150^{\circ}$. The distillate was collected at $110-120^{\circ}$. From 16.1 g of (I), after distillation through a column, we obtained 3.4 g of a mixture of (IV) and 2,4-dichloro-2-butene, bp 71-73° (100 mm), in a respective ratio of 3:2, and 3.1 g of (I).

2,2,4-Trichloropentane (III). The dehydrochlorination of (III) was run at $110-120^{\circ}$. After the calculated amount of HCl had evolved the reaction product was distilled off at $70-135^{\circ}$ (135 mm), and then redistilled through a column. From 70 g (0.4 mole) of (III) we obtained 14.1 g of (VI) and 17.5 g of (III).

Alkaline Dehydrochlorination

<u>1,1,3,3-Tetrachlorobutane (II)</u>. With stirring, a solution of 18.4 g of KOH in methyl cellosolve was added to 58.8 g of (II) at 5-10°. After stirring for 4-5 h the mixture was diluted with water. The organic layer was separated, washed with water, and dried over $CaCl_2$. Distillation through a column gave 41.7 g of a mixture of (VII) and (VIII) in a respective ratio of 35:65.

2,2,4-Trichloropentane (III). In the same manner as the preceding, at 20°, from 35.2 g of (III) and 12.6 g of KOH, after distillation through a column, we obtained 6.5 g of (IX), 1.2 g of (X), and 8.8 g of (III).

From 17.5 g of (III) and 18.0 g of KOH under the same conditions we obtained 1.4 g of (IX) and 5.8 g of (X).

<u>Isomerization of 1,3,3-Trichloro-1-butene (VII) to 1,1,3-Trichloro-2-butene (VIII).</u> A catalytic amount of ZnCl_2 was added at 80° to 4.8 g of mixed isomers (VII) and (VIII), obtained by the alkaline dehydrochlorination of (II). After 10 min the reaction mixture was cooled and decanted from the precipitate into a distillation flask. Distillation gave 4.2 g (87%) of 1,1,3-trichloro-2-butene (VIII).

CONCLUSIONS

1. The catalytic dehydrochlorination of compounds of general formula $CH_3CCl_2CH_2CHCIX$ (X = H, Cl, CH₃) under the influence of Friedel-Crafts catalysts is accomplished via the chlorine of the dichloromethylene group toward both the methyl and the methylene groups.

2. The alkaline dehydrochlorination of the same compounds proceeds with the involvement of the hydrogen of the methylene group and the chlorine of both chlorine-containing groups.

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