DEHYDROCHLORINATION OF POLYCHLORO HYDROCARBONS BY POTASSIUM HYDROXIDE IN METHYL CELLOSOLVE MEDIUM

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In previous papers [1, 2] we proposed a two-step method for the preparation of substituted chloroprene homologs, starting with polychloro hydrocarbons of structure $Cl(CH_2)_nCCl_2CH_2CHClX$ [3]. The catalytic dehydrochlorination of such polychloro hydrocarbons by metal chlorides proceeds selectively, via the chlorine of the dichloromethylene group toward the less chlorinated and longer chain of the molecule, counting from the $-CCl_2$ group [1]. The further alkaline dehydrochlorination of the formed polychloroalkenes leads to the formation of substituted chloroprene homologs [2]. The obtained dienes are easily polymerized under radical conditions with the formation of self-extinguishing, film-forming polymers [4, 5].

The purpose of the present paper was to study the alkaline dehydrochlorination of polychloro hydrocarbons in order to ascertain if dienes can be obtained in one step and to establish the rules of alkaline dehydrochlorination. The dehydrochlorination was run with alkali in methyl cellosolve at $0-20^{\circ}$; the obtained results are given in Table 1. As can be seen from Table 1, all of the starting compounds contain either two (I)-(III) or three (IV)-(V) chlorine-containing functions. In contrast to catalytic dehydrochlorination, which proceeds selectively, the alkaline dehydrochlorination proceeds in a more complicated manner, with the involvement of at least two chlorine-containing functions.

The dehydrochlorination of 1, 3, 3, 5-tetrachloropentane (I) (here and subsequently the numbers are given in harmony with Table 1) leads to the formation of 3, 5-dichloro-1, 3-pentadiene (VI) and 3, 3, 5-tri-chloro-1-pentene (VII). In a special experiment it was shown that the further dehydrochlorination of (VII) leads to (VI)

 $\begin{array}{c} ClCH_{2}CH_{2}CCl_{2}CH_{2}CH_{2}Cl & \longrightarrow CH_{2} = CHCCl_{2}CH_{2}CH_{2}Cl \\ (I) & & & & & \\ (VII) & & & & \\ ClCH_{2}CH = CClCH_{2}CH_{2}Cl & \longrightarrow CH_{2} = CHCCl = CHCH_{2}Cl \\ (VI) & & & \\ \end{array}$

At the same time, as was shown by us previously [2], (VI) is easily formed from 1,3,5-trichloro-2pentene. However, 1,3,5-trichloro-2-pentene was not found in the reaction mixture (based on an authentic specimen by the GLC method), and for this reason it is difficult to say whether (VI) is formed only from (VII) or also partially from 1,3,5-trichloro-2-pentene.

As a result, on the example of (I) it is impossible to determine if the reaction proceeds in the first step only via the chlorine of the chloromethyl group or also partially via the chlorine of the dichloromethylene group. For comparison we ran the dehydrochlorination of 1, 3, 3-trichlorobutane (II). In this case the reaction proceeds with the involvement of the chlorine atoms of both chlorine-containing groups to approximately the same degree, and leads to 3, 3-dichloro-1-butene (IX), 1, 3-dichloro-2-butene (X), and also (XI) – the replacement product of the allylic chlorine by the β -methoxyethoxy group (subsequently called the alkoxy group). In a special experiment it was shown that the treatment of (I) with excess alkali in methyl cellosolve gives (VIII), i.e., compounds, containing an allylic chlorine atom, replace it under the synthesis conditions by the alkoxy group.

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		ło%	Bp, °C (p,	20	20	Found /	calcula	ted, %
Starting compounds	Reaction products	тіелі, тієла,	imm of Hg)	<u>d</u> u	d 4	υ	н	ច
ClCH2CH2CCl2CH2CH2Cl (I)	$CH_{a} = CHCCI = CHCH_{a}CI$ (VI)	20						
	CH2=CHCCl2CH2CH2Cl (VII)	25	70(21)	1,4852	1,2650	$\frac{34,69}{34,61}$	$\frac{3, 99}{4, 07}$	$\frac{60,89}{61,32}$
	$CH_{2} = CHCCl = CHCH_{2}OCH_{2}OCH_{3} * (VIII)$	36	98(12)	1,4830	1,0591	$\frac{54,23}{54,39}$	$\frac{7,38}{7,42}$	20,21 20,07
CH ₅ CCl ₂ CH ₂ CH ₂ CI (11)	$CH_{S}CCl_{2}CH=CH_{2}$ (IX) $CH_{S}CCl=CHCH_{2}Cl$ (X)	5 33						
	CH ₃ CCl=CHCH ₂ OCH ₂ CH ₂ OCH ₂ (XI)	∞	84(15)	1,4502	1,0432	$\frac{51,07}{51,06}$	$\frac{7,97}{7,96}$	$\frac{21,65}{21,54}$
CHaCClaCHaCH=CHCH2Cl (III)	CH ₃ CCl=CHCH=CHCH ₂ Cl (X11)	44	7778(12)	1,5340	1,1376	$\frac{47,56}{47,71}$	5,35 $5,34$	$\frac{46,98}{46,95}$
	CH ₃ CCl=CHCH=CHCH ₂ OCH ₂ CH ₂ OCH ₃ * (X111)	58	81(2)	1,4940	1,0424	56, 50 56, 69	$\frac{7,90}{7,93}$	$\frac{18,73}{18,60}$
CHCl ₂ CH ₃ CCl ₃ CH ₂ CH ₂ Cl (IV)	$CHCl_{2}CH = CClCH = CH_{2}$ (XIV)	36		-		00.06	9.0%	67 <u>98</u>
	$CHCl = CHCCl_2CH_2CH_2Cl (XV)$ $CHCl = CHCCl_2CH_2Cl^+ (XVI)$	2,5	75,5-76(4)	1,5170	1,4057	28,88	2,91	68,21
CHCl ₂ CH ₂ CCl ₂ CH ₂ CH ₂ CH ₂ Cl ₂ Cl (V)	CHCl ₂ CH=CCl(CH ₂) ₄ Cl (XVII)	29	112(4)	1,5060	1,2940	35,73 35,63	$\frac{4,31}{4,27}$	59,90 60,10
	$CHCl=CHCGl=CH(CH_2)sCl (XVIII)$ $CHCl_2C=C(CH_2)sCl (XIX)$	27				$\frac{41,92}{42,14}$	$\frac{4,59}{4,55}$	53, 57 53, 34

TABLE 1. Constants and Analyses of Obtained Compounds

*The yields are given from the experiments that were run specially to obtain these compounds. † Indentified by GLC employing an authentic specimen.

Com-	Config-	Solvent		δ, ppm	
pound	uration	OUTVOIL	CH3CCI=	CH-	CH₂X
х	Z E Z E	CCl4 C6H6	2,14 2,14 1,80 1,80	5,63 5,75 5,33 5,58	4 ,05 3 ,96 3 ,92 3 ,62
XI	Z E Z E	CCl ₄ C6H6	2,07 2,07 1,85 1,85	5,55 5,67 5,51 5,70	4,00 3,87 4,02 3,78

TABLE 2. Chemical Shifts of Protons for $CH_3CCl = CH \cdot CH_2X$, X = Cl(X); $OCH_2CH_2OCH_3$ (XI)

1, 5-Dichloro-2, 4-hexadiene (XII) was obtained from 1, 5, 5-trichloro-2-hexene (III), i.e., the reaction went via the allylic hydrogen atom and the chlorine of the dichloromethylene group. In a separate experiment it was shown that when (III) is treated with excess alkali the allylic chlorine in the formed (XII) is also replaced by the alkoxy group, forming (XIII).

In principle, the dehydrochlorination of 1, 1, 3, 3, 5-pentachloropentane (IV) and 1, 1, 3, 3, 7-pentachloroheptane (V) can proceed in four directions:



In the dehydrochlorination of (IV) were isolated 3, 5, 5-trichloro-1, 3-pentadiene (XIV) and 1, 3, 3, 5-tetrachloro-1-pentene (XV), and 1, 3, 5-trichloro-1, 3-pentadiene was identified by GLC employing an authentic specimen.

As the result of the dehydrochlorination of (V), from the reaction products were isolated 1, 1, 3, 7-tetrachloro-2-pentene (XVII) and a mixture that was composed of 1, 3, 7-trichloro-1, 3-heptadiene (XVIII) and 1, 1, 7-trichloro-2-heptene (XIX) in approximately equal amounts.

The obtained data make it possible to conclude that the dehydrochlorination of (IV) and (V) proceeds along directions 1 and 2 (see Scheme 1) via the most labile hydrogen atoms of the methylene group, located between the dichloromethyl and dichloromethylene groups. From a comparison of the obtained results it can be seen that the alkaline dehydrochlorination of the $CCl_2CH_2CH_2Cl$ grouping [compounds (I) and (II)] proceeds via the chlorine atoms of the chloromethyl and dichloromethylene groups in the same manner as the alkaline dehydrochlorination of tetrachloropropane [6]. If the molecule contains a $CHCl_2CH_2CCl_2CH_2CH_2$ grouping with different methylene groups and different CCl_2 groups [compounds (IV) and (V)] the reaction is accomplished via the methylene group with the most labile hydrogen atoms. The cleavage of the chlorine atoms is nonselective and proceeds with the involvement of both of the chlorine-containing groupings.

The structure of the compounds, listed in Table 1, was confirmed by the NMR spectra. For CH₃ \cdot CCl₂CH₂CH₂Cl (II) δ_{CH_3} 2.20, δ_{CH_2} 2.67, δ_{CH_2Cl} 3.77 ppm. For CH₂ = CHCCl₂CH₂CH₂Cl (VII) the spectrum represents the sum of the characteristic signals of the CCl₂CH₂CH₂Cl and $\frac{H_1}{H_1}$ C = C $\stackrel{H_2}{\longrightarrow}$ groups (δ_1 5.35, δ_1 , 5.68, δ_2 6.25 ppm, J_{1.2} 10, J₁'.2 16, J_{1.1}' < 1 Hz), while for CH₃CCl₂CH = CH₂ (IX) the spectrum represents the sum of the above indicated CH₂ = CH and CH₃CCl₂ fragments.

The NMR spectra of the unsaturated compounds, which will be discussed below, fail to contain signals that belong to any other groups, and consequently the discussion has to be limited only to the geometric isomers. To designate the geometric isomers we used the recently proposed nomenclature [7], which operates with the concepts of the E and Z forms.

The chemical shifts of the protons for (X) and (XI), obtained in benzene and in CCl_4 , are given in Table 2.

Compound	Formula	Configura-			ó, p	шd					J, Hz		
		tion	δı	δ1'	δ2	Ş ₃	Ş.	[§] CH ₂ R	$J_{1,2}$	J1',2	J _{2,3}	J _{3,4}	J4,5
VIII	\mathbf{H}_{1} , \mathbf{H}_{3} , \mathbf{H}	Z	5,35	5,57	6,30		5,87	4,20	10,5	16,2	1		5,7
	H_1 $C=0$ $G=0$ $G=0$ C $C=0$ $GH_2OCH_3OCH_3$												
	$\begin{array}{c} H_1 & \\ & 1 & 2 \\ G=G \\ & G=G \\ & 3 & 4 \end{array}$	Е	5,46	5,67	6,63		6,00	4,10	10,5	16,2	1	1	6,6
	Hr' C=C CI H.				<u> </u>				<u> </u>				
XII	GH ₃ H r-r H	Z, E	1		5,99	6, 42	5,70	4,01	!		10, 2	15,0	7,2
XIII	CH ₃ H	Z, E	[I	5,97	6,35	5,63	3,88		I	9,9.	15,0	5,7
	ci c=c H cH-och.ch.och.					<u> </u>							
IIIAX		E, Z	I	6,58	6,58	1	5,82	2,45	1	12,6	I		7,2
	H C=C H												
	cí cH₂CH₂CH₂CH												
	CH2CH2CH2CH2CH2CH	E, E		6,87	6,73	1	5,76	2,45	1	12,6	1		8,1
	H G=C												
* Also see § a	and J for $CH_2^{-}CHCC1^{-}CHCH_2C1$ [9].		•				-					-	

TABLE 3. Values of Chemical Shifts and J Constants for Dienes*

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As can be seen from Table 2, in the region of the vicinal and CH_2 protons are present signals that belong to both of the possible geometric isomers. Apparently, the signals of the CH_2X protons, which are shifted upfield, belong to the E isomer. This is in agreement with the fact that for (X) and (XI), J_{CH_3, CH_2}^Z > $J_{CH_3CH_2}^E$ (for (X), $J_{CH_3CH_2}^Z 0.9$, $J_{CH_3, CH_2}^E 0.5$ Hz), analogous to [8]. The ratio of the E and Z isomers for (X) and (XI) (1:3) was determined from the ratio of the integral intensities of the doublets from the CH_2X groups of both isomers, which are found quite apart in benzene.

The NMR spectrum for CHCl = CHCCl₂CH₂CH₂Cl (XV) is composed of the known CCl₂CH₂CH₂Cl fragment and the CHCl = CH group (AB system), the protons of which are found mainly in the E position (93%). J_{AB}^{E} 12.7 Hz, δ_{A}^{E} 6.72, δ_{B}^{E} 6.25 ppm. A small amount of the Z form (7%) gives an AB quadruplet with J_{AB}^{Z} 7.6 Hz, δ_{A}^{Z} 6.82, δ_{B}^{Z} 6.50 ppm.

The NMR spectrum for $CHCl_2CH = CCl(CH_2)_4Cl$ (XVII) contains the known = $CCl(CH_2)_4Cl$ fragment and the $CHCl_2CH = CCl$ group (AB system, J_{AB} 9.1 Hz, δ_A 6.55, δ_B 6.00 ppm). A noticeable amount of the second isomer is absent. By analogy with the other alkaline dehydrochlorination products it is possible to assume that (XVII) is found in the Z form.

Dienes (VI), (VIII), (XII), (XIII), (XIV), (XVI), and (XVII) can represent a mixture of the E and Z forms. The structure of compounds (VI), (XIV), and (XVI) was discussed earlier [9]. In Table 2 are given the values of the chemical shifts and the spin-spin coupling constants for the dienes that were obtained in the present paper.

Diene (VIII) is a mixture of the Z and E isomers in a 6:1 ratio. For the E forms the δ_2^E are shifted downfield (analogous to that mentioned in [9]) when compared with δ_2^Z ; $J_{4,5}^E > J_{4,5}^Z$, as was observed for dienes of similar structure [10].

Dienes (XII) and (XIII) contain mainly the Z, E form (70-80%). This is corroborated by the values of J_{CH_3} , C_{H_2} 1.2, $J_{3,4}$ 15, $J_{2,3}$ 9.9-10.2 Hz. Analogous values for the spin-spin coupling constants were observed in [8, 10]. In the region of the vicinal protons of (XII) and (XIII) are present signals that belong to other possible isomers, but the total amount of these isomers in the mixture does not exceed 20%. The assignment of these isomers has not been made as yet.

Diene (XVIII) was obtained by us previously [9] in two steps by catalytic and alkaline dehydrochlorination. In the present paper we obtained diene (XVIII) by the one-step alkaline dehydrochlorination of 1, 1, 3, 3, 7-pentachloroheptane (V). In the region of the vicinal protons of the NMR spectrum of compound (XVIII) are observed an AB quadruplet, a singlet and two triplets, which apparently belong to the E, E and E, Z isomers. The AB quadruplet with a center at δ 6.73 and the triplet at δ 5.76 ppm were assigned by us to the E, E configuration, by analogy with the data given in [9, 10], since $J_{4,5}^{E} > J_{4,5}^{E} Z$, while $\delta_{11}^{E, E}$ and δ_{2}^{E} , E are found further downfield than $\delta_{11}^{E, Z}$ and δ_{2}^{E} , Z (see Table 3).

The singlet at δ 6.58 and the triplet at δ 5.82 ppm were assigned to the E, Z configuration, since $J_{1',2}$ 12.6 Hz (established by the accumulation of the signals of the ¹³C satellites), J_{13C2H2} 163.8, J_{13C1H1} 195.3 Hz, which is in good agreement with the data given in [11]; in addition, in the NMR spectrum, obtained in benzene, the signals of the H₁ and H₂ protons, which are equivalent in CCl₄ (singlet), were found to be apart by 0.26 ppm with a constant of $J_{1,2}$ 12.6 Hz. The ratio of the E, Z and E, E forms is respectively equal to ~45:55.

The presence of acetylene (XIX) in the mixture was confirmed by the presence of a triplet in the NMR spectrum with δ 6.20 ppm and $J_{1,4}$ 1.9 Hz, and by the data of the Raman spectrum, where the intense band of $\nu_{C=C} = 2238 \text{ cm}^{-1}$ is present.

EXPERIMENTAL

The spectra were obtained on a Hitachi-Perkin-Elmer R-20 instrument at 60 MHz, equipped with an L. P-4050 accumulator of the weak signals, using 30% solutions of the compounds in either CCl_4 or benzene (tetramethylsilane was used as the standard). The parameters of the spectra were determined from a first order calculation of the spectra. It was verified that the second order corrections do not affect the conclusions regarding the structure of the compounds. In Table 3 are given the values of the "apparent" spin-spin coupling constants J', which for the sake of convenience will subsequently be designated by J. The chemical shifts of the protons were determined from the center of gravity of the multiplets (recorded on a scale of 3 Hz/cm), and the error does not exceed $\pm 3 \text{ Hz}$ (0.05 ppm). The GLC was run on an instrument equipped with a flame-ionization detector, column (1 m \times 0.2 cm), stationary phase 8% SE-30, solid phase Chromosorb W. 80-100 mesh, and carrier gas = nitrogen.

Dehydrochlorination of 1, 3, 3, 5-Tetrachloropentane (I). With stirring, to 105 g of (I) was added 61 g of KOH in 150 ml of methyl cellosolve. The mixture was stirred for a day and then allowed to stand overnight. After treatment with water the organic layer was separated, washed twice with water, and dried over CaCl₂. Distillation over hydroquinone through a column gave 14 g of (VI) and 21.9 g of (VII). In a similar manner, from 17.3 g of 3, 3, 5-trichloro-1-pentene (VII) and 5.2 g of KOH was obtained (VI) in 38% yield (the yield was determined by GLC).

Under the same conditions, from 52.5 g of (I) and 56 g of KOH was obtained 15.9 g of (VIII).

Dehydrochlorination of 1, 3, 3-Trichlorobutane (II). Compound (II) was obtained in 27% yield from 1, 1, 1-trichloroethane and ethylene by the procedure given in [3], bp 84° (72 mm); n_D^{20} 1.4662; d_4^{20} 1.2673. Found: C 30.14; H 4.43; Cl 65.50%; MR 35.30. C₄H₇Cl₃. Calculated: 29.75; H 4.36; Cl 65.86%; MR 35.27. The dehydrochlorination was run in the same manner as the preceding. From 335 g of (II) and 135 g of KOH was obtained 60.2 g of (IX), bp 95-95.5°, n_D^{20} 1.4428; d_4^{20} 1.1079, cf. [12]; 51.2 g of (X), bp 127-129°, n_D^{20} 1.4665, d_4^{20} 1.1573, cf. [13], and 25.5 g of (XI).

Dehydrochlorination of 1,5,5-Trichloro-2-hexene (III). In the same manner as the preceding, from 47 g of (III), obtained as described in [14], and 16.8 g of KOH at 10-15°, in the presence of hydroquinone, was obtained 16.8 g of (XII). Under the same conditions, from 28 g of (III) and 16.8 g of KOH was obtained 16.7 g of (XIII).

Dehydrochlorination of 1, 1, 3, 3, 5-Pentachloropentane (IV). In the same manner as the preceding, at $5-10^{\circ}$, in the presence of hydroquinone, from 97 g of (IV) and 50 g of KOH were obtained 24.5 g of (XIV) and 2 g of (XV).

Dehydrochlorination of 1, 1, 3, 3, 7-Pentachloroheptane (V). In the same manner as the preceding, at $0-5^{\circ}$, from 55 g of (V) and 22.5 g of KOH were obtained 13.7 g of (XVII) and 10.8 g of a mixture of (XVIII) + (XIX) with bp 91-93° (2 mm).

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CONCLUSIONS

1. A one-step method was proposed for the preparation of 3-chloro-5-(β -methoxyethoxy)-1, 3-pentadiene, (2-chloro-6-(β -methoxyethoxy)-2, 4-hexadiene, and 2, 5-dichloro-2, 4-hexadiene from the corresponding polychloro hydrocarbons by the action of potassium hydroxide in methyl cellosolve.

2. The alkaline dehydrochlorination of the $CCl_2CH_2CH_2Cl$ and $CHCl_2CH_2CCl_2CH_2CH_2$ groupings is accomplished via the chlorine of both chlorine-containing groups. The cleavage of the hydrogen proceeds selectively, and specifically from the methylene group that contains the most labile hydrogen atoms.

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