## HOMOLYTIC ADDITION OF POLYHALOMETHANES TO $\alpha$ -OLEFINS CONTAINING CHCl<sub>2</sub> AND CCl<sub>2</sub>=CH GROUPS IN THE $\omega$ -POSITION TO THE C=C BOND

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The homolytic addition of electrophilic reagents, like CHCl<sub>3</sub>, CCl<sub>3</sub>Br or HBr, to polychloro olefins that contain polychlorinated groups in the  $\omega$ -position to the C=C bond was studied on the example of compounds of the type  $CCl_3(CH_2)_nCH=CH_2$  (n = 0,1,2,4). It was found that when n = 0 or 1 the  $CCl_3$  group hinders the addition of the indicated addenda [1]. In the present paper we studied the radical addition of some polyhalomethanes  $CCl_3X(X=H, Cl, Br)$  to  $\alpha$ -olefins of the even series, in which the CHCl<sub>2</sub> and CCl<sub>2</sub>=CH groups are separated from the terminal C=C bond by two or more methylene groups.

We studied the compounds  $CHCl_2(CH_2)_3CH=CH_2$  (I) and  $CCl_2=CH(CH_2)_nCH=CH_2$  (II)-(IV), n = 2,4,6. The synthesis and structure of compounds (I) and (III) (n = 4) were described previously [2]. Compounds (II) and (IV) were obtained in a similar manner. The structure of (II) was confirmed by bromination at the unsubstituted C=C bond, and by the IR and NMR spectra. The structure of (IV) was confirmed by the IR spectral data. The addition reaction was initiated with either dicyclohexyl peroxydicarbonate (DCHPDC) or benzoyl peroxide (BP). The conditions of the addition reactions and the obtained products are given in Tables 1 and 2.

As can be seen from Table 1, the reaction of 6,6-dichloro-1-hexene (I) with the indicated polyhalomethanes gives the addition products (V)-(VII) in good yields, in which connection the yield of the adduct with chloroform, as is customary, is lower than with the other  $CCl_3X$ .

The addition of CCl<sub>3</sub>X (X=H, Cl, Br) to  $\alpha, \alpha$ -dichlorodienes CCl<sub>2</sub>=CH(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>, where n = 2,4,6, goes at the unsubsituted CH<sub>2</sub>=CH group. The yields of the adducts are somewhat lower than in the case of (1), and vary as a function of the distance between the  $CC1_2$ =CH and the  $CH_2$ =CH groups. Thus, 1,1-dichloro-1,5-hexadiene (II) gives adducts with all of the CCl<sub>3</sub>X in 20-68% yields. From 1,1-dichloro-1,7octadiene (III) the adduct was obtained only with  $CCl_3Br$  (63%), while with  $CCl_3H$  and  $CCl_4$  the yields of the

Olefin (amount, M)	·x	Amount, M	Initiator	Olefin con- version, %	Adduct	Yield % of theory
(I) (0,07) (I) (0,07) (I) (0,08) (II) (0,07) (II) (0,07) (II) (0,07) (II) (0,07) (III) (0,07) (III) (0,08) (IV) (0,08) • The yields	H Cl Br H Cl Br Br H are	1,3 1,26 0,35 1,3 1,26 0,36 0,15 1,3 based	DCHPDC† BP DCHPDC "† " BP DCHPDC† on the distil	100 60 70 80 100 100 77 1ed pr	$\begin{array}{llllllllllllllllllllllllllllllllllll$	40 73 85 17 25 53 ‡ 63 ‡ 63 ‡ 33

TABLE 1. Addition of CCl<sub>3</sub>X(X=H, Cl, Br) to Olefins (I)-(IV) in Presence of DCHPDC or BP (8 mole % of DCHPDC, 60-65°, or 5 mole % of BP, 90°)

‡ The yields are based on the sum of the isomers.

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adducts do not exceed 2-3%, with a diene conversion of respectively 40 and 50%. These adducts were not isolated in the pure state. The addition of chloroform to 1,1-dichloro-1,9-decadiene (IV) proceeds with the formation of the adduct in 30% yield. It is possible to assume that the anomalous behavior of diene (III) (n = 4) with CHCl<sub>3</sub> and CCl<sub>4</sub>, which are poorer carriers of the reaction chain than trichlorobromomethane, is apparently associated with the intramolecular transformations of the intermediate radical CCl<sub>2</sub> = CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CHCH<sub>2</sub>CCl<sub>3</sub>, which lead to chain termination.

The formation of the isomeric adducts in amounts of 10-15 rel.% was observed in the reactions of dienes (II) and (III) (n = 2,4) with all of the addenda  $CCI_3X$ . The fractions of the adducts that, based on the GLC data, contain up to 20 rel.% of the isomers, have the same elemental composition [(IXa), (Xa), (XIa), see Table 2], and based on the data of the IR and NMR spectra, do not contain a terminal  $CH_2$ =CH group. The structure of the isomeric adducts was not studied in more detail.

The structure of adducts (V)-(XII), isolated in the pure state, was confirmed by the IR and NMR spectra. Frequencies at 660 and 750 cm<sup>-1</sup> are observed in the IR spectra of adducts (V)-(VII), which are characteristic for the CHCl<sub>2</sub>CH<sub>2</sub> group; the spectra of adducts (VIII)-(XII) have frequencies at 465, 610-615, 880-885, 1620, and 3040 cm<sup>-1</sup>, which correspond to the CCl<sub>2</sub>=CH group. The obtained data correspond to those reported in [1-4]. The NMR spectra of adducts (V)-(XI) respectively have the triplets of the proton of the CHCl<sub>2</sub>CH<sub>2</sub> group with  $\delta$  5.67, 5.71, and 5.72 ppm, and of the CCl<sub>2</sub>=CHCl<sub>2</sub>group, with  $\delta$  5.80, 5.85, 5.81, and 5.80 ppm. A multiplet of the protons of the CCl<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> group, with  $\delta$  2.65 ppm, is observed in the spectra of the adducts with chloroform [(V), (VIII)]. In the spectra of the adducts, containing the CCl<sub>3</sub>CH<sub>2</sub>CHX (X =Cl, Br) group, the protons of the CH<sub>2</sub> group give a spectrum of the AB type, with  $\delta \sim 3.18$  ppm [in adduct (VI)] and ~3.30 ppm [in adducts (VII), (IX)-(XI)]. The multiplets of the CH<sub>2</sub>CHXCH<sub>2</sub> group are found at  $\delta \sim 4.25$  ppm. The integral intensities do not contradict the structure of the adducts. The obtained results are found to be in agreement with the literature data [1, 2, 5].

## EXPERIMENTAL METHOD

The NMR spectra were taken for 25-30% CCl<sub>4</sub> solutions on a Hitachi-Perkin-Elmer R-20 instrument, 60 MHz, relative to TMS.

All of the experiments were run in an argon atmosphere. The polychloromethanes, as well as the starting and obtained chloro olefins, were distilled in an argon stream; their purity was determined by GLC (instrument equipped with a flame-ionization detector, glass columns ( $2 \text{ m} \times 4 \text{ mm}$  and  $1 \text{ m} \times 3 \text{ mm}$ ), either 10% poly(ethylene glycol adipate) or 6% Silicone E-301 deposited on Chromosorb W (80-100 mesh), 135-165°).

<u>1,1-Dichloro-1,5-hexadiene</u>. As described in [2], from 17.9 g of 1,1,3-trichloro-1-propene in an equal volume of ether and allylmagnesium bromide (from 37.5 g of allyl bromide, 17 g of Mg and 300 ml of ether [6]) we obtained 20.5 g (90%) of 1,1-dichloro-1,5-hexadiene, bp 77.5° (70 mm);  $n_D^{20}$  1.4720;  $d_4^{20}$  1.0889. Found: C 47.71; H 5.38; Cl 46.40%; MR 38.84. C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>. Calculated: C 47.71; H 5.34; Cl 46.95%; MR 38.71. The frequencies 465, 610, 880, 912, 1620, 1640, and 3040 cm<sup>-1</sup> in the IR spectrum, assigned to the CCl<sub>2</sub>=CH and CH=CH<sub>2</sub> groups, correspond to the data given in [2-4].

The data of the NMR spectrum of  $CCl_2$ =CHCH<sub>2</sub>CH<sub>2</sub>CH=C  $H_i$  ( $\delta$ , ppm): c 5.78, i 5.66, j 4.88, k 4.88;  $H_i$ 

 $J_{cd} = 7.05$ ,  $J_{ik} = 17.0$ ,  $J_{ij} = 9.3$ , and  $J_{ih} = 6.0$  Hz, correspond to the analogous data given in [2, 5]. The integral intensities and the multiplets of the protons of the groups correspond to the given structure.

The reaction of 1,1-dichloro-1,5-hexadiene with bromine quantitatively gives 1,1-dichloro-5,6-dibromo-1-hexene, bp 131.5° (8 mm);  $n_D^{20}$  1.5510;  $d_4^{20}$  1.8228. Found: C 23.09; H 2.52; Hal 74.35%; MR 54.40. C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>Br<sub>2</sub>. Calculated: C 23.29; H 2.59; Hal 74.23%; MR 54.70. The data of the IR and NMR spectra for the CCl<sub>2</sub>=CHCH<sub>2</sub> group are: 465, 610, 885, 1620, 3040 cm<sup>-1</sup> and  $\delta$  5.82 ppm.

<u>1,1-Dichloro-1,9-decadiene</u>. Operating as described in [2], we obtained 1,1-dichloro-1,9-decadiene from 1,1-dichloro-7-bromo-1-heptene [7] and a 3-fold molar excess of  $CH_2=CHCH_2MgBr$  in THF. After distillation through a column, bp 137° (70 mm);  $n_D^{20}$  1.4730;  $d_4^{20}$  1.0150; yield 75%. Found: C 57.97; H 7.79; Cl 34.03; MR 57.24.  $C_{10}H_{16}Cl_2$ . Calculated: C 57.97; H 7.79; Cl 34.23%; MR 57.18. The IR spectral data for the  $CCl_2=CH$  and  $CH_2=CH$  groups are: 460, 610, 885, 910, 1620, 1640, and 3040 cm<sup>-1</sup>.

					MR. 1			
Adduct	Formula	Bp, °C (p, mm of	D B D	$d_4^{20}$	Found		Calculated	7/0
		A11			Calculated	υ	н	Ð
Ś	CHCl <sub>a</sub> (CH <sub>2</sub> ) <sub>5</sub> CCl <sub>a</sub>	125-126(5)	1,4965	1,3501	59,07	31,07	4,06	64,92
					58,86	30,85	4,07	65,08
(I A)	CHCl <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CHClCH <sub>3</sub> CCl <sub>3</sub>	145—146(5)	1,5222	1,4506	63,52	27,46	3,28	69,03
					71,60	AC, 12	3,28	69,31
(III)	CHCl <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CHBrCH <sub>2</sub> CCl <sub>5</sub>	136,5(2)	1,5310	1,6400	66,30	23,92	2,87	73,38
					00,02	50°07	2,87	73,20
(III)	$CCl_2 = CH(CH_2)_4 CCl_3$	140-140, 5(13)	1,5103	1,3960	57,97 58,39	31, 33 31, 09	3,35 3,35	65,12 65,56
(IX)	CCI <sub>3</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> CHCICH <sub>2</sub> CCI <sub>3</sub>	130-130, 5(5)	1,5225	1,4754	63,08	27,64	2,65	69,23
				•	63,26	27,58	2,64	69,78
(IXa)	$(IX) + isomer (\sim 20\%)$	132-133,5(5)	-			27,58	2,63	69,48
(X)	CCl <sub>3</sub> =CH(CH <sub>2</sub> ) <sub>2</sub> CHBrCH <sub>2</sub> CCl <sub>3</sub>	135,5(4)	1,5390	1,6632	65,80	24,11	2.38	73.69
	-	-			66, 16	24,07	2,31	73.68
(Xa)	$(\mathbf{X})$ + isomer (~20%)	152(8)	1,5405			24,00	2,26	73,24
(XI)	CCl <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>4</sub> CHBrCH <sub>2</sub> CCl <sub>5</sub>	150(1,5)	1,5335			28,57	3,42	67,98
	1 · ·					28,64	$\frac{3}{20}$	68,15
(XIa)	(XI) + isomer (~15%)	151 - 153(1,5)	1,5342	-		28,71	3,40	67,82
(IIX)	COL=CH(CH_ACC).	162 5-163(4)	1.4980	1.2442	76,94	40,62	5,21	54,05
	Stop S(Stro) Trop Stop				18,91	40,45	5,24	54,30
		-					-	

TABLE 2. Constants and Analyses of Obtained Adducts

Addition of Chloroform to 6,6-Dichloro-1-hexene (I). With stirring, 10.3 g of (I) in 25 ml of CHCl<sub>3</sub> and 2.2 g of DCHPDC in 25 ml of CHCl<sub>3</sub> were added simultaneously in 2.5 h to 60 ml of CHCl<sub>3</sub> at 60°. The mixture was then heated for 7 h at 60-65°, after which the solvent and starting dichloro olefin were distilled off. The residue was distilled to give 7.7 g (40%) of 1,1,1,7,7-pentachloroheptane (see Table 2).

The 1,1,7,7-pentachloroheptane was hydrolyzed with 94%  $H_2SO_4$  solution (90°, 2 h) to give  $\omega,\omega$ -dichloroenanthic acid, bp 146° (4 mm):  $n_D^{20}$  1.4768;  $d_4^{20}$  1.2240. Found: C 42.67; H 6.0; Cl 36.44%; MR 45.95.  $C_7H_{12}Cl_2-O_2$ . Calculated: C 42.23; H 6.07; Cl 35.62%; MR 45.80.

The same procedure was used to add  $CCl_4$  to 6,6-dichloro-1-hexene [adduct (VI)], and chloroform to 1,1-dichloro-1,5-hexadiene and 1,1-dichloro-1,9-decadiene [adducts (VIII) and (XII), see Tables 1 and 2].

Addition of Trichlorobromomethane to 6,6-Dichloro-1-hexene (I). A mixture of 70 g of CCl<sub>3</sub>Br, 12 g of (I) and 0.8 g of BP (added in two portions) was heated at 90° for 6 h. Distillation gave 24 g (85%) of 1,1,-1,7,7-pentachloro-3-bromoheptane with bp 146-150° (2 mm). The constants of the adduct are given in Table 2.

Addition of  $CCl_4$  to 1,1-Dichloro-1,5-hexadiene (II). The experiment was run under the same conditions as the addition of  $CHCl_3$  to olefin (I). For reaction we took 10.6 g of (II), 120 ml of  $CCl_4$  and 1.6 g of DCHPDC. After distilling off the  $CCl_4$  and starting (II) the residual oil was distilled. We obtained: 9.2 g of fraction I with bp 135-141° (3 mm), and 2.2 g of fraction II with bp 142-148° (3 mm); the undistillable residue weighed 7.5 g. Based on the GLC data, fractions I and II are adduct (IX), contaminated with 10-15 rel.% of the isomer. The yield of the adducts was 50%. Distillation of fractions I and II (from two experiments) through a column gave the pure adduct (IX) (see Table 2).

Addition of Trichlorobromomethane to 1,1-Dichloro-1,7-octadiene (III). The experiment was run the same as with olefin (I). From 5 g of (III), 30 g of CCl<sub>3</sub>Br and 0.2 g of BP, after the usual workup and distillation, we obtained: 0.4 g of fraction I with bp 64-104° (1.5 mm), 2.7 g of fraction II with bp 162-168 (1.5 mm), and 3.7 g of fraction III with bp 168-178° (1.5 mm); the undistillable residue weighed 2.5 g. Based on the GLC data, fraction II is the nearly pure adduct (XI), while fraction III contains the adduct and 11-13 rel. % of the isomers. From fraction II after two distillations we isolated the pure adduct (XI), devoid of isomers. The constants are given in Table 2.

Adduct (X) was obtained in a similar manner (see Tables 1 and 2).

## CONCLUSIONS

1. The homolytic addition of some polyhalomethanes  $CXCl_3(X=H, Cl, Br)$  to the  $\alpha$ -olefins:  $CHCl_2-(CH_2)_3CH=CH_2$  and  $CCl_2=CH(CH_2)_nCH=CH_2$  (n = 2, 4, 6), was accomplished. The adducts were obtained in good yields.

2. The adduct from the diene with n = 4 is formed only when an efficient carrier of the reaction chain (CCl<sub>3</sub>Br) is used.

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