RADICAL ADDITION OF HALOGEN-CONTAINING ADDENDS TO UNSATURATED COMPOUNDS CONTAINING ELECTRON-ACCEPTOR GROUPS

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In this work we studied the homolytic addition of various electrophilic addends: chloroform, bromotrichloromethane, and hydrogen bromide, to unsaturated compounds with a terminal double bond, containing electron-acceptor groups, such as CCl_3- and $CCl_3C(=O)O-$, separated from the double bond by various numbers of methylene units. In the reaction with $CHCl_3$, we investigated trichloroalkenes with the structure $CCl_3(CH_2)_nCH=CH_2$, n = 0, 2, 4 (Table 1). The addition of $CHCl_3$ to 3,3,3-trichloropropene practically did not take place. The main reaction product, despite a tenfold excess of the addend, was a dimer of the original monomer. In the case of the other trichloroalkenes (n = 1, 2, 4), adducts with the structure $CCl_3 \cdot (CH_2)_{n+2}CCl_3$ with yields of 10, 71, and 46%, respectively, were obtained. The structure of the $\alpha,\alpha,\alpha,\omega,\omega,\omega$-hexachloroalkanes was demonstrated by the PMR method. The hydrolysis of 1,1,1,6,6,6-hexachlorohexane, leading to adipic acid, was also conducted.

Bromotrichloromethane was added to 5,5,5-trichloro-1-pentene, allyl and vinyl esters of trichloroacetic acid (Table 2). The corresponding adducts were isolated in good yields. In the dehydrobromination of 1,1,1,6,6,6-hexachloro-3-bromohexane with diethylamine, 1,1,1,6,6,6-hexachloro-3-hexene was obtained in an 80% yield. The structure of 1,1,1,6,6,6-hexachloro-3-bromohexane and 1,1,1,6,6,6-hexachloro-3-hexene was demonstrated by the PMR method (Table 3). Hydrolysis of adducts with the structure $CCl_3C \cdot (=O)OCHBrCH_2CCl_3$ and $CCl_3C(=O)OCH_2CHBrCH_2CCl_3$ with aqueous ammonia in both cases led to the formation of the amide of trichloroacetic acid, and, in the latter case, an alcohol with the composition $C_4H_6 \cdot Cl_3BrO$, probably with the structure $CCl_3CH_2CHBrCH_2OH$.

The addition of hydrogen bromide to 4,4,4-trichloro-1-butene and 5,5,5-trichloro-1-pentene led to the formation of adducts with a good yield (see Experimental section). The structure of 1,1,1-trichloro-4-bromobutane was demonstrated by converting it to trichlorovaleronitrile, hydrolysis of which gave glutaric

TABLE 1. Addition of $CHCl_3$ (S) to $CCl_3(CH_2)_nCH=CH_2$ (M) in the Presence of 8 Mole % Dicyclohexylperoxydicarbonate at 60°, M:S = 1:13

No. in order	n	Adducts	Yield, % of theoretical	Mp, °C	Found, %			Calculated, %		
					C	H	Hal	C	H	Hal
1	0	$CHCl_2CHClCH_2CCl_3$ *	1†							
2	1	$CCl_3(CH_2)_3CCl_3$	10	31,5—32,5	21,76	2,14	75,39	21,54	2,17	76,30
3	2	$CCl_3(CH_2)_4CCl_3$	71	67—68	24,75	2,79	72,71	24,61	2,75	72,64
4	4	$CCl_3(CH_2)_6CCl_3$	46	28	30,10	3,84	66,00	29,94	3,77	66,29

* The adduct was determined by the GLC method by identification with a known sample.

† The basic reaction product is a dimer with the structure $CCl_2=CHCH_2CCl_2CHClCH_2Cl$ [1].

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*Deceased.

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TABLE 2. Addition of $CBrCl_3$ to Unsaturated Compounds in the Presence of 1-3 Mole % Benzoyl Peroxide at 80°

No. in order	Unsaturated compound (amount, M)	$CBrCl_3$, M	Adduct	Yield, % of theoretical	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found /calculated	Found, %			Calculated, %		
									C	H	Hal	C	H	Hal
1	$CCl_3(CH_2)_2CH{=}CH_2$ (0,01)	0,02	$CCl_3(CH_2)_2CHBrCH_2CCl_3$	85	126 (4)	1,5364	1,7443	66,50/66,87	19,60	1,89	78,56	19,39	1,86	78,75
2	$CCl_3C({=}O)OCH_2CH{=}CH_2$ (0,24)	0,74	$CCl_3C({=}O)OCH_2CHBrCH_2CCl_3$	86	135—137 (1)	1,5262	1,8040	68,40/68,54	18,07	1,28	72,15	17,94	1,26	72,60
3	$CCl_3C({=}O)OCH{=}CH_2$ (0,12)	1,2	$CCl_3C({=}O)OCHBrCH_2CCl_3$	56	96—97 (1,5)	1,5218	1,8409	64,22/63,91	16,19	0,79	74,19	15,99	0,78	74,48

acid. The structure of 1,1,1-trichloro-5-bromopentane was demonstrated by identification with a known sample by the method of gas–liquid chromatography (GLC). It is interesting to note that in the case of the reaction with 5,5,5-trichloro-1-pentene, in addition to the adduct 1,1,1-trichloro-5-bromopentane, 1,1-dichloro-5-bromopentane is formed (5% of the sum of the reaction products), identified also by the GLC method. The formation of 1,1-dichloro-5-bromopentane is apparently associated with partial reduction of the trichloromethyl group of the adduct under the conditions of the reaction.

A comparison of the yields of the adducts obtained in the reactions that we studied, as well as a comparison of these results with the literature data (the reaction of bromotrichloromethane with 3,3,3-trichloropropene [2] and 4,4,4-trichlorobutene [3]) shows that in these reactions the effect of polar factors is manifested. This action is especially noticeable in the reaction of $CHCl_3$ with trichloroalkenes with the structure $CCl_3(CH_2)_nCH{=}CH_2$, n = 0, 1, 2, 4. In the case of the reaction of $CHCl_3$ with 3,3,3-trichloropropene, the radical formed with structure $CCl_3\dot{C}H\cdot CH_2CCl_3$ is rearranged to a radical with structure $\dot{C}Cl_2CHClCH_2CCl_3$ (analogously to the reaction of 3,3,3-trichloropropene with hydrogen bromide, bromotrichloromethane [2]). The rearranged radical with a radical center on the dichloromethyl group, being electrophilic, is incapable of continuing the chain with an electrophilic addend $-CHCl_3$. Therefore, in this reaction practically no adduct formation is observed.

In the addition of chloroform to 4,4,4-trichloro-1-butene, the radical $CCl_3CH_2\dot{C}HCH_2CCl_3$ formed, as a result of the influence of the two trichloromethyl groups in the α-position to the radical center, is also sufficiently electrophilic; therefore, its reaction with $CHCl_3$ is hindered, which also explains the low yield of the adduct. The removal of one trichloromethyl group two and four methylene units from the radical center in radicals with the structure $CCl_3(CH_2)_n\dot{C}HCH_2CCl_3$ (in the case of 5,5,5-trichloro-1-pentene and 7,7,7-trichloro-1-heptene) evidently reduces the electrophilicity of the intermediate radical, which promotes the subsequent substitution reaction with $CHCl_3$. Therefore in these reactions the yield of the adduct is considerably higher (5-7 fold).

We should also mention the following. In all the examples studied (with the exception of the reaction of $CHCl_3$ with 3,3,3-trichloropropene), adducts were isolated retaining the trichloromethyl group of the initial unsaturated compound, i.e., no products due to rearrangement of radicals with migration of chlorine from the trichloromethyl group to the distant radical center were found among the isolated products in radicals with the structures $CCl_3(CH_2)_n\dot{C}HCH_2X$ (n = 1, 2, 4) and $CCl_3C({=}O)O(CH_2)_m\dot{C}H\cdot CH_2X$ (m = 0, 1).

EXPERIMENTAL

Addition of Chloroform to Unsaturated Compounds. To 100 ml $CHCl_3$, 17.3 g 5,5,5-trichloro-1-pentene in 30 ml $CHCl_3$ and 2.2 g dicyclohexylperoxydicarbonate in 30 ml $CHCl_3$ were added simultaneously from two funnels over a period of 2 h with mixing at 60° in a stream of argon, after which the reaction mixture was heated for 6 h at 60°. After the starting materials and the decomposition products of the peroxide were distilled off, the reaction product was redistilled under vacuum. We obtained 20.9 g (71%) 1,1,1,6,6,6-hexachlorohexane (example 3, see Table 1). Hydrolysis of it with 92-93% H_2SO_4 at 90° led to adipic acid with a yield of 84%.

TABLE 3. Parameters of the PMR Spectra of the Compounds Obtained

Formula of compound	Chemical shifts δ, ppm				
	CH_2CCl_3	$-\underline{CH_2}CH_2CCl_3$	$-\underline{CH_2}(CH_2)_2CCl_3$	$=CH-$	$-CHBr-$
$CCl_3CH_2CH_2CH_2CCl_3$	2,68	2,27	—	—	—
$CCl_3CH_2CH_2CH_2CH_2CCl_3$	2,72	1,91	—	—	—
$CCl_3CH_2CH_2CH_2CH_2CH_2CH_2CCl_3$	2,70	1,86	~1,57	—	—
$CCl_3CH_2CHBrCH_2CH_2CCl_3$	~2,98	2,49	—	—	4,38
$CCl_3CH_2CH{=}CHCH_2CCl_3$	2,80	—	—	6,27	—

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* The PMR spectra were taken on a Perkin-Elmer P-12 instrument, 60 MHz. The chemical shifts are cited in the δ-scale (zero on tetramethylsilane); hexamethyldisiloxane (δ = 0.05 ppm) was used as an internal standard. The ratios of the integral intensities correspond to the assignments made.

The addition of $CHCl_3$ to 3,3,3-trichloropropene, 4,4,4-trichloro-1-butene, and 7,7,7-trichloro-1-heptene (examples 1,2,4, see Table 1) was conducted analogously. 7,7,7-Trichloro-1-heptene was produced according to the method of [4] from 1,1,1-trichloro-7-iodoheptane with a yield of 19%; bp 73° (10 mm); n_D^{20} 1.4711; d_4^{20} 1.1545. Found: C 41.74; H 5.46; Cl 52.74%; MR 48.66. $C_7H_{11}Cl_3$. Calculated: C 41.70; H 5.51; Cl 52.75%; MR 48.83.

Constants of 1,1,1-trichloro-7-iodoheptane: bp 90° (1 mm); n_D^{20} 1.5353; d_4^{20} 1.6520. Found: C 25.34; H 3.79%; MR 62.12. $C_7H_{12}Cl_3I$. Calculated: C 25.52; H 3.67%; MR 61.93.

Addition of Bromotrichloromethane to Unsaturated Compounds. When 1.7 g 5,5,5-trichloro-1-pentene and 4 g bromotrichloromethane were heated in the presence of 1 mole % benzoyl peroxide for 3 h at 80°, we obtained 3.1 g (85%) 1,1,1,6,6,6-hexachloro-3-bromohexane (example 1, see Table 2). Dehydrogenation of the adduct with diethylamine in methanol at room temperature yielded 1,1,1,6,6,6-hexachloro-3-hexene, mp 62°, with an 80% yield. Found: C 25.00; H 2.08; Cl 73.03%. $C_6H_6Cl_6$. Calculated: C 24.77; H 2.08; Cl 73.15%. The products of the addition of bromotrichloromethane to the allyl and vinyl esters of trichloroacetic acid are given in Table 2, examples 2 and 3.

Addition of Hydrogen Bromide to Unsaturated Compounds. In the presence of 1 mole % benzoyl peroxide, HBr was passed through a solution of 35 g 5,5,5-trichloro-1-pentene in 50 ml CCl_4 at 80° for 5 h. We obtained 19.5 g (38%) of the adduct. An analysis of the fraction corresponding to the adduct by the method of GLC indicated that it consisted of 1,1,1-trichloro-5-bromopentane (95%) and 1,1-dichloro-5-bromopentane (5%). Identification with known samples was performed on two phases of different polarities. 1,1-Dichloro-5-bromopentane and 1,1-trichloro-5-bromopentane were produced according to the method of [5]. Constants of 1,1,1-trichloro-5-bromopentane: bp 64° (1 mm); n_D^{20} 1.5140; d_4^{20} 1.6065. Found: MR 47.67; calculated MR 47.65. According to the data of [6]: bp 110° (2 mm). The picrate of the isothiuronium derivative of 1,1,1-trichloro-5-bromopentane, produced according to the method of [7], showed no depression of the melting point when mixed with a sample synthesized from 1,1,1,5-tetrachloropentane.

The addition of HBr to 4,4,4-trichloro-1-butene was carried out analogously to that described above by passing through HBr until the change in the index of refraction ceased. The yield of 1,1,1-trichloro-4-bromobutane was 66%; bp 84-85° (10 mm); n_D^{20} 1.5142; d_4^{20} 1.6885. Found: C 20.08; H 2.44%; MR 42.87. $C_4H_6 \cdot Cl_3Br$. Calculated: C 20.03; H 2.52%; MR 43.04.

From 1,1,1-trichloro-4-bromobutane and sodium cyanide we obtained trichlorovaleronitrile; bp 125-127° (20 mm); n_D^{20} 1.4834; d_4^{20} 1.3363. Found: C 32.18; H 3.39; Hal 56.83%; MR 39.88. $C_5H_3Cl_3N$. Calculated: C 32.20; H 3.24; Hal 57.06%; MR 39.63. Hydrolysis of trichlorovaleronitrile led to glutaric acid.

CONCLUSIONS

The radical addition of $CHCl_3$ to trichloroalkenes with the structure $CCl_3(CH_2)_nCH=CH_2$; n = 0,1,2,4; that of bromotrichloromethane to 5,5,5-trichloro-1-pentene, allyl and vinyl esters of trichloroacetic acid; and the addition of hydrogen bromide to 4,4,4-trichloro-1-butene and 5,5,5-trichloro-1-pentene were studied.

LITERATURE CITED

1. V. N. Kost, T. T. Vasil'eva, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Otd. Khim. N., 1254 (1962).
2. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, Dokl. Akad. Nauk SSSR, 81, 199 (1951).

3. M. S. Kharash and M. Sage, J. Organ. Chem., 14, 82 (1949).
4. R. Kh. Friedlina, E. Ts. Chukovskaya, N. A. Kuz'mina, and A. A. Kamyshova, Izv. Akad. Nauk SSSR, Ser. Khim., 1319 (1963).
5. N. V. Kruglova and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1028 (1971).
6. W. A. Skinner, E. Bishop, D. Tieszen, and J. D. Johnston, J. Organ. Chem., 23, 1710 (1958).
7. R. Kh. Freidlina and B. V. Kopylova, Izv. Akad. Nauk SSSR, Otd. Khim. N., 172 (1961).