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HOMOLYTIC REACTIONS OF THE 2,2-DICHLOROVINYL GROUP

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Electrophilic addition reactions are known for compounds containing the $CCl_2 = CH$ group [1], but homolytic addition to compounds of this kind has been little studied. In the present investigation we studied the radical addition of various reagents to compounds containing a 2,2-dichlorovinyl group. At ordinary temperatures in presence of ultraviolet radiation and at higher temperatures in presence of peroxides the addition of hydrogen bromide to the 2,2-dichlorovinyl group was not observed. This is probably related to the reversibility of the addition of a bromine atom by the scheme (1):

$$Br + CCl_2 = CHR \rightleftarrows \cdot CCl_2CHBrR\ . \tag{1}$$

By conducting the reaction at low temperature we were able to effect the homolytic addition of hydrogen bromide to 1,1,3-trichloropropene and other compounds containing the $CCl_2 = CH$ group by the scheme (2):

$$\begin{gathered} CCl_2 = CHCH_2Y + HBr \rightarrow HCCl_2CHBrCH_2Y \\ Y = Cl,\ Br,\ -(CH_2)_2Cl\ . \end{gathered} \tag{2}$$

Lowering the reaction temperature to -35° appears to shift the equilibrium (1) to the right. Thus, at between -35 and -37° under ultraviolet irradiation hydrogen bromide readily adds to 1,1,3-trichloropropene, 3-bromo-1,1-dichloropropene, and 1,1,5-trichloro-1-pentene. Without irradiation or in presence of hydroquinone HBr does not react with 1,1,3-trichloropropene. The structure of the reaction product was proved for the case of the addition of HBr to 3-bromo-1,1-dichloropropene. The dibromodichloropropane obtained was found to be identical to the 2,3-dibromo-1,1-dichloropropane synthesized by the bromination of 3,3-dichloropropene in acetic acid by the scheme (3):

$$CHCl_2CH = CH_2 \xrightarrow[CH_3COOH]{Br_2} CHCl_2CHBrCH_2Br. \tag{3}$$

The picrates of the isothiuronium derivatives of these two dibromides ($CHCl_2CHBrCH_2SC(=NH)NH_2 \cdot C_6H_2(NO_2)_3OH$) both melted at 146-147°, and a mixture melted without depression.

The reactions of 1-butanethiol and benzenethiol with 1,1,3-trichloropropene at between -35 and -37° under ultraviolet irradiation led to the formation of sulfides of structure $CHCl_2-CH(SR)CH_2Cl$. By the oxidation of these sulfides with hydrogen peroxide in acetic acid we obtained sulfones, the formation of which was accompanied by the elimination of HCl. The structures of the sulfides were confirmed by independent synthesis by the reactions of 1-butanesulfenyl chloride and of benzenesulfenyl chloride with 3,3-dichloropropene by the scheme (4):

$$CHCl_2CH = CH_2 + ClSR \rightarrow CHCl_2CH(SR)CH_2Cl. \tag{4}$$

The sulfones prepared from the sulfides synthesized in these two ways were identical. The reaction with 1-butanethiol goes better than that with benzenethiol, and a good yield is obtained of 2-(butylthio)-1,1,3-trichloropropane

TABLE 1. Constants and Analyses

Expt. No.	Formula	B.p., °C (p, mm)	d_4^{20}	n_D^{20}	*MR*		Found, %		Calculated, %	
					found	calculated	C	H	C	H
1	$CHCl_2CHBrCH_2Cl$	76(11)	1,8330	1,5290	38,08	38,42	16,48	1,74	15,92	1,78
2	$CHCl_2CHBrCH_2Br$	71(3)	2,1485	1,5615	40,85	41,32				
3	$CHCl_2CHBr(CH_2)_3Cl$	100(5)	1,6566	1,5267	47,29	47,66	23,87	3,13	23,60	3,17
4	$CHCl_2CHBrCH_2C_6H_5$	127—129(3)	1,5329	1,5703	57,40	57,66	40,63	3,15	40,34	3,38
5	$CHCl_2CHBrCH_2Br$	75(5)	2,1520	1,5616	40,79	41,32	13,25	1,57	13,31	1,49
6	$CHCl_2CH(SC_4H_9)CH_2Cl$	100(5)	1,2404	1,5130	57,09	57,13	36,13	5,24	35,68	5,58
7	$CHCl_2C(SC_4H_9)=CH_2$	83(3)	1,1585	1,5175	52,07	51,79	42,04	5,91	42,22	6,07
8	$CHCl_2CH(SC_4H_9)CH_2Cl$	97—100(4)	1,2396	1,5133	57,17	57,13				
10	$CHCl_2CH(SC_6H_5)CH_2Cl$	122(3)	1,3642	1,5900	63,23	63,26	43,00	3,56	42,29	3,55
11	$CHCl_2C(CH_3)(SC_4H_9)CH_2Cl$	125(5)	1,2195	1,5138	61,61	61,74	38,63	5,97	38,49	6,06

By the dehydrochlorination of this sulfide with alkali we obtained 2-(butylthio)-3,3-dichloropropene by the scheme (5)

$$CHCl_2CH(SC_4H_9)CH_2Cl \xrightarrow{KOH} \underset{(I)}{CHCl_2C(SC_4H_9) = CH_2} \quad (5)$$

and the structure of this was proved by its conversion into methylglyoxal osazone by its hydrolysis with sulfuric acid in presence of 2,4-dinitrophenylhydrazine.

We also carried out the homolytic addition of 1-butanethiol and of benzenethiol to 1,1,3-trichloropropene at room temperature and at 60° (in the case of 1-butanethiol) under ultraviolet irradiation, but lower yields of addition products were obtained. In all the cases studied the homolytic addition of HBr and of thiols to the $CCl_2 = CH$ group went with formation of compounds containing a terminal dichloromethyl group, i.e.,the radical X· added at the 1-position of the 2,2-dichlorovinyl group $CCl_2 = CH$:

$$HX \xrightarrow{h\nu} H\cdot + X\cdot; \quad CCl_2 = CHR + X\cdot \rightarrow \cdot CCl_2CHXR\,(A)$$
$$CCl_2CHXR + HX \rightarrow HCCl_2 = CHXR + X\cdot$$

Thus, in this case the direction of addition is determined by the higher stability of the radical A (carrying the unpaired electron on the dichloro-substituted carbon) as compared with the secondary radical of structure $XCCl_2\dot{C}HR$, which could be formed in the attack by the radical X on the 2-position of the $CCl_2 = CH$ group. It should be noted that the introduction of substituents in the 1-position of the 2,2-dichlorovinyl group ($CCl_2 = CYR$, in which Y = Cl, CH_3) hinders the radical addition of HBr and thiols.

EXPERIMENTAL

Addition of HBr to 1,1,3-Trichloropropene (Expt. 1). The experiments were conducted in an unsilvered quartz Dewar vessel furnished with a thermocouple, tubes for passing gas in and out, and a condenser inserted inside the vessel. The vessel was irradiated with a PRK-4 mercury lamp at a distance of 10 cm. 5 ml of colorless dry liquid HBr was added to a solution of 14.5 g of freshly distilled $CCl_2 = CHCH_2Cl$ in 20 g of heptane cooled to between -45 and - 55°. The temperature of the solution was then kept between -35 and -37° for 2.5 h under ultraviolet irradiation. The reaction mixture was washed with water and sodium carbonate solution and was dried over $CaCl_2$. The 2-bromo-1,1,3-trichloropropane obtained was distilled through a column; yield 70%. The constants and analyses of the compounds obtained are given in Table 1.

The addition of HBr to $CCl_2 = CHCH_2Br$, to $CCl_2 = CH(CH_2)_3Cl$ and to $CCl_2 = CHCH_2C_6H_5$ was conducted similarly as in Expt. 1. In the case of $CCl_2 = CH(CH_2)_3Cl$ the reaction required four hours at between -35 and -45° (Experiments 2-4, see Tables 1 and 2). Isothiuronium derivatives were prepared from $CHCl_2CHBrCH_2Br$ and $CHCl_2CHBr(CH_2)_3Cl$ the melting points of the picrates were 147-148° and 141-142° (from alcohol) respectively. Analyses of picrates are given in Table 3.

TABLE 2. Addition of HBr to $CCl_2 = CHCH_2X$ with Formation of $HCCl_2CHBrCH_2X$

Expt.	X	Amt. taken		Yield, %
		halo olefin, g	HBr, ml	
2	Br	20	10	77 *
3	$(CH_2)_2Cl$	26	7	90
4	C_6H_5	18,8	7	12,6

*Based on the amount of halo olefin that reacted; in the other cases the yields are based on the amount of halo olefin taken for reaction.

Bromination of $CHCl_2CH = CH_2$ (Expt. 5). 5 ml of bromine in 5 ml of glacial acetic acid was added slowly at room temperature to a solution of 11.1 g of 3,3-dichloropropene in 5 ml of glacial acetic acid. We obtained 17 g (62.7%) of 2,3-dibromo-1,1-dichloropropane (see Table 1). Isothiuronium derivative: picrate m.p. 146-147.5° (from alcohol), identical to the sample obtained in Expt. 2.

Addition of 1-Butanethiol to 1,1,3-Trichloropropene (Expt. 6). A solution of 26.7 g of $CCl_2 = CHCH_2Cl$ in 30 ml (25.2 g) of 1-butanethiol was exposed to ultraviolet radiation at between -35 and -37° with stirring with a stream of argon for a period of 12.5 h. Two fractionations gave 33.9 g (79.9%) of 2-(butylthio)-1,1,3-trichloropropane (see Table 1). Sulfone: m.p. 39.5-40° (from alcohol) (see Table 3).

TABLE 3. Analyses of Compounds Obtained

Expt.	Formula	Found, %		Calculated, %	
		C	H	C	H
2	$CHCl_2CHBrCH_2SC(=NH)NH_2$ *	13,90 †		14,15 †	
3	$CHCl_2CHBr(CH_2)_3SC(=NH)NH_2$ *	27,96	3,11	27,55	2,70
6	$CHCl_2C(SO_2C_4H_9) = CH_2$ ‡	36,17	5,01	36,37	5,23
7	$CHCl = C(SC_4H_9)CH_2SC(=NH)NH_2$ *	36,29	3,89	35,94	3,88
7	2,4-Methylglyoxal-2,3-dinitrophenylosazone	41,51	2,78	42,03	2,80
9	$CHCl_2C(SO_2C_6H_5) = CH_2$ ‡	43,24	3,41	43,05	3,21

*Picrate.

†Analysis for nitrogen.

‡Or $CHCl = C(SO_2R)CH_2Cl$, the structure was not investigated.

Dehydrohalogenation of 2-(Butylthio)-1,1,3-trichloropropane (Expt. 7). 28.8 g of the sulfide was treated in the cold with 8 g (25% excess) of KOH in 2-ethoxyethanol with stirring. After two hours the reaction mixture was washed several times with water, dissolved in ether, and dried over $CaCl_2$. After two fractionations we obtained 2-(butylthio)-3,3-dichloropropene (see Table 1). Yield 19.7 g (80.8%). Sulfone, m.p. 38.5-39.5° (from alcohol), identical to the sample from Expt. 6. Isothiuronium compound: picrate m.p. 135-135.5° (see Table 3). In the hydrolysis of 1 g of the sulfide in 7 ml of alcohol with 1.5 ml of H_2SO_4 in 7 ml of alcohol in presence of 0.7 g of 2,4-dinitrophenylhydrazone with heating we obtained 0.5 g of methylglyoxal osazone, which was washed with alcohol and then melted at 291-293° (decomp.).

Addition of 1-Butanesulfenyl Chloride to 3,3-Dichloropropene (Ext. 8). 19 g (30% excess) of 1-butanesulfenyl chloride was added dropwise with stirring to 12.9 g of 3,3-dichloropropene cooled to 0°. The reaction mixture was left overnight. We obtained 24.6 g of a sulfide (see Table 1). Sulfone, m.p. 38.5-39.5° (from alcohol), identical to the sulfone obtained in Expt. 6.

Addition of Benzenethiol to 1,1,3-Trichloropropene (Ext. 9). A solution of 21.7 g of $CCl_2 = CHCH_2Cl$ and 20.3 ml of C_6H_5SH in 20 g of heptane was irradiated for 8.5 hours at between -26 and -37° with stirring with a stream of argon. We obtained 3.8 g (10%) of 1,1,3-trichloro-2-(phenylthio)propane, b.p. 155-160° (5 mm) and n_D^{20} 1.5885. Sulfone, m.p. 90-91° (see Table 3).

Addition of Benzenesulfenyl Chloride to 3,3-Dichloropropene (Expt. 10). The procedure was as in Expt. 8, but at room temperature. From 20 g of $CHCl_2CH = CH_2$ in 35 ml of dry CCl_4 and 25.8 g of C_6H_5SCl in 15 ml of CCl_4 we obtained 23.1 g of 1,1,3-trichloro-2-(phenylthio)propane (see Table 1). Sulfone, m.p. 91-91.5° (from alcohol), identical to the sulfone from Expt. 9.

Addition of n-C_4H_9SH to $CCl_2 = C(CH_3)CH_2Cl$ (Expt. 11). A solution of 16 g of $CCl_2 = C(CH_3)CH_2Cl$ in 15.7 ml of n-C_4H_9SH was irradiated with ultraviolet with stirring with a stream of argon at between -35 and -37° for ten hours. We obtained 3.2 g (13%) of 2-(butylthio)-1,1,3-trichloro-2-methylpropane (see Table 1).

SUMMARY

1. A study was made of the photochemical addition of HBr to 1,1,3-trichloropropene, 3-bromo-1,1-dichloropropene, and 1,1,5-trichloro-1-pentene, and also of 1-butanethiol to 1,1,3-trichloropropene and 1,1,3-trichloro-2-methylpropene and of benzenethiol to 1,1,3-trichloropropene at low temperature.

2. The homolytic addition of hydrogen bromide and of thiols to the $CCl_2 = CH$ group goes with the formation of compounds containing a terminal dichloromethyl group.

LITERATURE CITED

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