## THE REARRANGEMENT OF POLYHALOALKYL RADICALS IN SOLUTION WITH 1,2-CHLORINE ATOM MIGRATION\*

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Abstract—Radicals  $XCCl_2CYCH_2Z(l; X = Cl,H,F,CH_3; Y = H,CH_3,Cl,Br; Z = Br,Cl,CCl_3,SR)$ were generated by homolytic addition of various addenda to unsaturated compounds  $XCCl_2CY = CH_2$ . Radicals (I) were shown to rearrange in solution into radicals  $XCCl_-CYCl_-CH_2Z(II)$ , the latter being more stable than the former. It was found that compounds  $XCCl_2CBr = CH_2$  with  $X = Cl,CH_3$ , F could isomerize under the action of initiators of radical processes to compounds  $XCCl = CClCH_2Br$ . This isomerization was proved to be of a radical chain character and involves the 1,2-chlorine migration in the intermediate radical  $XCCl_2CBrCH_2Br$  (III). The dependence between the structure of starting radicals and their ability to undergo rearrangement in solution has been established and the effect of the nature of addendum on the reaction course investigated. The polyhaloalkyl radicals were arranged in a sequence according to their relative stability.

INTRAMOLECULAR radical rearrangements can now be regarded as the reactions of the radical with itself. This allows their separation in accordance with the radical reactions into three main groups.

## 1. Substitution Reactions

This group covers a large number of rearrangements, with the migration of different atoms or groups, to be schematically pictured as follows:

$$\begin{array}{c} X & X \\ \dot{A} - B - C \rightarrow \dot{A} - \dot{B} - C \\ X & X \\ \dot{A} - (B)_n C \rightarrow \dot{A} - (\dot{B})_n \dot{C} \end{array}$$

X being the migrating atom or group.

## 2. Addition Reactions

The reactions discussed are those involving the ring closure, such as



## 3. Degradation Reactions

This group involves rearrangements with the rupture of the ring as well as some allylic rearrangements. They are characterized by the rupture of the link (bond) at  $\beta$ -atom to form a new  $\alpha,\beta$ -double bond.

$$\dot{A}$$
 - B - C  $\rightarrow$  A = B  $\dot{C}$   
 $\begin{vmatrix} & | & | \\ & | & | \\ X - Y & X - Y \end{vmatrix}$ 

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There is as yet little information about the reactions of the second and third types. The best known rearrangement of the first type is that with the migration of hydrogen,

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chlorine, aryls and alkyls. Unfortunately there are very few reviews on the rearrangement of radicals but some data is recorded by Walling<sup>1</sup>.

The present work involves the rearrangement of polyhaloalkyl radicals in solution we have discovered. The study of chemical conversions of polychlorohydrocarbons containing a trichloromethyl group has revealed that the CCl<sub>3</sub> group is active in homolytic reactions.<sup>2</sup> Thus, the reaction of  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes and organomagnesium compounds in the presence of cobaltous chloride leads to the attack of the CCl<sub>3</sub> group to give compounds of the structure Cl(CH<sub>2</sub>)n-CCl<sub>2</sub>CCl<sub>2</sub>(CH<sub>2</sub>)n-Cl. Such is also the case when  $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes react with copper or nickel. The reaction seems to proceed through the homolytic cleavage of the chlorine atom from the tetrachloroalkane molecule according to the scheme:

$$\begin{split} \dot{R} + CCl_3(CH_2)nCl \rightarrow RCl + \dot{C}Cl_2(CH_2)nCl \\ 2Cl(CH_2)n\dot{C}Cl_2 \rightarrow Cl(CH_2)nCCl_2 - CCl_2(CH_2)nCl \end{split}$$

It will be noted that the abstraction of the chlorine atom from the trichloromethyl group is effected under extremely mild conditions, and it is possible that the readiness of cleavage is still greater in the polychlorohydrocarbon radical, just as hydrogen is more labile in free hydrocarbon radicals than in saturated hydrocarbon molecules.<sup>1</sup> The ready cleavage of the chlorine atom and the known stability of radicals with a carbon atom bearing an odd electron and linked to two chlorine atoms<sup>3</sup> both must favour the rearrangement of radicals of type A into those of type B

$$\begin{array}{c} \mathsf{CCI}_3\dot{\mathsf{C}} \swarrow \to \dot{\mathsf{C}CI}_2\mathsf{CCI} \swarrow \\ \mathsf{A} & \mathsf{B} \end{array}$$

In the investigations of such a rearrangement the radicals were obtained from the homolytic addition of various compounds to olefins containing a polyhalomethyl group.<sup>4-15</sup> The addition of hydrogen bromide, bromotrichloromethane, bromine, thiophenole, and mercaptans to compounds  $XCCl_2CY=CH_2$ , where  $X=Cl,F,H,CH_3$ , and  $Y=Cl,H,Br,CH_3$  has been studied and the results summarized in Tables 1, 2, and 3.

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No.Polychorocetin (yokul in % of checry)Non-rearranged IT (yokul in % of checry)Rarranged IT (yokul in % of checry)Rearranged IT (% did in % did in % of checry)Rearranged IT (% did in % d				Reaction Prod	ducts			
1. $CCI_3CH-CH_2$ $CCI_4H-CHC-CH_2 Br (5N)$ $CCI_4H-CHC-CH_2 Br (5N)$ $I00$ 4         2. $CCI_3CH-CH_2$ $CCI_4H-CHC-CH_2 Br (5N)$ $CH_{10}-CCI-CH_2 Br (1N)$ $I00$ 5         3. $CCI_3CH-CH_2$ $CCI_4D-CH_2$ $CCI_4D-CHC-CH_2 Br (5N)$ $CHCI_{1-}CCI-CH_2 Br (1N)$ $I00$ 5         4. $CCI_3C-CH_2$ $CHCI_2-CCI-CH_2 Br (5N)$ $CHCI_2-CCI-CH_2 Gr (11)$ $CCI_2-CH_2 Br (1S)$ $I00$ 7         5. $CHCI_2-CH-CH_2$ $CHCI_2-CCI_2-CH_2 Br (5N)$ $CHCI_2-CCI_2-CH_2 Gr (11)$ $CCI_2-CH_2 Br (1S)$ $I00$ 7         6. $CH_3CCI_2-CH-CH_2$ $CHCI_2-CCI_2-CH_2 Br (5N)$ $CHCI_2-CCI_2-CH_2 Br (1S)$ $I00$ $S_1$ 7.* $CCI_2-CH-CH_2$ $CHCI_2-CH_2-CH_2 Br (1S)$ $CHCI_2-CCI_2-CH_2 Br (1S)$ $I00$ $S_1$ 8. $CHCI_2-CH_2-CH_2$ $CHCI_2-CH_2-CH_2 Br (1S)$ $CHCI_2-CCI_2-CH_2 Br (1S)$ $I00$ $S_1$ 9. $CHCI_2-CCI_2-CH_2 Br (30)$ $CHCI_2-CCI_2-CH_2 Br (1S)$ $I00$ $S_1$ 9. $CHCI_2-CCI_2-CH_2 Br (30)$ $CHCI_2-CCI_2-CH_2 Br (1S)$ $I00$ $I00$ $I00$ $I00$ $I00$ $I$	.00	Polychloro-olenn	Non-rearranged 1 <sup>†</sup> (yield in % of theory)	Rearranged II† (yield in % of theory)	Rearranged IV <sup>†</sup> (yield in % of theory)	Non-saturated product III† (yield in % of theory)	Rearrangement (%‡)	References
2.* $CCI_3CH=CH_3$ CCI_4H=CH_4 $CCI_4H=CH_4$ $CCI_4H=CH_4$ $I00$ 5         3. $CCI_5C=CH_4$ $CL_4$ $CCI_4$ $CH_3$ $CH_3$ $I00$ 5         4. $CCI_5C=CH_4$ $CHC_2$ $CH_2$ $CH_2$ $CH_4$ $CH_3$ $I00$ 5         5. $CHC_1-CH_2$ $CHC_2-CH_2-CH_3$ $CHC_3-CH_2-CH_3$ $CHC_3-CH_4$ $I00$ 7         6. $CHC_3-CH_2-CH_3$ $CHC_3-CH_2-CH_3$ $CHC_3-CH_2-CH_3$ $I00$ $20$ $8.9$ 7. $CHC_3-CH_2-CH_3$ $CHC_3-CH_3-CH_3$ $CHC_3-CH_2-CH_3$ $I00$ $90$ $8.9$ 7. $CHC_3-CH_2-CH_3$ $CHC_3-CH_3-CH_3$ $CHC_3-CH_3-CH_3$ $I00$ $90$ $8.9$ 7. $CHC_3-CH_2-CH_3$ $CHC_3-CH_3-CH_3$ $CHC_3-CH_3-CH_3$ $I00$ $90$ $8.9$ 8. $CHC_3-CH_3-CH_3$ $CHC_3-CH_3-CH_3$ $CHC_3-CCH_3-CH_3$ $I00$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ $90$ <td></td> <td>CCI3CH-CH2</td> <td></td> <td>CCI<sub>3</sub>H—CHCI—CH<sub>2</sub>Br (77)</td> <td></td> <td></td> <td>100</td> <td>4</td>		CCI3CH-CH2		CCI <sub>3</sub> H—CHCI—CH <sub>2</sub> Br (77)			100	4
3. $CCI_3C=CH_4$ $CCI_3C=CH_4$ $CHCI_3=CCH_2H_4$ $CHCI_3=CCH_2H_4$ $IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII$	2 <b>.</b> *	cci <sub>s</sub> ch—cH <sub>2</sub>		CCI <sub>2</sub> H—CHCI—CH <sub>2</sub> Br (88)			100	S
4.       CCI <sub>3</sub> CCI=CH <sub>2</sub> CHCI <sub>3</sub> -CCI <sub>2</sub> -CCI <sub>2</sub> -CCI <sub>2</sub> -CCI <sub>2</sub> Br (34)       CHCI <sub>3</sub> -CCI <sub>2</sub> -CH <sub>2</sub> Br (15)       100       7         5.       CHCI <sub>3</sub> -CH=CH <sub>2</sub> CHCI <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> Br (5)       CH <sub>2</sub> CI-CHCI-CH <sub>2</sub> Br (46)       CHCI <sub>2</sub> -CCI <sub>2</sub> -CH <sub>2</sub> Br (15)       90       8,9         6.       CH <sub>3</sub> CCI <sub>2</sub> -CH=CH <sub>2</sub> CHCI <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> Br (19)       CHCI <sub>2</sub> -CHCI-CH <sub>2</sub> Br (18)       CHCI <sub>2</sub> -CCI       90       8,9         7.*       CFCI <sub>2</sub> -CH=CH <sub>2</sub> CFCI <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> Br (19)       CFCIH-CH <sub>2</sub> Br (18)       CHCI <sub>2</sub> -CCI       90       90       9         8.       CHCI <sub>2</sub> -CCI=CH <sub>2</sub> CHCI <sub>2</sub> -CCI+CH <sub>2</sub> Br (19)       CFCIH-CCH <sub>2</sub> Br (18)       CHCI <sub>2</sub> -CC-CH <sub>2</sub> Br (10)       0       7         9.       CHCI <sub>2</sub> -CC -CH <sub>2</sub> CHCI <sub>2</sub> -CCI-CH <sub>2</sub> Br (34)       CICH <sub>2</sub> -CCI-CH <sub>2</sub> Br (30)       CHCI <sub>2</sub> -CC-CH <sub>2</sub> Br (12)       47       9       7         9.       CHCI <sub>2</sub> -C -CH <sub>2</sub> CHCI <sub>2</sub> -CCI-CH <sub>2</sub> Br (34)       CICH <sub>2</sub> -CCI-CH <sub>2</sub> Br (30)       CHCI <sub>2</sub> -CCC-CH <sub>2</sub> Br (12)       7       9       7	r,	ccı <sub>s</sub> c—cH <sub>2</sub> CH <sub>3</sub>		CHCl <sub>2</sub> —CCl—CH <sub>2</sub> Br (59) CH <sub>3</sub>	снсі <sub>2</sub> —ссі—сн <sub>2</sub> сі (11) сн <sub>3</sub>	$\operatorname{CCl}_{2} = \operatorname{C-CH}_{2}\operatorname{Br}(15)$ CH <sub>3</sub>	100	৬
5. $CHCI_{3}-CH-CH_{3}$ $CHCI_{2}-CH_{3}-CH_{3}Br(5)$ $CH_{3}CI_{-}CH-CH_{3}Br(5)$ $CH_{3}CI_{-}CH-CH_{3}$ 90       8.9         6. $CH_{3}CCI_{3}-CH-CH_{3}$ $CH_{3}-CH_{-}CH_{3}Br(13)$ $CH_{3}-CH-CH_{2}Br(13)$ $CH_{3}-CH-CH_{2}Br(13)$ 90       8.9         7.* $CFCI_{2}-CH=CH_{2}$ $CFCI_{2}-CH_{3}-CH_{2}Br(13)$ $CFCIH-CH_{2}Br(13)$ $CFCIH-CH_{2}Br(13)$ $7$ 90       7         8. $CHCI_{3}-CCI=CH_{2}$ $CHCI_{3}-CCIH-CH_{2}Br(13)$ $CFCIH-CCH_{2}Br(13)$ $CFCIH-CH_{2}Br(13)$ $9$ $9$ 9. $CHCI_{3}-CC-CH_{3}$ $CHCI_{3}-CCI-CH_{2}Br(13)$ $CICH_{3}-CCI-CH_{2}Br(13)$ $0$ $7$ 9. $CHCI_{3}-CC-CH_{3}$ $CHCI_{3}-CCI-CH_{2}Br(13)$ $CICH_{3}-CCI-CH_{2}Br(13)$ $0$ $7$ 9. $CHCI_{3}-CC-CH_{3}$ $CHCI_{3}-CCI-CH_{2}Br(13)$ $CICH_{3}-CCI-CH_{2}Br(13)$ $0$ $0$ $7$	4	ccl3ccl=cH2		CHCl <sub>3</sub> —CCl <sub>2</sub> —CH <sub>2</sub> Br (34)	CHCl <sub>3</sub> —CCl <sub>2</sub> —CH <sub>2</sub> Cl (14)	CCl <sub>2</sub> —CCl—CH <sub>2</sub> Br (15)	100	7
6. $CH_3CCI_4-CH-CH_2$ 6. $CH_3CCI_4-CH-CH_2$ CH_3CHCI-CHCI-CH_2Br (73)       100       9         7.• $CFCI_2-CH=CH_3$ CFCI_2-CH_2-CH_2Br (39)       CFCIH-CCIH-CH_2Br (18)       30       5         8. $CHCI_2-CCI=CH_2$ CHCI_2-CCIH-CH_2Br (30)       CFCIH-CCIH-CH_2Br (18)       0       7         9. $CHCI_2-C-CH_4$ CHCI_2-CH_2-CH_2Br (34)       CICH_2-CCI-CH_2Br (30)       CHCI_2-C-CH_2Br (12)       47       9         0. $CHCI_2-C-CH_4$ CHCI_2-CH_2-Br (34)       CICH_2-CCI-CH_2Br (30)       CHCI_2-C-CH_2Br (12)       47       9	5.	CHCl <sub>3</sub> —CH—CH <sub>2</sub>	CHCl2-CH2-CH2Br (5)	CH2CI-CHCI-CH2Br (46)			06	8,9
7.* $CFCl_2-CH=CH_2$ $CFCl_2-CH_2-CH_2$ $CFCl_2-CH_2-CH_2$ 30       5         8. $CHCl_2-CCI=CH_2$ $CHCl_2-CCIH-CH_2$ $CFCH_2$ $0$ 7         9. $CHCl_2-C_2-CH_2$ $CHCl_2-CCI-CH_2$ $CICH_2-CCI-CH_2$ $0$ 7         9. $CHCl_2-C_2-CH_2$ $CHCl_2-CCI-CH_2$ $CICH_2-CCI-CH_2$ $0$ 7         0. $CHCl_2-C_2-CH_2$ $CHCl_2-CCI-CH_2$ $CICH_2-CCI-CH_2$ $0$ 7	6.	CH3CCI2-CH-CH2		CH <sub>3</sub> CHCI—CHCI—CH <sub>2</sub> Br (73)			100	6
8. $CHCl_{2}-CCl=CH_{2}$ $CHCl_{2}-CCl=CH_{2}$ $CHCl_{2}-CCH-CH_{2}Br (30)$ $CHCl_{2}-C-CH_{2}$ $CHCl_{2}-CH-CH_{2}Br (34)$ $CICH_{2}-CL-CH_{2}Br (30)$ $CHCL-C-CH_{2}Br (12)$ $47$ $9$ $CHCL-C-CH_{2}Br (12)$ $47$ $9$	7.*	CFCI2-CH=CH2	CFCl <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br (39)	CFCIH—CCIH—CH <sub>2</sub> Br (18)			30	ŝ
9. $CHCl_2-C-CH_2$ $CHCl_2-CH-CH_2Br$ (34) $CICH_2-CCI-CH_2Br$ (30) $CHCI_2-C-CH_2Br$ (12) 47 9 $CH_3$ $CH_3$ $CH_3$ $CH_3$	×.	CHCI2-CCI=CH2	CHCl2-CCIH-CH2Br (30)				0	7
	<i>б</i>	cHCl2CCH2 CH3	CHCl2-CHCH2Br (34)	CICH <sub>2</sub> CCICH <sub>2</sub> Br (30) CH <sub>3</sub>		CHCICCH <sub>2</sub> Br (12) CH <sub>3</sub>	47	6

In Table 1 are listed data for the reaction of hydrogen bromide with a number of polyhalo-olefins in the presence of benzoyl peroxide or when exposed to ultra-violet light. It is well known, that the hydrogen bromide addition to olefins in the presence of peroxides proceeds by a chain radical mechanism. The homolytic character of reactions presented in Table 1 is the more evident from the fact that in the absence of initiators of radical processes hydrogen bromide fails to react with compounds listed in the table. The chain character of the reactions is substantiated by the fact that addition of a minute quantity of inhibitors completely stops the reaction. Addition of hydrogen bromide was carried out by saturating the benzoyl peroxide solution (0.5 g) in polyhaloalkene (0.1-0.6 mole) at  $50-70^\circ$ . Some tests were carried out in solutions (carbon tetrachloride and n-heptane) without markedly affecting the reaction. Generally the reaction resulted in a mixture of products

$$\begin{array}{c|c} & \text{SCHEME 1.} \\ & \xrightarrow{} XCCl_2CHYCH_2Br & I \\ & \xrightarrow{} HCCIXCYCICH_2Br & II \\ & \xrightarrow{} CCIX = CYCH_2Br & III \\ & \xrightarrow{} HCCIXCYCICH_2CI & IV \\ & \xrightarrow{} dimers & V \\ & \xrightarrow{} polymers & VI \end{array}$$

The following mechanism was suggested to account for this process



This scheme is analogous to that of Kharash's 'peroxide effect' but involves at steps b and b' the rearrangement of radicals A and A' into radicals B and B' and the elimination of a chlorine atom at step (e). The elimination of chlorine atoms results in a chain process quite similar to the main process (steps a, b, d) due to the liberation of bromine atoms into the system. The elimination of chlorine leading to

			<b>Peaction</b>		Reaction proc	lucts		
cut	Initiator	Solvent	temp.	Non-rearranged I* (yield in % of theory)	Rearranged II* (yield in % of theory)	Rearranged IV* (yield in % of theory)	Unsaturated III* (yield in % of theory)	Ref.
	(C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O <sub>2</sub>		100°		BrCCl <sub>3</sub> —CHCl—CH <sub>2</sub> CCl <sub>3</sub> (18)	BrCCI <sub>2</sub> CHCICH <sub>2</sub> CI (14)	CCI2-CH-CH2CCI3 (26)	4
		сн3соон	$20^{\circ}$	CCI <sub>3</sub> —CHBr—CH <sub>2</sub> Br (80)				10
	Exposed to electric light (150 W)	CHCI <sub>3</sub>		CCl <sub>3</sub> —CHBr—CH <sub>2</sub> Br (70)†	CCl₂Br—CHCl—CH₂Br (30)†			10
	(C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O <sub>2</sub>	cc14	80°	CCl <sub>3</sub> —CHBr—CH <sub>2</sub> Br (47)↑	CCl₂Br—CHCl—CH₂Br (53)↑			10
\$H‡			115°	CCl <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> (27)				Ξ
HS	Exposed to electric light (150 W)		80-90°		CHCl <sub>2</sub> —CHCl—CH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> (30)		CCl <sub>2</sub> -CH-CH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub> (11)	п
CH <sub>2</sub> SF	Exposed to electric light (150 W)		110-115°		CHCl <sub>2</sub> —CHCl—CH <sub>2</sub> —SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> (11)		CCI <sub>2</sub> -CH-CH <sub>2</sub> -SCH <sub>2</sub> - C <sub>6</sub> H <sub>5</sub> (39)	П
H <sub>13</sub> SF	Exposed to electric light (150 W)		110-115°				CCl <sub>2</sub> =CHCH <sub>2</sub> SC <sub>6</sub> H <sub>13</sub> -n (30)	12

TABLE 2. ADDITION OF DIFFERENT REAGENTS TO 1,1,1-TRICHLOROPROPENE

7 % of the overall yield. ‡ The reaction carried out in the presence of sulphur as inhibitor of homolytic processes.

the stabilization of intermediate radicals is common to homolytic reactions.<sup>16,17</sup>

A number of factors affect the chemical behaviour of radicals in solutions and, in particular, the ratio of products obtained following scheme (1); the main factors being the relative stability of starting and rearranged radicals and the relative rate of their interaction with the reaction chain carrier such as HBr, Br<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>SH.

Reactions listed in Table 1 were run with the same carrier, namely hydrogen bromide, under comparable conditions. The comparison of results supports the conclusion that there is a connection between the structure of the radical and its capacity to undergo rearrangement with 1,2-chlorine migration. Thus, the reaction of 1,1,2-trichloropropene-2 (Ex. 8, Table 1) with hydrogen bromide proceeds without rearrangement as, in accordance with the general rule, the starting secondary radicals CHCl<sub>2</sub>CClCH<sub>2</sub>Br are more stable than the primary radicals CHClCCl<sub>2</sub>CH<sub>2</sub>Br that could have been formed on rearrangement. The radicals whose odd electron is bound

to the group 
$$\dot{C}Cl_2$$
—C—appear to be more stable than the secondary  $(-C-\dot{C}H-C)$ ,

 $\left( \stackrel{\frown}{\longrightarrow} C \stackrel{-\dot{C}Cl}{\longrightarrow} C \stackrel{-\dot{C}}{\longrightarrow} C \stackrel{-\dot{C}}{\longrightarrow} C \stackrel{-\dot{C}}{\longleftarrow} C \stackrel{-\dot{C}}{\longrightarrow} C \stackrel{-\dot{C}}{\rightarrow} C$ 

rearrange into radicals A', B', C' (Ex. 1, 2, 3, 4, Table 1).

$$\begin{array}{c} {\rm CCl}_{s}\dot{{\rm C}}{\rm HCH}_{2}{\rm Br}\rightarrow\dot{{\rm C}}{\rm Cl}_{s}{\rm CH}{\rm CH}_{2}{\rm Br}\\ {\rm A} {\rm A}'\\ {\rm CCl}_{s}\dot{{\rm C}}{\rm Ci}{\rm CH}_{s}{\rm Br}\rightarrow\dot{{\rm C}}{\rm Cl}_{s}{\rm CCl}_{s}{\rm CH}_{s}{\rm Br}\\ {\rm B} {\rm B}'\\ {\rm CCl}_{s}\dot{{\rm C}}{\rm -CH}_{s}{\rm Br}\rightarrow\dot{{\rm C}}{\rm Cl}_{s}{\rm CC}{\rm I}{\rm CH}_{s}{\rm Br}\\ {\rm -}\\ {\rm -}\\ {\rm -}\\ {\rm CH}_{s} {\rm CH}_{s}\\ {\rm C} {\rm C}'\end{array}$$

The primary radicals, bound to chlorine are somewhat more stable than the secondary ones bound to hydrogen. Accordingly, radicals D rearrange into radicals D'.

> $CHCl_2\dot{C}HCH_2Br \rightarrow \dot{C}HClCHClCH_2Br$  (Ex. 5, Table I) D D

It follows, of course, that the secondary radical E rearranges into a more stable secondary radical E'.

$$\begin{array}{c} CH_{3}CCI_{2}\dot{C}HCH_{2}Br \rightarrow CH_{3}CCICHCICH_{2}Br \quad (Ex. \ 6, \ Table \ I) \\ E \qquad \qquad E \\ \end{array}$$

It is to be noted that the introduction of fluorine or hydrogen into the trihalomethyl group of unsaturated compounds (Ex. 5 and 7, Table 1 and Ex. 3, Table 3) hinders the rearrangement of radicals under study and gives rise both to rearranged and non-rearranged products.

Table 2 lists some data characteristic of homolytic reactions of 3,3,3-trichloropropene with a number of carriers of the chain reaction such as bromotrichloromethane, bromine, and mercaptans. Considering that the rearrangement of radicals

 <sup>&</sup>lt;sup>16</sup> L. P. Schmerling, I. P. West, J. Amer. Chem. Soc. 75, 6216 (1953).
 <sup>17</sup> K. E. Wilzbach, F. R. Mayo, R. Van Meter, J. Amer. Chem. Soc. 70, 4069 (1948).

according to the scheme  $CCl_3CHCH_2Z \rightarrow CCl_2CHClCH_2Z$  ( $Z = CCl_3,Br,SR$ ) is not markedly affected by the nature of the group Z, that is remote from the centres of rearrangement, one can consider the differences in reactions compared in Table 2 as essentially dependent on the nature of the addenda.

The first of addenda listed is bound to trichloropropene only by a chain radical mechanism (Ex. 1, Table 2), the reaction proceeding according to scheme (1). Bromine addition to 3,3,3-trichloropropene can be effected heterolytically in a polar solvent such as acetic acid in the absence of initiators (Ex. 2, Table 2). This leads to a non-rearranged addition product  $CCl_3CHBrCH_2Br$ . When the reaction is carried out in a non-polar solvent exposed to electric light (Ex. 3, Table 2) or in the presence of benzoyl peroxide (Ex. 4, Table 2) a mixture of a rearranged product (BrCCl\_2CHClCH\_2Br) and non-rearranged product is obtained.

Similarly, addition of thiophenol to trichloropropene can be effected either heterolytically using sulphur to inhibit the homolytic process (Ex. 5, Table 2) or homolytically (Ex. 6, Table 2). In the first case yields a non-rearranged product  $CCl_3CH_2CH_2SC_6H_5$ , the second a rearranged product and an unsaturated compound  $HCCl_2CHClCH_2SC_6H_5$  and  $CCl_2=CH=CH_2SC_6H_5$ , the latter in very small yield. When thiophenol is substituted by benzylmercaptan (Ex. 7, Table 2) or n-hexylmercaptan (Ex. 8, Table 2) the main products are the unsaturated compounds  $CCl_2=CHCH_2SC_6H_5$  and  $CCl_2=CHCH_2SC_6H_{13}$  respectively. It is of interest that in these cases the eliminated chlorine is not taken up by trichloropropene but reacts with benzylmercaptan and n-hexylmercaptan to form hydrogen chloride.

These facts indicate that whenever the reaction is carried out in the presence of radical initiators (Ex. 1, 3, 4, 6, 7), the starting radicals  $CCl_3\dot{C}HCH_2Z$  ( $Z = CCl_3$ , Br,  $C_6H_5S$ ) rearrange into more stable radicals  $\dot{C}Cl_2CHClCH_2Z$ . The different nature of chain reaction carriers affect only the relative yield of the products of the type I-VI [scheme (1), p. 97]. This also substantiates the suggestion that it is the high stability of the rearranged radical that is primarily responsible for the rearrangement taking place.

Comparison of examples 6 and 8 in Table 2 suggests that the less effective reaction chain carriers prolong the life of intermediate radicals and thus seem to favour the stabilization of radicals by eliminating chlorine [e.g. step e, scheme (2)] to form unsaturated compounds.

In some instances the reactions proceed with the formation of rearranged products together with 'normal' addition products.

m		(Ex. A. Table 2)
(1)	$CCI_3CH = CI_2 + BI_2 \longrightarrow BrCCI_2CHCICH_2Br$	(EX. 4, 1201e 2)
(2)		(Ex. 7 Table I)
(2)		(EX. 7, Table I)
(3)		(Ex. 2 Table 2)
(3)	$CFCI_2CBI = CH_2 + HBI \longrightarrow CFCI = CCICH_2Br$	(EX. 5, 1401e 5)
(4)		(Ev. E. Tabla I)
(ד)	$CHCl_2 - CH = CH_2 + HBI \rightarrow CH_2CI - CHCI - CH_2Br$	(EX. 5, Table I)
(5)	$CHCI = C(CH) = CH + UP_{2} \rightarrow CHCI_{2} - C(CH_{3})H - CH_{2}Br$	
(3)	$CH_2 - C(CH_3) = CH_2 + HBT \longrightarrow CH_2CI - CCI(CH_3) - CH_2Br$	(EX. 7, Table I)

In all but the first case, one must exclude the possibility of non-rearranged products being formed as a result of simultaneous heterolytic addition reactions, as in the absence of benzoyl peroxide or electric light the reactions do not go. Further, the addition of traces of inhibitors stops the formation both of rearranged and nonrearranged products.

It is possible that the life of starting radicals F, G, H, T (CFCl<sub>2</sub>CHCH<sub>2</sub>Br, CFCl<sub>2</sub>CBrCH<sub>2</sub>Br, CHCl<sub>2</sub>CHCH<sub>2</sub>Br, CHCl<sub>2</sub>—C(CH<sub>3</sub>)—CH<sub>2</sub>Br) and of the corresponding rearranged radicals F', G', H', T' (CFClCHClCH<sub>2</sub>Br, CFClCBrClCH<sub>2</sub>Br, CHClCHCl—CH<sub>2</sub>Br, CHCl—CCl(CH<sub>3</sub>)—CH<sub>2</sub>Br) is of about the same duration and so leads to a mixture of rearranged and non-rearranged products.

The investigation of 1,2-chlorine migration in radicals led to an interesting example of homolytic conversion of  $CCl_3CBr=CH_2$  into its isomer  $CCl_2=CCl=CH_2Br$  (Ex. 1, Table 3).

The compound  $CCl_3CBr=CH_2$  after 1-2 days or after exposure without heating to a mercury lamp for a few minutes fully isomerizes:

$$CCI_3CBr = CH_2 \rightarrow CCI_2 = CCICH_2Br$$

The radical chain mechanism of this rearrangement was proved by the following observations.

The rearrangement is initiated by exposure to ultra-violet light and inhibited by small additions of hydroquinone or dimethylaniline. The course of the homolytic isomerizations of this compound is different from that of its heterolytic anionotropic isomerization which proceeds according to the allylic type:

$$CCl_{3}CBr=CH_{2} \xrightarrow{hv} CCl_{2}=CCICH_{2}Br$$

$$CCl_{3}CBr=CH_{2} \xrightarrow{CCl_{3}} CCl_{2}=CBrCH_{2}Cl_{3}$$

The following scheme is suggested for the homolytic isomerization:

$$\begin{array}{c} \mathsf{Br} + \mathsf{CCl}_{3}\mathsf{CBr} = \mathsf{CH}_{2} \xrightarrow{a} \mathsf{CCl}_{3}\mathsf{CBr}\mathsf{CH}_{2}\mathsf{Br} \\ \uparrow \\ \mathsf{Br} + \mathsf{CCl}_{2} = \mathsf{CCICH}_{2}\mathsf{Br} \xleftarrow{c} \mathsf{CCl}_{2}\mathsf{CBr}\mathsf{CICH}_{2}\mathsf{Br} \end{array}$$

SCHEME 3.

The results obtained in other cases of such isomerization are listed in Table 3.

Compounds of the type  $XCCl_2CBr=CH_2$  (X = CH<sub>3</sub> or F) are also isomerized when exposed to ultra-violet light or heated with benzoyl peroxide according the scheme:

$$XCCl_2CBr = CH_2 \rightarrow XCCl = CClCH_2Br$$

3,3-Dichloro-2-bromobutene-1 (Ex. 2, Table 3) undergoes heterolytic isomerization under the action of SbCl<sub>5</sub> to its allylic isomer, 2,4,-dichloro-3-bromobutene-2, but under the action of ultra-violet light it isomerizes homolytically to 2,3-dichloro-4bromobutene-2. 1-Fluoro-1,1-dichloro-2-bromopropene (Ex. 3, Table 3) when exposed to ultra-violet light isomerizes homolytically to 1-fluoro-1,2-dichloro-3bromo-propene-1, with a simultaneous formation of a dimer whose structure is considered to be  $CH_2BrCHBrCH_2CCI=CCIF$ 

				Interaction with di	fferent reagents			
Polyhaloalkenes	Aniontropic isomerization	Homolytic isomerization		Reaction P	roducts	Vield Re	carrangement	Ref.
			Kcagents	Unsaturated	Addition products	theory	C(2)	
1. CCl <sub>3</sub> CBr—CH <sub>2</sub> *	CCI2-CBr-CH2CI	ccl <sub>2</sub> =cclcH <sub>2</sub> Br†						13
			C <sub>6</sub> H <sub>5</sub> SH	CCI2_CCI-CH2SC6H5		22	100	12
			C4H9SH	CCI <sub>2</sub> =CCI-CH <sub>2</sub> SC <sub>4</sub> H <sub>9</sub>		30	100	12
			C <sub>6</sub> H <sub>5</sub> SH + S	CCI <sub>3</sub> CHBr—CH <sub>2</sub> SC <sub>6</sub> H <sub>5</sub>		38	0	12
2. CH <sub>3</sub> CCI <sub>2</sub> CBr-CH <sub>2</sub> *	CH3CCI-CBr-CH2CI	CH3CCI⇒CCI→CCI→Br†						14
			$(HBr+C_6H_5CO_2)_2$	CH <sub>3</sub> CCI		06	100	
3. CFCI <sub>2</sub> CBr—CH <sub>2</sub> *		CFCI-CCI-CH2Brt						
		+ dimer*(C)		~~~~~~				
			HBr(UV light)	CFCICCICH <sub>2</sub> Br (A)	CFCl <sub>2</sub> —CHBrCH <sub>2</sub> Br (B)	78(B) 3(A)	<del>4</del> 8.	
					dimer (C)*	9(C)		15
			Heating with (C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub>	CFCI-CCICH <sub>2</sub> Br (A)	dimer (C)*	46(A) 49(C)	100§	
* After some inductio Reaction of 1, 2, 3 v	m period, 1 and 2 undergo 1 with dialkylamine leads to an	homolytic isomerisation to C nines CXCI-CBr-CH <sub>2</sub> NR <sub>2</sub>	CCIX==CCICH <sub>2</sub> Br (X) (X==CI,F,CH <sub>3</sub> ).	-Cl, CH <sub>3</sub> ); 3-on standing	give rise to (C)dimer: C	H2Br-CHB	r	FCI.

TABLE 3. HOMOLYTIC ISOMERIZATION OF COMPOUNDS XCCl2-CBr=CH2

Under the action of ultra-violet light.
 Heating or exposing to ultra-violet light.
 Not accounting for dimers.

The isomerization of  $XCCl_2CBr = CH_2$  to  $XCCl = CClCH_2Br$  is accounted for by the fact that radicals with linkages -C - C - Br readily split off bromine and are

stabilized to form unsaturated compounds. Therefore, in compounds of the type  $XCCl_2CBr=CH_2$ , where X is Cl or CH<sub>3</sub>, we failed to effect the homolytic addition of even hydrogen bromide or thiophenol which are known to be very effective chain carriers (Ex. 1 and 2, Table 3).

The starting radicals XCCl<sub>2</sub>CBrCH<sub>2</sub>Z where X is Cl or CH<sub>3</sub> and Z is Br or C<sub>6</sub>H<sub>5</sub>S isomerize in all cases to split off bromine and form unsaturated compounds XCCl= CClCH<sub>2</sub>Z. Only in the case of hydrogen bromide addition to 1-fluoro-1,1-dichloro-2-bromopropene under the action of ultra-violet light (Ex. 3, Table 3) was there a saturated addition product (CFCl<sub>2</sub>CHBrCH<sub>2</sub>Br) formed together with the unsaturated compound (CFCl=CClCH<sub>2</sub>Br). But the saturated product resulted from the nonrearranged radical T whilst the rearranged radical T' was stabilized only by abstraction of bromine to give an unsaturated compound [see Scheme (4)].

$$CFCl_{2}CBr = CH_{2} + Br \rightarrow CFCl_{2}CBrCH_{2}Br$$

$$T$$

$$CFCl_{2}CBrCH_{2}Br \xrightarrow{rearrangement} CFClCCIBrCH_{2}Br$$

$$SCHEME 4.$$

$$HBr \qquad T' \downarrow$$

$$CFCl_{2}CHBrCH_{2}Br + Br \qquad CFCl = CCICH_{2}Br + Br$$

It is to be noted that 1,2-chlorine migration was also observed in other reactions. Thus, Urry<sup>18</sup> investigating the reaction of diazomethane and carbon tetrachloride under the action of light obtained tetrachloromethylmethane as the sole product in a 60 per cent yield. Since the reaction is very slow in the dark, is accelerated by light and is inhibited by diphenylamine it follows a radical chain mechanism.

The reaction of diazomethane with trichloromethane, chloroform and methyl trichloroacetate proceeds similarly.<sup>18</sup> Methyldiazoacetate reacts with chloroform, carbon tetrachloride and bromotrichloromethane to form rearranged products.<sup>19</sup>

The reaction of olefins and sulphuryl chloride in the presence of tertiary butyl peroxide proceeds as follows;<sup>20</sup>

$$\begin{array}{l} \mathsf{RCH}{=}\mathsf{CH}_2 + \mathsf{SO}_2\mathsf{Cl}_2 \xrightarrow{\rightarrow} \mathsf{RCHCICH}_2\mathsf{Cl} \\ \xrightarrow{\rightarrow} (\mathsf{RCHCICH}_2)_2\mathsf{SO}_2 \end{array}$$

and the authors suggest rearrangement of radicals with 1,3-chlorine migration from sulphur to carbon according to the scheme:

$$\begin{array}{c} \text{RCH}{=}\text{CH}_2 + \dot{\text{SO}}_2\text{CI} \rightarrow \text{RCHCH}_2\text{SO}_2\text{CI} \\\\ \text{RCHCICH}_2\text{SO}_2\text{CH}_2\dot{\text{CHR}} \xleftarrow{} \text{RCH}{=}\text{CH}_2 \\\\ \downarrow \text{SO}_2\text{CI}_2 \\\\ (\text{RCHCICH}_2)_2\dot{\text{SO}}_2 + \dot{\text{SO}}_2\text{CI} \end{array}$$

<sup>18</sup> W. H. UITY, J. R. Eiszner, J. Amer. Chem. Soc. 74, 5822 (1952).
 <sup>19</sup> W. H. UITY, J. W. Wilt, J. Amer. Chem. Soc. 76, 2594 (1954).
 <sup>20</sup> M. S. Kharasch, A. F. Zavist, J. Amer. Chem. Soc. 73, 964 (1951).

On the basis that the rearrangement of polyhaloalkyl radicals gives rise to more stable radicals, their relative stability has been tabulated as follows:

$$\begin{split} \mathsf{CCI}_3\dot{\mathsf{CH}}_2 &< \dot{\mathsf{CCI}}_2\mathsf{CH}_2\mathsf{CI}^{18} \\ \mathsf{CH}_2\mathsf{CICCI}_2\dot{\mathsf{CH}}_2 &< \mathsf{CH}_2\mathsf{CI}\dot{\mathsf{CCIH}}_2\mathsf{CI}^{18} \\ (\mathsf{CH}_2\mathsf{CI})_2\mathsf{CCI}\dot{\mathsf{CH}}_3 &< (\mathsf{CH}_2\mathsf{CI})_2\dot{\mathsf{CCIH}}_2\mathsf{CI}^{18} \\ \dot{\mathsf{CHCICCI}}_2\mathsf{CH}_3\mathsf{Br} &< \mathsf{CHCI}_2\dot{\mathsf{CCIH}}_2\mathsf{Br}^7 \\ \mathsf{CCI}_3\dot{\mathsf{CHCH}}_2\mathsf{X} &< \dot{\mathsf{CCI}}_2\mathsf{CHCICH}_2\mathsf{X} \\ \mathsf{X} &= \mathsf{CI},^4 \; \mathsf{Br},^4 \; \mathsf{CCI}_3,^4 \; \mathsf{SC}_6\mathsf{H}_5^{11} \\ \mathsf{CCI}_3\dot{\mathsf{CHCOOCH}}_3 &< \dot{\mathsf{CCI}}_2\mathsf{CHCICOOCH}_3^{19} \\ \mathsf{CCI}_3\dot{\mathsf{CHCOOCH}}_3 &< \dot{\mathsf{CCI}}_2\mathsf{CHCICOOCH}_3^{19} \\ \mathsf{CCI}_3\dot{\mathsf{CCICH}}_2\mathsf{Br} &< \dot{\mathsf{CCI}}_2\mathsf{CCIBrCH}_2\mathsf{Y} \\ \mathsf{Y} &= \mathsf{Br},^{10} \; \mathsf{SC}_6\mathsf{H}_5^{12} \\ \mathsf{CH}_3\mathsf{CCI}_2\dot{\mathsf{CHCH}}_2\mathsf{Br} &< \mathsf{CH}_3\dot{\mathsf{CCI}} \; \mathsf{CHCICH}_2\mathsf{Br}^9 \\ \mathsf{CCI}_3\dot{\mathsf{C}}(\mathsf{CH}_3)\mathsf{CH}_2\mathsf{Br} &< \mathsf{CHCICHCICH}_2\mathsf{Br}^{*8}, 9 \\ \mathsf{CHCI}_2\dot{\mathsf{C}}(\mathsf{CH}_3\mathsf{CH}_2\mathsf{Br} &\leq \mathsf{CHCICHCICH}_2\mathsf{Br}^{*,5}, 9 \\ \mathsf{CHCI}_2\dot{\mathsf{C}}(\mathsf{CH}_3\mathsf{CH}_2\mathsf{Br} &\leq \dot{\mathsf{CHCICCI}}(\mathsf{CH}_3\mathsf{DCH}_2\mathsf{Br}^{*,5} \\ \mathsf{CHCI}_2\dot{\mathsf{C}}(\mathsf{CH}_2\mathsf{Br} &\leq \dot{\mathsf{CFCICHCICH}}_2\mathsf{Br}^{*,5} \\ \mathsf{CFCI}_2\dot{\mathsf{CH}}_2\mathsf{Br} &\leq \dot{\mathsf{CFCICHCICH}}_2\mathsf{Br}^{*,15} \\ \mathsf{CFCI}_2\dot{\mathsf{C}}\mathsf{B}\mathsf{CH}_2\mathsf{Br} &\leq \dot{\mathsf{CFCICCIBrCH}}_2\mathsf{Br}^{*,15} \end{split}$$

From this table the following sequence of increasing stability of radicals may be deduced:

$$\mathsf{R\dot{C}H}_2 < \mathsf{R}_2\dot{\mathsf{C}H} < \mathsf{R}_3\dot{\mathsf{C}} \leqslant \mathsf{R\dot{C}HCI} < \mathsf{R}_2\dot{\mathsf{C}CI} < \mathsf{R\dot{C}CI}_2$$

with R being the polyhaloalkyl radical.

The agreement between the first three of this sequence with the stability of the hydrocarbon radicals (primary < secondary < tertiary) emphasizes the validity of the suggestion that the rearrangement is essentially due to the formation of radicals which are more stable under the conditions studied.

In accordance with the experimental evidence the rearrangement under investigation proceeds with an intramolecular chlorine atom migration. Thus the homolytic hydrogen bromide addition to 1,1,1-trichloropropene may proceed as follows:

SCHEME 5.  

$$Br + CCI_{3}CH = CH_{2} \longrightarrow CCI_{3}CHCH_{2}Br$$

$$I$$

$$Br + HCCI_{2}CHCICH_{2}Br \longrightarrow CCI_{2}CHCICH_{2}Br$$

$$III$$

Alternatively the chlorine atom is split off with subsequent addition to the double bond to give a rearranged radical as follows:

\* The life of investigated radicals under selected conditions is of about the same duration. There are still not enough data to speak more precisely about the relative stability of these radicals but that of the radicals to the right seems to be higher or near to that of the radicals to the left. It is, however, known that the chlorine atom adds more readily to compounds of Type I than II, and hence scheme (6) cannot predominantly lead to the formation of the rearranged compound III as has been observed.

The main argument in support of intramolecular chlorine atom migration is the fact that in some cases studied the rearrangement does not proceed with the formation of any products due to intermolecular chlorine migration.

Thus, the following schemes exemplify rearrangements that result in almost quantitative yields of a single product:

$$CCI_{3}CBr=CH_{2} \xrightarrow{hv} CCI_{2}=CCICH_{2}Br$$

$$CH_{3}CCI_{2}CBr=CH_{2} \xrightarrow{Bz_{2}O_{2}} CH_{3}CCI=CCICH_{2}Br$$

$$HBr$$

$$CCI_{3}CH=CH_{2} + HBr \xrightarrow{Bz_{2}O_{2}} HCCI_{2}CHCICH_{2}Br$$

But in those reactions where the intramolecular chlorine migration is accompanied by intermolecular migration additional products are always formed. Thus, for example, scheme (7) shows a homolytic addition of thiols to 1,1,1-trichloropropene to yield both rearranged compounds V according to scheme a, b, c, and unsaturated compounds IV as well as hydrogen chloride following the scheme a, d, e:

SCHEME 7.  

$$SR + CCI_{3}CH = CH_{2} \xrightarrow{a} CCI_{2}CH = CH_{3}SR \xrightarrow{d} CCI_{2} = CH_{-}CH_{2}SR + CI$$
  
 $\downarrow IV$   
 $\downarrow V$   
 $\downarrow V$