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The Synthesis of Substituted Cyclopropanes and Cyclopropenes by the Reductive Cyclisation of Polychloroalkanes

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The methods of synthesis of three-carbon rings—substituted cyclopropanes and cyclopropenes, obtained by the action of various metals on polychloroalkanes with chlorine-containing groups in the 1,3-positions relative to one another, are reviewed. Reductive cyclisation with zinc of compounds having the groups $-CCl_2CH_2CCl<$ or $CCl_3CH_2CCl<$ gives rise to new possibilities for the synthesis of substituted cyclopropanes. A new method of synthesising 1,2-disubstituted cyclopropenes from compounds with the group $-CCl_2CH_2CCl_2$ is examined.

The bibliography includes 87 references.

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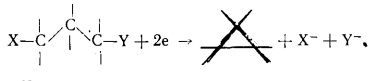
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I. INTRODUCTION

The chemistry of compounds of the cyclopropane and cyclopropene series has attracted the constant attention of investigators. This is indicated particularly by the appearance of annual reviews of literature on the synthesis of these compounds[1-8]. During recent years, reviews have been published on individual methods of synthesis of substituted cyclopropanes: the carbene method[9,10], the Simmons–Smith method[11], synthesis with the aid of the copper-isonitrile complex[12,13], and the electrochemical method[14,15]. Cyclopropene compounds are usually obtained by β-elimination from halogenocyclopropanes, by the addition of carbenes to acetylenes, or by the intramolecular cyclisation of the corresponding unsaturated aliphatic compounds[16,17]. Reviews have been devoted to the properties and reactions of three-carbon rings[18-32].

The structures of these rings have been confirmed by infrared, Raman, and ^1H NMR spectroscopy[33-35]. ^{13}C NMR has been used with an increasing frequency in recent years for the solution of problems of the structure of cyclopropanes[36-40]. cyclopropanes with an exocyclic double bond[41,42], or cyclopropenes[43-45].

Among the numerous methods for the synthesis of three-carbon rings, our attention was attracted to the intramolecular cyclisation of aliphatic chloro-compounds, particularly the 1,3-elimination (or γ-elimination) reaction[46] involving the removal of two halogen atoms with formation of a new C–C bond. The 1,3-dehalogenation reaction permits the direct conversion of an aliphatic halogenohydrocarbon into cyclopropane homologues with the same number of carbon atoms. The stoichiometry of this process is represented by the following equation in a general form:



Metals are usually employed as electron donors.

The aim of the present review is a survey of studies devoted to the synthesis of three-carbon rings from polychloroalkanes with chlorine-containing groups in the 1,3-positions relative to one another. Examples of such reactions have been mentioned in certain reviews, but they have never been surveyed and examined from the standpoint of their suitability for the synthesis of compounds of cyclopropane and cyclopropene series. Furthermore, new possibilities for the synthesis of a wide variety of cyclopropanes and cyclopropenes by reductive 1,3-dechlorination have been discovered in recent years, which necessitates a special discussion of all the results concerning this field. This review deals with the literature data published up to January, 1981.

II. 1,3-DECHLORINATION OF DICHLOROALKANES AND DICHLOROALKENES

The synthesis of cyclopropane by the 1,3-dechlorination of 1,3-dibromopropane by sodium was first described by Freund[47]. Gustavson[48] showed that the application of zinc dust in alcohol as the dehalogenating agent is more convenient. Subsequently it was found that the Gustavson 1,3-dehalogenation is of general importance for the synthesis of compounds of the cyclopropane series[49,50]. However, it was discovered that, whereas the use of 1,3-dibromoderivatives gives rise to satisfactory results, 1,3-dichloroderivatives are less valuable[50,51].

Without dwelling on numerous examples of the synthesis of substituted cyclopropanes from 1,3-dibromo-compounds, we shall consider below the 1,3-elimination of chlorine from organic polychloro-compounds.

Table 1 presents all the examples of the synthesis of cyclopropane and cyclopropene derivatives from 1,3-dichloro-compounds known at the present time. It is seen that, in order to achieve a high yield of cyclopropane, Na_2CO_3 and NaI have been added[52] to the 1,3-dichloropropane (see No.1 in Table 1), coverting thereby the dichloro-compound into the more reactive di-iodo-derivative. n-Pentylcyclopropane has been obtained by the same method from 1,3-dichlorooctane (Table 1, No.6). It has been observed[54] that satisfactory results are obtained when 1,3-dichloropropane or 1,3-dichlorobutane is treated with the $Cr(ClO_4)_2$-ethylenediamine complex (Table 1, Nos.4 and 5).

Magnesium in tetrahydrofuran can also be used successfully as the dechlorinating agent (Table 1, Nos.8 and 9). It has been shown[57] that the configuration of the dichloro-compound

is very important in the dechlorination of bicyclic systems. Thus the 1,3-dechlorination of *anti*-8-*exo*-4-dichlorodibenzobicyclo[3.2.1]octadiene proceeds with formation of the cyclopropane ring (Table 1, No.9), while in the case of *syn-exo*- and *syn-endo*-dichloro-compounds the benzyl chlorine undergoes hydrogenolysis. The replacement of chlorine by hydrogen occurs also when the zinc–copper[57] or sodium–potassium[62] alloy is used as the dechlorinating agent. Furthermore, on treatment with sodium in ethanol, the dibromo-compound of analogous structure gives rise to a high yield of a hydrocarbon containing the cyclopropane ring[62]. Table 1 presents also examples (Nos.3, 7, 10, and 11) for which 1,3-dichlorination by a wide variety of reducing agents proceeds with low yields of cyclopropane derivatives.

Proceeding to the synthesis of substituted cyclopropenes or their isomers with an exocyclic double bond from unsaturated 1,3-dichloro-compounds, one must note that attempts to obtain methylenecyclopropane by the dechlorination of 3-chloro-2-chloromethyl-1-propene by zinc proved unsuccessful[63]. The use of magnesium as the dechlorinating agent led to the formation of methylenecyclopropane in a low yield (Table 1, No.12). The electrochemical dechlorination of 1,3-dichloroalkenes, leading to substituted cyclopropenes (Table 1, No.13), has been achieved. Birch reduction, leading to cyclic compounds containing the 1,2,3-trichloroalkenyl group and a ring larger than that of cyclohexene, proceeds as reductive dechlorination with formation of bicyclo[*n*.1.0]alkanes (Table 1, No.14).

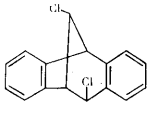
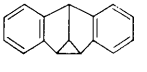
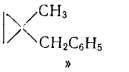
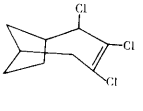
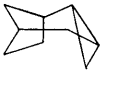
In conclusion of the examination of the 1,3-dechlorination of dichloroalkanes and dichloroalkenes, one should note that these reactions have been achieved in relation to a small number of examples and only some are suitable for the synthesis of three-carbon rings on a preparative scale; in the reviews published recently[7,8] the method of synthesis of three-carbon rings by 1,3-dechlorination is not mentioned at all. 1,3-Dichloro-derivatives containing functional groups are also without importance for the synthesis of cyclopropanes with functional substituents[64].

III. 1,3-DECHLORINATION OF COMPOUNDS WITH THE GROUPS $CCl_3CH_2CCl<$ or $-CCl_2CH_2CCl<$

1. The Interaction of Polychloroalkanes with $LiAlH_4$ and CH_3Li; Electrochemical Dechlorination

The 1,3-dechlorination of polychloroalkanes containing the $CCl_3CH_2CCl<$ or $-CCl_2CH_2CCl<$ groups by $LiAlH_4$ and CH_3Li or electrochemically, which leads to compounds of the cyclopropane series, has been described in relation to isolated examples. Thus treatment of 1,1,1,3-tetrachloro- or 1,1,1,3-trichloro-octane with $LiAlH_4$ in dioxan has been

Table 1. 1,3-Dechlorination of dichloroalkanes and dichloroalkenes.

№	Initial compound	Reductant	Solvent	Cyclopropane derivatives	Yield, %	References
1	$ClCH_2CH_2CH_2Cl$	Zn, NaI + Na_2CO_3	C_2H_5OH/H_2O**		95	[52]
2	$ClCH_2CH_2CH_2Cl$	Na	$(C_6H_5)_2O$	»	64	[52]
3	$ClCH_2CH_2CH_2Cl$	Ti	—	»	14	[53]
4	$ClCH_2CH_2CH_2Cl$	Cr^{II}en***	DMF/H_2O	»	86	[54]
5	$CH_3CHClCH_2CH_2Cl$	Cr^{II}en	DMF/H_2O		94	[54]
6	$ClCH_2CH_2CHClC_5H_{11}$	Zn, NaI + Na_2CO_3	C_2H_5OH/H_2O		39	[55]
7	$ClCH_2CH_2CHClC_5H_{11}$	$LiAlH_4$	dioxan	»	—	[55]
8	$ClCH_2CH_2CH_2C(CH_3)(CH_2Cl)_2$	Mg	THF		68	[56]
9		Mg	THF		94	[57]
10	$C_6H_5CH_2C(CH_3)(CH_2Cl)_2$	$LiAlH_4$	dioxan		18	[58]
11	$C_6H_5CH_2C(CH_3)(CH_2Cl)_2$	$LiAlH_4$	THF	»	4	[58]
12	$CH_2=C(CH_2Cl)_2$	Mg	THF		17	[59]
13	$R_2CClCH=CHCl$*****	electrochemically	DMF		—	[60]
14		Na	NH_3 (liq.)		55	[61]

*Here and in the other tables the yields are expressed as percentages of the theoretical yield.
**When the reaction was carried out in CH_3CONH_2 the yield of cyclopropane was 80%.
***en = $NH_2(CH_2)_2NH_2$.
****The product is formed by the carbonylation of the Grignard reagent obtained from



*****Analogous products have also been obtained from $R_2C = CHCHX_2$ (R = CH_3 or C_6H_5).

found to result in the formation of n-pentylcyclopropane (up to 22%) together with the main reaction product—n-octane:[55]

$$XCCl_2CH_2CHClC_5H_{11} \xrightarrow[\text{dioxan}]{LiAlH_4} n\text{-}C_8H_{18} + \triangleright\!-C_5H_{11}\ .$$
X=H, Cl

The electrolysis of CCl_4 or ethyltrichloroacetate in the presence of compounds with polar double bonds (acrylonitrile, ethyl acrylate, etc.) can be classified as cyclisation with participation of geminal polyhalogenoalkyl groups[65]. Electrolysis at a mercury cathode leads to the two-electron cleavage of the added component. The anion, generated electrochemically, attacks the monomer with formation of the anionic adduct (I). The latter is converted into products via several pathways in accordance with the following scheme:

$$(C_2H_5CO_2CCl_2)^- + CH_2{=}CHX \rightarrow (C_2H_5CO_2CCl_2CH_2CHX)^- \rightarrow$$
$$\xrightarrow{a} C_2H_5CO_2CCl_2CH_2CH_2X$$
$$\xrightarrow{b} \text{Cl, } CO_2C_2H_5\text{-substituted cyclopropane, X}$$
$$\xrightarrow{c} C_2H_5CO_2CCl_2CH_2CHClX\ ;$$
X=CN, $CO_2C_2H_5$.

Stage *a* involves the protonation of the anionic adduct (I), stage *b* involves its cyclisation, including the intramolecular substitution of the halogen, and stage *c* involves the abstraction of the halogen from the initial polyhalogeno-compound. This reaction, carried out in dimethylformamide (DMF) in the presence of lithium chloride at room temperature, leads to a substituted cyclopropane (80%) and an adduct (20%). It must be emphasised that under the given conditions the second chlorine atom of the *gem*-dichloromethylene group is retained.

Mixed polyhalogeno-compounds containing chlorine and bromine, such as $CHBr_2CH_2CH_2Cl$ or $CHClBrCH_2CH_2Br$, undergo 1,3-dehalogenation by methyl-lithium[66]. Cyclisation then proceeds via the 1,3-elimination of bromine atoms and leads to a 45–50% yield of chlorocyclopropane. The presence of a chlorine atom in the γ-position relative to the geminal group sharply reduces the yield of the halogenocyclopropane. Thus in the case of 1,1-dibromo-3-chloropropane the yield of bromocyclopropane was 3–5% and the main product proved to be 1,6-dichlorohex-3-ene (40%).

Thus the 1,3-dehalogenation of *gem*-polyhalogeno-compounds with participation of bromine is also much easier than the reaction with participation of chlorine.

2. Reductive Cyclisation of Polychloro-derivatives

The ready availability of polychloroalkanes of the type of $CCl_3CH_2CClR^1R^2$ or $RCCl_2CClR^1R^2$, obtained by the addition of CCl_4 or $RCCl_3$ to the $>C=C<$ bond[67,68], makes it attractive to develop on their basis a method of synthesising compounds of the cyclopropane series. The study of chemical reactions of such polychloroalkanes suggested a new approach to the synthesis of cyclopropane and its substituted derivatives by the reductive cyclisation of the above compounds by zinc in boiling ethanol in a stream of HCl.[69]

In the present review reductive cyclisation is a term given to the process involving 1,3-dechlorination with formation of a new carbon–carbon bond (closure of a three-membered ring) and hydrogenolysis of one or two C–Cl bonds [mechanisms (2) and (3)]. It is noteworthy that the 1,3-elimination of two chlorine atoms from aliphatic compounds of the type of $RR^1CClCH_2CClR^2R^3$ with formation of the corresponding cyclopropane derivative is also sometimes referred to as reductive cyclisation[54] or reductive 1,3-elimination[5]. In the present review we shall refer to the reaction via mechanism (1) as 1,3-dechlorination in order to demonstrate its difference from reactions (2) and (3). Together with the above processes, hydrogenolysis, which does not lead to cyclopropane derivatives [reaction (4)], is also possible:

$$RCCl_2CH_2CClR^1R^2 \rightarrow \text{Cl, } R^1, R, R^2\text{-substituted cyclopropane}\ , \quad (1)$$

$$RCCl_2CH_2CClR^1R^2 \rightarrow \text{H, } R^1, R, R^2\text{-substituted cyclopropane}\ , \quad (2)$$

$$CCl_3CH_2CClR^1R^2 \rightarrow \text{H, H, } R^1, R^2\text{-substituted cyclopropane}\ , \quad (3)$$

$$RCCl_2CH_2CClR^1R^2 \rightarrow RCH_2CH_2CClR^1R^2 + RCH_2CH_2CHR^1R^2\ . \quad (4)$$

3. The Influence of the Nature of the Hydrogen Donor on the Yield of Cyclopropanes in the Reductive Cyclisation of Polychloroalkanes

The influence of various hydrogen donors on the yields of substituted cyclopropanes has been studied in relation to the compounds $(ClCH_2CH_2)_2CCl_2$ and $CH_3CCl_2CH_2CHClCH_3$ [70] (Table 2). In order to obtain comparable results, all the experiments, whose results are presented in Table 2, were performed up to ~100% conversion of the initial polychloroalkanes by heating the reaction mixture for 1–3 h.

Table 2. The yield of cyclopropanes in the reductive cyclisation of polychloroalkanes with zinc in various media[70].

Initial compound	Cyclopropane	Solvent				
		C_2H_5OH in stream of HCl	C_2H_5OH	CH_3CO_2H	$(CH_3)_2NCHO$	$[(CH_3)_2N]_3PO$
$(ClCH_2CH_2)_2CCl_2$	$\triangleright\!-CH_2CH_2Cl$	91	91	61*	53	70
$CH_3CCl_2CH_2CHClCH_3$	H_3C, CH_3 (*cis*:*trans*)	78 (7:1)	57 (6:1)	31 (4:1)	48 (10:1)	— —

*1,5-Dichloropentane (16%) was also obtained.

Table 2 shows that the best results have been obtained in experiments performed in boiling ethanol in a stream of HCl. Subsequently these conditions were used in the synthesis of a wide variety of cyclopropanes by the reductive cyclisation of polychloro-derivatives.

4. The Synthesis of Cyclopropane and Monosubstituted Cyclopropanes

Compounds having the structures CCl_3CH_2CHClR or $RCCl_2CH_2CH_2Cl$, containing the *gem*-polyhalogeno-group, readily react with zinc via one of the following mechanisms

$$RCCl_2CH_2CH_2Cl \xrightarrow[C_2H_5OH]{Zn} \triangleright\!\!-R \quad , \qquad (5)$$
$$R=(CH_2)_2Cl,\ (CH_2)_4Cl$$

$$CCl_3CH_2CHClR^1 \xrightarrow[C_2H_5OH]{Zn} \triangleright\!\!-R^1 \quad ; \qquad (6)$$
$$R^1=H,\ Alk.$$

The initial compound for the synthesis of cyclopropane is 1,1,1,3-tetrachloropropane [mechanism (6), $R^1 = H$], which can be readily obtained by the radical addition of CCl_4 to ethylene[67].

Reactions (5) and (6) involve both the *gem*-dichloromethylene and the *gem*-trichloromethyl groups. In both cases monosubstituted cyclopropanes are formed in high yields (Table 3). Under the chosen conditions, the formation of chlorocyclopropanes is not observed. Chloroalkanes [hydrogenolysis via mechanism (4)] have been obtained among the side products. Thus propyl chloride[71], 1,1,3-trichlorohexane[72], and 1,5-dichloropentane[69] have been isolated in low yields.

Table 3. The yields of cyclopropane and monosubstituted cyclopropanes* having the general formula $\triangleright\!\!-R$.

Initial compound	Yield, %	R	References
$CCl_3CH_2CH_2Cl$	75	H	[71]
$CCl_3CH_2CHClC_3H_7$	81	C_3H_7	[72]
$CCl_3CH_2CHClC_8H_{17}$	87	C_8H_{17}	[72]
$CCl_2(CH_2CH_2Cl)_2$	91	$(CH_2)_2Cl$	[69]
$ClCH_2CH_2CCl_2(CH_2)_4Cl$	86	$(CH_2)_4Cl$	[73]

*The reactions were performed in boiling ethanol with gaseous HCl passed for 1–3 h. The reactant ratio was polychloroalkane : zinc = 1 : 4.

5. The Synthesis of Monosubstituted Cyclopropanes with the Cyano- or Ester Group in the Aliphatic Chain

Polychloro-derivatives of the type $ClCH_2CH_2CCl_2CH_2.CClR^1X$ ($R^1 = H$ or CH_3; $X = CO_2CH_3$ or CN), containing a functional group in the α-position relative to the C–Cl bond, exhibit certain characteristic features in the reductive cyclisation reactions.

Table 4. The yields of monosubstituted cyclopropanes with functional groups in the side chain having the general formula $\triangleright\!\!-CH_2CHXR^1$ [74]*.

№	Initial compound	Yield, %	R^1	X
1	$ClCH_2CH_2CCl_2CH_2CHClCO_2CH_3$	67	H	CO_2CH_3
2	$ClCH_2CH_2CCl_2CH_2CCl(CH_3)CO_2CH_3$	63	CH_3	CO_2CH_3
3	$ClCH_2CH_2CCl_2CH_2CHClCN$	69	H	CN

*For the reaction conditions, see the footnote to Table 3.

The reaction proceeds selectively with respect to the $ClCH_2CH_2CCl_2$-fragment, while the chlorine atom in the α-position relative to the electron-accepting group (CN, CO_2R) is replaced by hydrogen and is not involved in the reductive cyclisation:

$$ClCH_2CH_2CCl_2CH_2CClXR^1 \xrightarrow[EtOH\ or\ MeOH]{Zn} \triangleright\!\!-CH_2CHXR^1 \ ;$$
$$R^1=H,\ CH_3;\ X=CN,\ CO_2CH_3 \ .$$

As a result, high yields of monosubstituted cyclopropanes with electron-accepting groups in the side chain are produced (Table 4).

Among the side reactions, mention may be made of the hydrogenolysis of the $>CCl_2$ group. For example, $Cl(CH_2)_5CO_2CH_3$ has been obtained in a low yield from $ClCH_2CH_2CCl_2CH_2CHClCO_2CH_3$. The hydrolysis of the cyano-group on cyclisation of $ClCH_2CH_2CCl_2CH_2CHClCN$ to the acid with subsequent esterification, leading to cyclo-$C_3H_5CH_2CH_2CO_2C_2H_5$ with a low yield, has also been noted.

6. The Syntheses of Di-, Tri-, and Tetra-substituted Alkyl-, Chloroalkyl-, Phenyl-, and Chlorophenyl-cyclopropanes

If the substituents R, R^1 and R^2 in the initial polychloroalkanes $CCl_3CH_2CClR^1R^2$ or $RCCl_2CH_2CClR^1R^2$ are varied, it is possible to obtain disubstituted cyclopropanes (vicinal or geminal) as a result of reductive cyclisation and also tri- and tetra-substituted cyclopropanes by one of the following mechanisms:

$$CCl_3CH_2CClR^1R^2 \xrightarrow[C_2H_5OH]{Zn} \text{(1-Cl-2-R}^1\text{-3-R}^2\text{-cyclopropane)} + \text{(2-R}^1\text{-3-R}^2\text{-cyclopropane)} + \text{(1,2-Cl}_2\text{-3-R}^1\text{-cyclopropane)} \ ; \qquad (7)$$

$$RCCl_2CH_2CClR^1R^2 \xrightarrow[C_2H_5OH]{Zn} \text{(1-R-2-R}^1\text{-3-R}^2\text{-cyclopropane)} + \text{(1-Cl-2-R}^1\text{-3-R}^2\text{-cyclopropane)} \ ; \qquad (8)$$

$R=CH_3;\ R^1=H,\ CH_3;\ R^2=CH_3,\ C_6H_5.$

Examples of these reactions are given in Table 5.

Table 5. The yields and configurations of di-, tri-, and tetra-substituted cyclopropanes*.

№	Initial compound	Substituted cyclopropanes	Configuration**	Yield, %	Refs.
1	$CH_3CCl_2CH_2CHClCH_3$	1,2-dimethyl-3-Cl	*Z*	68	[75]
			E	10	
2	$CH_3CCl_2CH_2CHClC_6H_5$	1-Me-2-Ph-3-Cl	*Z*	3	
			E	3	
		1-Me-2-Ph-3-Cl	*Z*	17	[71]
			E	39	
3	$CCl_3CH_2CHClC_6H_5$	1-Ph-2-Cl	—	38	
			Z	4	[71]
		1,2-Cl$_2$-3-Ph	*E*	11	
		1,2-Cl$_2$-3-Ph	—	11	
4	$CCl_3CH_2CCl(CH_3)_2$	1,2,2-trimethyl-3-Cl	—	44	[76]
5	$CH_3CCl_2CH_2CCl(CH_3)_2$	1,2,2,3-tetramethyl	—	46	[76]
		1,2,2,3-tetramethyl-3-Cl	—	13	

*For the reaction conditions, see the footnote to Table 3.

**The geometrical isomers are designated in terms of the nomenclature of Blackwood et al.[77], based on the concepts of the *E*- and *Z*-forms.

Evidently the chlorine atom at a secondary carbon atom is readily involved in the reductive cyclisation. We may note that the synthesis of vicinal dialkylcyclopropanes results in the preferential formation of the *cis*-isomer (Table 5, No.1). The secondary benzylic chlorine atom can also be involved in the reaction. A characteristic feature of the reductive cyclisation of compounds with a benzylic chlorine atom is the formation of chlorocyclopropanes (Table 5, Nos.2 and 3), which indicates the influence of the bulk of the substituent at a secondary carbon atom linked to a single chlorine atom on the hydrogenolysis of the C–Cl bond in the CCl_2 or CCl_3 group on cyclisation of compounds of the type $XCCl_2CH_2.CHClC_6H_5$ (X = Cl or alkyl). For examples under discussion, the formation of n-propyl- or n-butyl-benzenes (in low yields) as side products has been noted.

The chlorine atom at a tertiary carbon atom is also involved in the reductive cyclisation. The resulting *gem*-dimethylcyclopropane is insufficiently stable under the experimental conditions (Table 5, No.4) and isomerises with ring opening. This entails the formation of 2-methylbut-1-ene and 3-methylbut-1-ene with an overall yield of 36%. Chlorocyclopropanes have been obtained not only by the reductive cyclisation with involvement of a benzylic chlorine atom but also in the case where the chlorine atom is linked to a tertiary carbon atom (Table 5, No.5). This shows that the number of substituents at the carbon atom linked to the chlorine atom influences the hydrogenolysis of the C–Cl bond in the dichloromethylene group. Evidently in the instances indicated above such hydrogenolysis is hindered, which leads to the formation of chlorocyclopropanes.

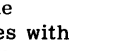
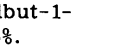
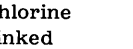
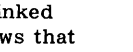
Consideration of the results of the reaction of 1,1,1,3-tetrachloro-3-phenylpropane with zinc shows that the overall yield of substituted cyclopropanes is 64% and that the products represent as it were all the stages in the reductive cyclisation: 1,1-dichloro-2-phenylcyclopropane, which is the 1,3-dechlorination product, and 1-chloro-2-phenyl- and 1-phenyl-cyclopropanes, which are the products of the successive substitution of chlorine by hydrogen. However, the chlorocyclopropanes formed are not intermediates whose hydrogenolysis leads to the formation of their hydrocarbon analogues, because it is known that chlorocyclopropanes are inert to reduction by zinc in alcohol[78]. Furthermore, special experiments have established that the interaction of 1,1-dichloro-2-phenylcyclopropane or 1-chloro-1-methyl-2-phenylcyclopropane with zinc under the conditions of reductive cyclisation leads to the formation of reduction products—1-chloro-2-phenylcyclopropane or 1-methyl-2-phenylcyclopropane—only in insignificant yields (2–7%).[70]

At the end of this discussion of the reductive cyclisation of polychloroalkanes with the $XCCl_2CH_2CCl<$ (X = Cl or alkyl) group, one may conclude that, in those cases where a single chlorine atom is linked to a primary or secondary carbon atom, the reaction proceeds smoothly and leads to the formation of mono- or di-substituted cyclopropanes in high yields. In those cases were a benzylic chlorine atom or a chlorine atom attached to a tertiary carbon atom is involved in the reaction, there is a possibility of the formation of a mixture of cyclopropane derivatives containing chlorocyclopropanes.

7. Competing Pathways in the Reductive Cyclisation of Polychloroalkanes with Several Chlorine-containing Groups

If there are several different chlorine-containing groups in the polychloroalkane molecule, the mode of reaction of this compound with zinc depends on the relative positions of the chlorine atoms. The study of the competing processes made it possible to establish the limits of the applicability of the given method of synthesis of cyclopropane compounds and to obtain data from which the reaction mechanism can be inferred. Certain examples of such reactions are given in Table 6.

Table 6. The reactions of monofunctional polychloroalkanes*.

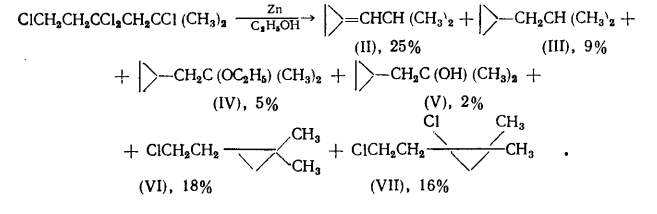
№	Initial compound	Products	Yield, %	References
1	$ClCH_2CH_2CCl_2CH_2CHClCH_3$		38	[75]
		 (*cis*)	32	
2	$ClCH_2CH_2CCl_2CH_2CHCl_2$		60 (72)**	[75]
			11 (2)	
3	$ClCH_2CH_2CCl_2CH_2CHClCH_2Cl$		60	[74]
4	$(ClCH_2CH_2CCl_2)_2$	$(ClCH_2CH_2CCl{=})_2$	92	[74]

*For the reaction conditions, see the footnote to Table 3.

**The yields of products obtained under the following reaction conditions are indicated in brackets: 25 °C, solvent—DMF.

***The 1,2-dechlorination products, namely 6-chlorohex-1-ene and 3-cyclopropylpropene, were not detected.

Table 6 shows that, if the reductive cyclisation can proceed with participation of the chlorine atom at a primary or secondary carbon atom, then both possible pathways operate to approximately equal extents and a mixture of mono- and di-substituted cyclopropanes is obtained (Table 6, No.1). On the other hand, if there is a possibility of competition between 1,3-dechlorination with participation of the chlorine atom at a primary or tertiary carbon atom, the reaction is more complex[76] and a number of products are formed:



Compounds (II)–(V) are then produced as a result of reductive cyclisation with participation of the chlorine atom at a primary carbon atom, while compounds (VI) and (VII) result from 1,3-dechlorination involving the chlorine atom at a tertiary carbon atom. The overall yields of compounds formed on cyclisation via both competing pathways amounted to 41 and 34% respectively. This shows that the two processes take place to approximately equal extents. It is noteworthy that 1,3-dechlorination with participation of a single chlorine atom at a tertiary carbon atom leads to the formation of chlorocyclopropane (VII). Cyclopropane (II), having an exocyclic double bond, has been obtained with an

appreciable yield. Its formation is due to the 1,3-dechlorination of the $ClCH_2CH_2CCl_2$ fragment and subsequent transformations of the intermediate

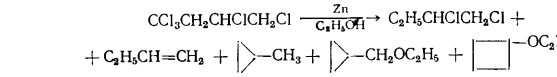


The $CHCl_2$ group in 1,1,3,3,5-pentachloropentane is involved in reductive cyclisation with much more difficulty than the $ClCH_2$ group (Table 6, No.2). Indeed, 60% of the reaction products were obtained by the cyclisation of the $ClCH_2CH_2CCl_2$ fragment. The formation of $CHCl_2(CH_2)_4Cl$ (5%) as a result of the hydrogenolysis of the CCl_2 group as well as the formation of a mixture of unsaturated chloroalkenes and the ethers $CH_2 = C(CH_2CH_2Cl)CH_2OC_2H_5$ and $CH_2 = C(CH_3)CH_2CH_2Cl$ (overall yield 12%) as a result of isomerisation with ring opening have also been noted. The formation of products of hydrogenolysis and isomerisation with ring opening does not occur if the reaction is carried out in DMF. The reductive cyclisation of the $CHCl_2CH_2CCl_2$ fragment is examined in greater detail below (see Section IV).

Results important for the understanding of the mechanism of the reductive cyclisation have been obtained in a study of polychloroalkanes which can undergo either 1,3- or 1,2-dechlorination. These compounds include $XCCl_2CH_2.CHClCH_2Cl$ (X = Cl, CH_3, or $ClCH_2CH_2$) and $(ClCH_2CH_2.CCl_2)_2$.

Table 6 shows that, when there is a possibility of the competitive 1,3-dechlorination of the $ClCH_2CH_2CCl_2$ group and the 1,2-dechlorination of single chlorine atoms, then the main reaction pathway is 1,3-dechlorination (Table 6, No.3). On the other hand, if 1,3-dechlorination of the same group or 1,2-dechlorination of vicinal dichloromethylene groups is possible, the only reaction pathway becomes 1,2-dechlorination of the $-CCl_2CCl_2-$group (Table 6, No.4). These results indicate unambiguously that the reaction begins with attack by the zinc atom on the $>CCl_2$ group.

Further confirmation of this has been obtained in the study of the interaction of polychloroalkanes of the type $XCCl_2.CH_2CHClCH_2Cl$ (X = Cl or CH_3) with zinc[71,74]. In relation to $CCl_3CH_2CHClCH_2Cl$, the reaction proceeds via the mechanism

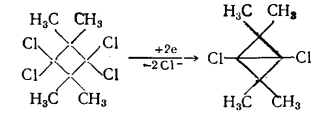


Similar results have been obtained in the study of the interaction of 2,2,4,5-tetrachloropentane with zinc in alcohol. The main products of these reactions are 1,2-dichloroalkanes and alk-1-enes—formed with an overall yield of 50–60% as a result of the hydrogenolysis of the CCl_3 or $>CCl_2$ groups. Cyclisation of the $CCl_2CH_2CHClCH_2Cl$ fragment containing the CH_2Cl group in the α-position relative to the single Cl atom is much more difficult (see also Table 6, No.3). The overall yield of cyclic products is only 6–9%.

Thus in these cases too the reaction begins with attack by zinc on the $>CCl_2$ group. The hydrogenolysis of the *gem*-polychloroalkyl group in the absence of the chlorine atom in the γ-position relative to this group becomes the only reaction pathway. Indeed, under the conditions of reductive cyclisation, mainly 1,1,5-trichloropentane is obtained from 1,1,1,5-tetrachloropentane[72].

IV. 1,3-DECHLORINATION OF COMPOUNDS WITH THE GROUPS $-CCl_2CH_2CCl_2-$ or $CCl_3CH_2CCl_2-$

1,3-Dechlorination of compounds with the $-CCl_2CH_2CCl_2-$ group is known to occur in a few isolated examples. Thus, 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane has been reduced electrochemically at a mercury cathode in DMF:[79]



The reaction proceeds with formation of 1,3-dichlorotetramethylbicyclobutane.

Polychloroalkanes with two $>CCl_2$ groups in the 1,3-positions (of the type of $RCCl_2CH_2CCl_2CH_3$) can be readily achieved by adding $RCCl_3$ to 2-chloropropene[80,81]. It might be supposed that 1,2-disubstituted cyclopropenes would be formed from these compounds under the conditions of reductive cyclisation. However, it was found that the results of the reaction depend greatly on the structure of the geminal groups (CCl_3, CCl_2, or $CHCl_2$) and on the reaction conditions.

Table 7 presents data obtained for various polychloroalkanes when the latter are refluxed with zinc in ethanol. It was shown that the reaction proceeds in a complex manner with formation of a mixture of saturated and unsaturated cyclic and aliphatic compounds. Cyclopropenes have been obtained only from $CHCl_2CH_2CCl_2CH_3$; the formation of chlorocyclopropanes has also been noted[82]. The presence of branched unsaturated products in the mixtures can be explained by the fact that chlorocyclopropanes are apparently unstable under the reaction conditions and isomerise with ring opening. In all three examples in Table 7 products of the hydrogenolysis of the $>CCl_2$ group are formed.

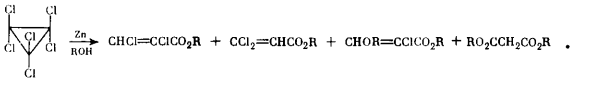
Table 7. The yields of the products of reductive cyclisation with participation of the $-CCl_2CH_2CCl_2-$group in C_2H_5OH (78 °C, 3 h).

Initial compound	Cyclic compounds	Yield, %	Aliphatic compounds	Yield, %	Refs.
$CHCl_2CH_2CCl_2CH_3$		30	$CHCl_2CH_2CH_2CH_3$	12	
		4	$CH_2=C(CH_3)CH_2OC_2H_5$	19	[75]
		10	$CH_2=C(CH_3)_2$	9	
$CH_3CCl_2CH_2CCl_2CH_3$		4	$CH_2=C(CH_3)CH(CH_3)OC_2H_5$	30	
			$CH_2CH=C(CH_3)CH_2OC_2H_5$	3	
		9	$CH_3(CH_2)_3CH_3$	1	[82]
		4	$CH_3CH=CHC_2H_5$	11	
			$CH_2=C(CH_3)C_2H_5$		
			$CHCl_2CH_2CH_2Cl$	38	
			$CHCl_2CH_2CH_2OC_3H_7$	21	[74]
$CHCl_2CH_2CHCl_2$*	—	—	$CHCl_2CH_2CH_3$	20	
			$Cl(CH_2)_3Cl$	4	

*The reaction was carried out in $n\text{-}C_3H_7OH$ at 100 °C for 3 h.

$CHCl_2CH_2CHCl$ does not react with zinc in boiling ethanol. On the other hand, in boiling propanol the hydrogenolysis of the $CHCl_2$ group, and not 1,3-dechlorination, takes place with subsequent alkoxylation.

The formation of a complex mixture of products has been observed in a study of the action of zinc in ethanol on hexachlorocyclopropane[83]. Instead of the expected 1,2,3,3-tetrachlorocyclopropene, a mixture of unsaturated esters was obtained, the esters being formed, according to the authors[83], as a result of isomerisation with opening of the cyclopropane ring:



1. The Synthesis of Substituted Cyclopropenes

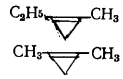
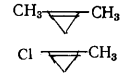
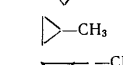
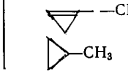
Reduction of the reaction temperature and especially the use of a different solvent (replacement of C_2H_5OH by DMF) enabled Kamyshova et al.[84] to propose a new method of synthesis of substituted cyclopropenes. The reaction proceeds via the mechanism



The availability of compounds of the type $RCCl_2CH_2CCl_2CH_3$ noted above leads to the possibility of synthesising the corresponding 1,2-disubstituted cyclopropenes; examples of such reactions are given in Table 8. Evidently, when R,R^1 = alkyl, the reaction leads to the formation of 1,2-dialkylcyclopropenes in high yields (Table 8, Nos.1 and 2). In those cases where the molecule contains only one CCl_2 group and the second geminal group is either CCl_3 (R = Cl, Table 8, No.3) or $CHCl_2$ (R = H, Table 8, No.4), the reaction is more complex and leads to a mixture of monosubstituted cyclopropanes and cyclopropenes.

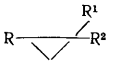
The synthesis of cyclopropenes from polychloroalkanes with the $-CCl_2CH_2CCl_2$-group by the action of zinc in DMF is extremely promising, since cyclopropenes are formed under mild conditions and in high yields.

Table 8. The synthesis of cyclopropenes by the dechlorination of compounds of the type $RCCl_2CH_2CCl_2CH_3$ with zinc in DMF at 25 °C.

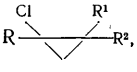
№	Initial compound	Cyclic compounds	Yield, %	Refs.
1	$CH_3CH_2CCl_2CH_2CCl_2CH_3$		77	[85]
2	$CH_3CCl_2CH_2CCl_2CH_3$		73	[84]
3	$CCl_3CH_2CCl_2CH_3$		29	[85]
			4	
4	$CHCl_2CH_2CCl_2CH_3$		56	[85]
			8	

V. THE PROBLEM OF THE MECHANISM OF THE REDUCTIVE CYCLISATION OF POLYCHLOROALKANES WITH FORMATION OF THREE-CARBON RINGS

The mechanism of the dehalogenation of 1,3-dihalogenoalkanes to compounds of the cyclopropane series by metals or salts of metals in the lowest valence state has been the subject of a series of studies (see, for example, Refs.54, 58, 66, 86, 87). It was found that the process is complex and consists of two or three stages[86,87]. In almost all the studies the possibility of the intermediate formation of a γ-halogeno-substituted organometallic compound was considered. For example, the cyclisation of 1,3-dihalogenopropane under the influence of the $Cr(ClO_4)_2$–ethylenediamine complex entails, according to Kochi and Singleton[54], the intermediate formation of $HalCH_2CH_2CH_2Cr^{II}en$, where en = ethylenediamine. The cyclisation of 2-benzyl-1,3-di-iodo-2-methylpropane by $LiAlH_4$ in ether is also believed[58] to involve the intermediate formation of the organoaluminium compound $PhCH_2C(CH_3).(CH_2I)CH_2LiAlH_3$. It is believed[66] that 1,1,3-dehalogenation of 1,1,3-trihalogenoalkanes with methyl-lithium proceeds via the intermediate formation of organolithium compounds of the type $RCHBrCH_2CHHalLi$. As regards the reductive cyclisation of compounds of the type $RCCl_2CH_2.CClR^1R^2$ by the action of zinc, which involves both 1,3-dechlorination and the hydrogenolysis of the C–Cl bond, one may claim that the hydrogenolysis of the CCl_2 group with formation of the fragment $\rangle CClCH_2CCl\langle$ is not the first reaction stage, since this fragment is dechlorinated with much more difficulty (see Section II), than the $-CCl_2CH_2CCl\langle$ group. One may also claim that the formation of the cyclopropanes



does not proceed via the intermediate chlorocyclopropanes

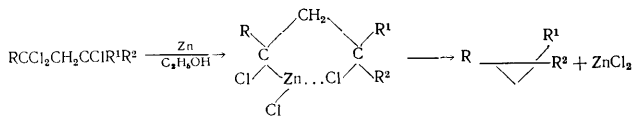


because, as already stated above, under the conditions of reductive cyclisation the hydrogenolysis of the chlorine atom linked to the ring proceeds to an insignificant extent (see Section III).

One may quote much evidence in support of the fact that reductive cyclisation with participation of *gem*-polyhalogeno-groups begins with attack by the zinc atom on such a group (CCl_2 or CCl_3). Thus there are two vicinal CCl_2 groups and the $ClCH_2$ group in the compound $(ClCH_2CH_2CCl_2)_2$; the reaction proceeds solely with the participation of the $-CCl_2CCl_2$-group, while the CH_2Cl group is not involved at all. On the other hand, the 1,3-dechlorination of the $ClCH_2CH_2CCl_2$ fragment in the $ClCH_2CH_2CCl_2CH_2CHClCH_2Cl$ molecule takes place much more readily than the 1,2-dechlorination of single chlorine atoms. The main reaction pathway for compounds of the type $XCCl_2CH_2CHClCH_2Cl$ (X = Cl or alkyl) is the hydrogenolysis of the $XCCl_2$ group. It has also been shown that $AlkCCl_2CH_2CHCl_2$ is 1,3-dechlorinated, whereas $CHCl_2CH_2CHCl_2$ is not involved in cyclisation. All these findings indicate the necessity for the presence in the molecule of the dichloromethylene or the trichloromethyl group for the reaction under consideration to occur. Finally reductive cyclisation proceeds just as readily when it involves a single Cl atom linked to a primary, secondary, or tertiary carbon atom.

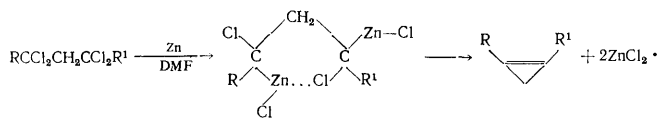
By analogy with the examples of the 1,3-dehalogenation of dihalogenoalkanes by metals with the intermediate formation of organometallic compounds, which were examined above, one can postulate that the reductive cyclisation of polychloroalkanes of the type $RCCl_2CH_2CClR^1R^2$ also proceeds via the intermediate formation of an organozinc compound. This hypothesis makes it possible to account for the ready

hydrogenolysis of the C–Cl bond in the α-position relative to the C–Zn bond:

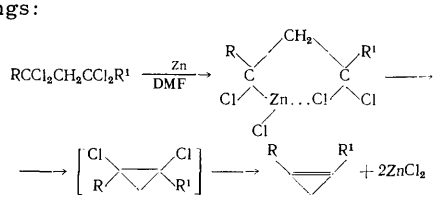


This hypothesis is also confirmed by the preferential formation of *cis*-1,2-disubstituted cyclopropanes mentioned above. The stereoselectivity of the process shows that an organozinc compound is formed as an intermediate in a specific conformation ensuring the coordination of zinc to γ-chlorine. The elimination of $ZnCl_2$ leads to the closure of the three-carbon ring.

1,2-Disubstituted cyclopropenes are apparently formed by a similar mechanism:



An alternative reaction involves the initial 1,3-dechlorination to 1,2-dialkyl-1,2-dichlorocyclopropane followed by 1,2-dechlorination of the vicinal chlorine atoms of the three-carbon rings:



Thus compounds with the groups CCl_3CH_2CCl <, $-CCl_2CH_2CCl$ <, or $-CCl_2CH_2CCl_2-$ can find extensive applications in the synthesis on their basis of a wide variety of three-carbon rings via dechlorination or reductive cyclisation reactions.

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