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Previously [1] it was shown that the reductive cyclization (RC) of polychloroalkanes proceeds with involvement of the CCl₂ group and the Cl atom found in the γ -position, and is a convenient method for the synthesis of substituted cyclopropanes. At the same time, RC via two dichloromethyl groups [2] fails to occur, while compounds with the CCl₂CH₂CHCl₂ grouping form under RC conditions a complex mixture of products [3]. This made it possible to assume that the reaction begins with the reaction of Zn with the most reactive CCl₂ group.

It seemed of interest to study the RC involving the two CCl_2 groups in $CH_3CCl_2CH_2CCl_2CH_3$ (I). It could be expected that the reaction will go in two directions: a) reduction of the CCl_2 groups, and b) 1,3-dechlorination:



The reaction was run under conditions comparable to those given in [1]: in refluxing aqueous ethanol, with vigorous stirring and activation of the zinc by iodine or HCl gas. In both cases the reaction proceeds easily and 100% conversion of (I) is reached in 1-1.5 h. Based on the GLC data, the reaction mixture contains \sim 15 compounds, and analyzed 17% of cyclic products (III)-(V), and less than 1% of pentane (II). As the main reaction products (Table 1) we isolated the isomeric ethers CH₂ = C(CH₃)CH(CH₃)OC₂H₅ (VI) and CH₃CH = C(CH₃)CH₂OC₂H₅ (VII) in an overall yield of 33% [(VI)/(VII) ratio = 10:1].

Besides (II) and (V) (cis/trans-2,3), we also identified 2-pentene (VIII) (cis/trans-2,6) and 2-methyl-1-butene (IX) among the hydrocarbon products by GLC. The overall yield of the hydrocarbons was 11%.

The formation of branched ethers (VI) and (VII) from the straight-chain polychloroalkane (I) is most probably due to opening of the cyclopropane ring (CPR) by the initially formed (IV) and subsequent alkoxylation. It is known that the solvolysis of chlorocyclopropanes by heating in alcohol in the presence of Ag^+ also leads to unsaturated ethers [4, 5].

It should be mentioned that the branched ketone $CH_3COCH(CH_3)_2$ (X) was detected among the reaction products. It is possible that dichlorocyclopropane (III), similar to monochloride (IV), isomerizes with opening of the ring to give $CH_3CCl_2C(CH)_3 = CH_2$, which by alkoxylation of the allylic Cl atoms, hydrolysis of the formed acetal, and reduction of the double bond is converted to ketone (X). The formation of this type of ketones was observed during the solvolysis of gem-dichlorocyclopropanes [6]. The yield of ketone (X) increases when the RC is run in the presence of HCl (Table 1).

The complex composition of the reaction mixture shows that, under conditions comparable to those for the RC of the $-\text{CCl}_2\text{CH}_2\text{CCl}$ fragment, the 1,3-dechlorination products of compounds with the $\text{CCl}_2\text{CH}_2\text{CCl}_2$ groupings are unstable and undergo various transformations: opening of the ring, and reduction of the Cl atom and its alkoxylation.

The structure of the isolated compounds was established via the PMR and IR spectra. The PMR spectral data are given in Table 2. The IR spectra of (III) and (IV) have a band at 1180 cm^{-1} (C-C in CPR), and also at 2980 and 3010 cm^{-1} (C-H in CPR). The IR spectra of com-

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TABLE 1. Ratio of Nonhydrocarbon Reaction Product

Method of activating Zn	Relative amount, in $\%$ of total products							
	(III)	(IV)	(VI)	(VII)	(X)	unidentified compounds		
l ₂ HCl	10 14	6 4	55 33	10 14	6 27	13 8		

TABLE 2. PMR Spectral Parameters of Isolated Compounds

Com- pound	Chemical shift of protons (8, ppm)								
	CH3	CH ₃ C=	CH2=CH	СНО	CH3CC1	CPR			
(III) (IV) (VI)	1,17 d 1,05 d 1,13 ^t	1,65 s	4,93 m	3,33 q 3,38 q	1,88 s 1,60 s	1,25 s 0,30-1,07 m			
(VII)	1,15t	1,60	5,48 m	3,80 q 3,40 q					
(X) *	1,08 d	2,10 s]	3,785					

*δ(CH) - 2.55 ppm (multiplet), cf. [8].

pounds (VI) and (VII) have bands at 1660 and 1680 cm^{-1} (C=C) and also at 3040 and 3080 cm^{-1} (H-C=). The IR spectrum of ketone (X) has a band at 1710 cm^{-1} (C=O) [7].

As a result, the obtained results show that under the selected conditions the RC involving two CCl₂ groups proceeds as 1,3-dichlorination to give chlorine-containing cyclopropanes, which partially undergo further transformations.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD chromatograph equipped with a katharometer. The following columns were used for the analytical determinations: A) 1 m \times 3 mm, packed with 5% SE-30, B) 2 m \times 3 mm, packed with 15% SE-301, and C) 1 m \times 3 mm, packed with 15% Carbowax 20M deposited on Chromaton N-AW-HMDS (0.16-0.20 mm), D) 3 m \times 3 mm, packed with 20% dinonyl phthalate, and E) 1 m \times 8 mm, packed with 20% Silicone E-301 deposited on Chromosorb P (0.16-0.20 mm) (column E was used for the preparative separation). The PMR spectra were obtained on a Hitachi-Perkin-Elmer R-20 instrument, using 50% CC1₄ solutions and TMS as the standard. The IR spectra were taken on a UR-20 instrument.

2,2,4,4-Tetrachloropentane was obtained from CH_3CCl_3 and 2-chloropropene as described in [9], bp 86-87° (18 mm), $n_D^{2°}$ 1,4853, $d_4^{2°}$ 1.3471. PMR spectrum (δ , ppm): 2.38 s (6H), 3.48 s (2H).

Reductive Cyclization of CH₃CCl₂CH₂CCl₂CH₃ (I). With vigorous stirring, to a suspension of 0.12 mole of Zn dust, activated with I_2 vapors, in 40 ml of 78% aqueous ethanol, heated to reflux, was added in drops 0.03 mole of (I). Based on the GLC data (column A, 100°C), the complete conversion of (I) is achieved after heating for 40 min. At the end of heating, the reaction mixture was distilled into a cooled trap to give a fraction with bp 25-78°, which was diluted with water, the water was frozen out, and the organic layer (1 g) was decanted and analyzed by GLC (column D, 45°). Here (II), (V), (VIII), and (IX) were identified by comparing with authentic specimens. One peak was not identified. The residual reaction mixture was diluted with water, and extracted in succession with pentane and CH₂Cl₂. The combined extracts were dried over MgSO₄ and the solvents were distilled off. Distillation of the residue gave 1.7 g of a fraction with bp 57° (200 mm) 60° (80 mm) and a residue of 0.3 g. This fraction was subjected to preparative GLC (column E, 60 and 75°) and here we isolated the pure (III), (IV), (VI), (VII), and (X). For 1-chloro-1,2-dimethylcyclopropane (IV). Found: C 57.62; H 8.98; Cl 33.96%. C5H9Cl. Calculated: C 57.42; H 8.68; Cl 33.90%. For 1,2-dichloro-1,2-dimethylcyclopropane (III). Found: C 43.77; H 5.91; Cl 50.06%. C₅H₈Cl₂. Calculated: C 43.19; H 5.80; Cl 51.01%. For 2,3-dimethyl-3-ethoxy-1-propene (VI). Found: C 73.13; H 12.40%. C7H140. Calculated: C 73.63; H 12.36%. The total yield of the products (% of theory) was: (II) 0.5, (III) 4, (IV) 9, (V) 4, (VI) 30, (VII) 3, (VIII) 4, (IX) 0.7, and (X) 4%.

2. The experiment was run and worked up the same as Expt. 1, but the zinc was activated by the steady passage of HCl gas. Here the complete conversion of (I) is achieved after heating for 1 h. The distribution of the reaction products in the reaction mixture, determined by GLC (column B, 80,), is given in Table 1.

CONCLUSIONS

The reductive cyclization of $CH_3CCl_2CH_2CCl_2CH_3$ proceeds as 1,3-dechlorination to give 1,2-dichloro-1,2-dimethyl- and 1-chloro-1,2-dimethylcyclopropanes. It was postulated that the formation of the esters $CH_2=C(CH_3)CH(CH_3)OC_2H_5$ and $CH_3CH=C(CH_3)CH_2OC_2H_5$ as the main reaction products is due to isomerization with opening of the chloro-substituted cyclopropane ring and subsequent solvolysis of the isomerization product.

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REACTION OF $\alpha, \alpha, \dot{\omega}$ -TRICHLOROALKENES WITH 1,1,1-TRICHLOROETHANE AND

1,1,1,3-TETRACHLOROPROPANE, ACCOMPANIED BY REARRANGEMENT OF RADICALS

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When CCl₄ is reacted with chloroolefins of type CCl₂=CH(CH₂)₂CH₂X, initiated either by peroxides or by coordination initiators (CI), for example Fe(CO)₅ + DMF, the main reaction products are compounds of structure HCCl₂CH(CCl₃)CH₂CH₂CH₂CHXCl (X = Cl (Ia), CN (Ib), with a Cl atom on the C⁵ atom attached to X [1, 2]. It was postulated that the (Ia, b) compounds are formed by the isomerization of the intermediate radical-adduct CCl₂CH(CCl₃)CH₂CH₂CH₂X (A) to the radical HCCl₂CH(CCl₃)CH₂CH₂CHX (B), with the 1,5-migration of H atom [1, 2]. A similar isomerization was observed in the reaction of CCl₃CH₂CH₂Cl with CH₂ = CCl₂ [3] and in the reduction of CCl₂(CH₂)_nY (Y = H, Cl, n = 4, 6) by the system: Fe(CO)₅ + hydrogen donor [4 and cited references].

In the present paper we studied under comparable conditions the reactions of other electrophilic addenda, $CC1_3CH_3$ (II) and $CC1_3CH_2CH_2C1$ (IV), with the electrophilic olefins $CC1_2 = CH(CH_2)_2CH_2C1$ (III) and $CC1_2 = CHCH_2C1$ (V), initiated by (CI), in order to search for the possible isomerization of the radical-adducts during the addition of gem-trichloroalkyl addenda.

Like in the reaction of CCl₄ with dichloroolefins $CCl_2=CHR$ [1, 2, 5], adducts of type CCl_3CH-R ($R'=CH_3$, CH_2CH_2Cl) are practically not formed from (II) and (III), and also from (IV) Ccl_3R'

and (V). 1,1,5,5,-Tetrachloro-2-(1,1-dichloroethyl)pentane (VI) (17% yield) and 1,1,3,3,5,5hexachloro-2-(chloromethyl)pentane (VIII) (21% yield), with a 30 and 54% conversion of (III)

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