REARRANGEMENT OF POLYCHLOROALKYL RADICALS WITH THE 1,5-MIGRATION OF HYDROGEN DURING THE REDUCTION OF 1,1,1,5-TETRACHLORO- AND 1,1,1-TRICHLOROPENTANES

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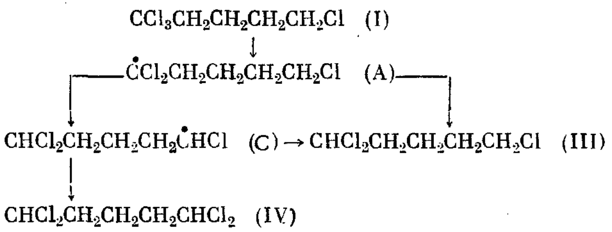
Polychloroalkyl radicals of type $R\dot{C}Cl_2$ undergo rearrangement with either the 1,5- or 1,6-migration of the H atom, and are converted to less stable radicals [1-3]. In order to ascertain the effect of the structure of the group, from which the H atom migrates, on the rearrangement we studied in the present paper the behavior of the radicals $\dot{C}Cl_2CH_2CH_2CH_2CH_2Cl$ (A) and $\dot{C}Cl_2CH_2CH_2CH_2CH_3$ (B). The A and B radicals were generated by the reduction of 1,1,1,5-tetrachloropentane (I) and 1,1,1-trichloropentane (II) using the system $i\text{-}C_3H_7OH$ + $Fe(CO)_5$.

Besides the reduction of (I) to 1,1,5-trichloropentane (III), under the studied conditions radical (A) rearranges to the radical $CHCl_2CH_2CH_2CH_2\dot{C}HCl$ (C) and the latter is converted to 1,1,5,5-tetrachloropentane (IV). Besides (III) and (IV), 2,4,8-trichloro-4-octene (V), 2,4,4,8-tetrachlorooctane (VI), and 1,5,6,10-tetrachloro-5-decene (VII) were isolated from the reaction mixture. It was also shown by GLC that 1,1,5-trichloro-1-pentene is present in the mixture. The formation of compounds (III)-(IV) can be described by a scheme that includes rearrangement.



Trichloropentane (III) can be formed from radicals A and C via their cleavage of H atoms from the solvent. The formation of products (V) and (VI) is explained by the addition of radical A to propylene and partial dehydrochlorination of the adduct [3, 4], while the formation of (VII) is explained by the dimerization of radical A and subsequent dehydrochlorination the same as described in [4, 5].

The reduction of 1,1,1-trichloropentane (II) under comparable conditions leads mainly to 1,1-dichloropentane (VIII), and also to 2,4-dichloro-4-octene (IX), 2,4,4-trichlorooctane (X), and 5,6-dichloro-5-decene (XI), i.e., to the same type of products as in the reduction of (I). However, 1,1,5-trichloropentane was not found in the reaction mixture, which should have been formed by the rearrangement of radical B to the radical $CHCl_2CH_2CH_2CH_2\dot{C}H_2$. Apparently, rearrangement with the 1,5-migration of hydrogen fails to occur in this case and the difference in the behavior of radicals A and B is related to the substantially greater difficulty of their intramolecular cleavage of hydrogen from the CH_3 group when compared with the CH_2Cl group.

The reduction of (I) performed in the present paper using various reducing systems disclosed that a decrease in the solution concentration of the H donor or in its efficiency

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TABLE 1

$CCl_3(CH_2)_4Cl$ (I) moles	H donor, moles	$Fe(CO)_5$, mmoles	Time, h	Conversion of (I), %	Reaction products and their yield, in % when based on reacted (I)		(III):(IV) ratio
					$CHCl_2\cdot(CH_2)_3CH_2Cl$ (III)	$CHCl_2(CH_2)_3CHCl_2$ (IV)	
0,1	i-C_3H_7OH (0,33)	4	3	52	44,5	2,2	20
0,1	i-C_3H_7OH (0,33)	8	5	69	58,5	2,7	22
0,1	i-C_3H_7OH (0,1)	8	5	36	59,6	5,9	10
0,1	CH_3OH (0.33)	4	3	11,5	55,5	8,7	6,5
0,05	$HCON(CH_3)_2$ (0.012)	4	3	13	51,6	14,6	3,5
0,05	$HCON(CH_3)_2$ (0,05)	4	3	11	63,0	15.4	4
0,03	$(C_2H_5)_3SiH$* (0,03)	4	3	97	89,0	–	–

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*The experiment was run as described in [7].

TABLE 2

Compound	n_D^{20}	d_4^{20}	Empirical formula	Found / Calculated		
				C	H	Cl
$CHCl_2CH_2CH_2CH_2CHCl_2$ (IV)	1,4945	1,3831	$C_5H_8Cl_4$	28,45 28,80	3,79 3,84	67.58 67,56
$CH_3CHClCH_2CCl_2(CH_2)_4Cl$ (VI)	1,4930	–	$C_8H_{14}Cl_4$	38.20 38,12	5,54 5,60	56,00 56,28
$CH_3CHClCH_2CCl_2{=}CH(CH_2)_2CH_3$ (IX)	1,4640	–	$C_8H_{14}Cl_2$	53,00 53,05	7.81 7,79	39,00 39,16
$CH_3CHClCH_2CCl_2(CH_2)_3CH_3$ (XI)	1.4695	1,1300	$C_8H_{15}Cl_3$	44,29 44,40	6,70 6,80	48,29 48,80

TABLE 3

Compound	δ, ppm				J, Hz		
	CH_3CHCl	CHCl	$CHClCH_2CCl_2$		J_{AB}	J_{AX}	J_{BX}
			H_A	H_B			
$CH_3CHClCH_2CCl_2CH_2CH_2CH_2CH_2Cl$ (VI)	1,60 d	4,35 m	2,77	2.63	−15.6	7,0	3,5
$CH_3CHClCH_2CCl_2CH_2CH_2CH_2CH_3$ (XI)	1,62 d	4,35 m	2,74	2,56	−15,2	5.9	4,9
$CH_3CHClCH_2CCl{=}CHCH_2CH_2CH_3$ (IX)	1,48 d	4,25 m	2,68*	2,52*	−14.7	7,9	5,3

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*The values of $\delta(H_A)$ and $\delta(H_B)$ are given for a solution of (IX) in C_6H_6, while in CCl_4 solution $\delta(H_A) = \delta(H_B) = 2.60$ ppm.

leads to an increase in the yield of (IV) (rearrangement product) relative to (III) (reduction product) (Table 1).

Compounds (IV)-(VII) and (IX)-(XI) were isolated from the reaction mixtures by preparative GLC. The composition and structure of compounds (IV), (VI), (IX), and (XI) were confirmed by elemental analysis and the NMR method (Tables 2 and 3). The spectrum of (IV) has signals that correspond to two types of protons: a triplet from the $CHCl_2$ group (δ_{CHCl_2} 5.81 ppm) and a multiplet of the methylene protons ($\delta_{CH_2} = 2.09$ ppm), while the integral intensities of the $CHCl_2$ and CH_2 groups have a 1:3 ratio, which corresponds to the adopted structure. The NMR spectra of compounds (VI), (XI), and (IX) represent the sum of the spectra of the known fragments [4, 6].

EXPERIMENTAL

1,1,1,5-Tetrachloropentane (I) [8], bp 94-95° (10 mm), n_D^{20} 1.4880, d_4^{20} 1.3472. 1,1,1-Trichloropentane (II) [8], bp 64° (27 mm), n_D^{20} 1.4550, d_4^{20} 1.1760. The purity of (I) and (II) was checked by GLC and NMR.

The GLC analysis was run on an LKhM-8MD chromatograph equipped with a katharometer, in a helium stream, and using 1.3 m × 4 mm columns packed with 15% Carbowax 20000 and 20% SKTPT-50Kh deposited on Chromaton (0.16-0.20 mm). The isolation of the compounds by preparative GLC was run on the same phases, but using 2.6 m × 9 mm columns. The NMR spectra were obtained on a Hitachi—Perkin—Elmer R-20 spectrometer (60 MHz) using 30% CCl_4 solutions of the compounds and HMDS as the internal standard.

Reduction of 1,1,1,5-Tetrachloropentane (I). a) A mixture of 0.3 mole of (I), 1 mole of $i-C_3H_7OH$, and 1 ml of $Fe(CO)_5$ was heated in an 0.5-liter stainless-steel autoclave for 4 h at 145°C. The isopropanol conversion products and its excess were distilled off, while the residue was dissolved in $CHCl_3$, washed with 1:1 HCl solution, then with water, and dried over $CaCl_2$. After distilling off the $CHCl_3$, the residue was vacuum-distilled. The products of three experiments were combined and distilled. Redistillation of the fraction with bp 84-89° (10-12 mm) (64.6 g) gave 1,1,5-trichloropentane (III) in 53% yield, n_D^{20} 1.4795, d_4^{20} 1.2407; cf [4].

Employing preparative GLC, from the fraction with bp 109-118° (10-12 mm)(5.9g) were isolated 1,1,5,5-tetrachloropentane (IV) and 2,4,8-trichloro-4-octene (V), n_D^{20} 1.4885, d_4^{20} 1.1757; cf. [4]. 2,4,4,8-Tetrachlorooctane (VI) was isolated in a similar manner from the fraction with bp 102-115° (2 mm) (1.9 g). Redistillation of the fraction with bp 116-160° (2 mm) (5.7 g) gave 2.5 g (2%) of 1,5,6,10-tetrachloro-5-decene (VII), bp 159-160° (2 mm), n_D^{20} 1.5070, d_4^{20} 1.2363; cf. [5]. The constants and elemental analysis of compounds (IV) and (VI) are given in Table 2.

b) The reaction of (I) with various reducing systems (see Table 1) was run in glass ampules, which were heated in metal jackets in a thermostat without stirring. In the case of the systems that contained $i-C_3H_7OH$ and CH_3OH the reaction products were worked up as described above, while the systems that contained DMF were washed several times with HCl solution, then with water, extracted with $CHCl_3$, dried, and the $CHCl_3$ was distilled off. In the case of systems that contained triethylsilane the reaction mixture was centrifuged to precipitate the iron salts. After the appropriate workup the reaction mixtures were analyzed by GLC.

Reduction of 1,1,1-Trichloropentane (II). A mixture of 17.5 g (0.1 mole) of (II), 0.38 mole of $i-C_3H_7OH$, and 0.4 ml of $Fe(CO)_5$ was heated in glass ampules, contained in metal jackets, in a thermostat for 4 h at 145°. The reaction products were worked up as in Expt. a). The products of three experiments were combined and distilled. Employing preparative GLC, from the fraction with bp 80-100° (100 mm) (32.7 g), which represented a mixture of (II) and 1,1-dichloropentane (VIII), we isolated (VIII), n_D^{20} 1.4390, d_4^{20} 1.0523; cf. [9]. In a similar manner, from the fraction with bp 90-100° (25-10 mm) (3.2 g) we isolated 2,4-dichloro-4-octene (IX), 5,6-dichloro-5-decene (X), n_D^{20} 1.4645, d_4^{20} 1.0173; cf. [10], and 2,4,4-trichlorooctane (XI). The constants and elemental analysis for (IX) and (XI) are given in Table 2. Based on the GLC data, the yield of (II), (VIII), (IX), (X), and (XI) is respectively 29, 38, 1.4, 3.4, and 1.5%.

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CONCLUSIONS

1. The reduction of 1,1,1,5-tetrachloropentane by various reducing systems gave 1,1,5-trichloropentane (as the main reaction product) and 1,1,5,5-tetrachloropentane. The formation of 1,1,5,5-tetrachloropentane testifies to the rearrangement of the $\dot{C}Cl_2CH_2CH_2CH_2CH_2Cl$ radical to the $CHCl_2CH_2CH_2CH_2\dot{C}HCl$ radical with 1,5-migration of the H atom.

2. The rearrangement product was not found when 1,1,1-trichloropentane was reduced under comparable conditions.

3. The reduction of 1,1,1,5-tetrachloropentane by various reducing systems disclosed that a decrease in the concentration of the H donor or in its efficiency leads to an increase in the relative yield of the rearranged product.

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EFFECT OF SUBSTITUENT AND NATURE OF SOLVENT ON ACYLOTROPY IN 3,6-DI-tert-BUTYL-2-ACYLOXYPHENOXYLS

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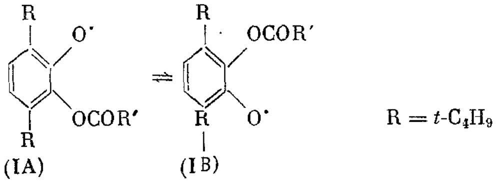
It was shown by us in a previous paper [1] that intramolecular migration of the acetyl group between the oxygen atoms is observed in 3,6-di-tert-butylacetoxyphenoxyl. The acylotropic transitions



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lead to a specific broadening of the lines of the hyperfine structure in the EPR spectra of the studied radicals, which makes it possible to estimate the kinetic parameters of these transitions. In the present paper the acylotropy phenomenon is discussed on the example of other 3,6-di-tert-butyl-2-acyloxyphenoxyls (Table 1). The EPR spectra of all of the studied radicals represent a doublet (a_H = 10.2 ± 0.2 Oe) due to the coupling of the unpaired electron with the ring proton in the p-position to the phenoxyl, each component of which is split into two lines (a_H = 1.95 ± 0.15 Oe) via the m-proton to the phenoxyl. A broadening of the extreme components in the EPR spectra of these radicals is observed when the temperature is raised to 120°C, which testifies to migration of the acyl groups between the oxygen atoms (Fig. 1). The indicated changes in the EPR spectra are completely reversible when the temperature is varied, and an analysis of the width of the lines made it possible to determine the acylotropy frequency (ν_{exchange}) [2]

$$\nu_{\text{exchange}} = \gamma_e \Delta (1/T_2)$$

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