HOMOLYTIC ADDITION OF ALIPHATIC ALCOHOLS TO TETRACHLOROETHYLENE IN THE LIQUID PHASE

L. K. Salamandra, Yu. B. Vol'kenshtein,
V. S. Bogdanov, M. Ya. Botnikov,
V. I. Kadentsev, and G. I. Nikishin

UDC 542.955:547.26:547.413.5

The free-radical reaction of tetrachloroethylene (TCE) with methanol in the liquid phase at 180°C and a pressure of 100 atm leads to the formation of trichloroallyl alcohol [1]. The aim of the present investigation was to study the reaction between TCE and other aliphatic alcohols: isopropanol, 1-butanol, 1-hexanol, 2-hexanol, and cyclohexanol, in the liquid phase. The reactions were initiated by tert-butyl peroxide (TBP) under a pressure of 50 atm. To compare the results with those previously obtained, we also included methanol in the range of alcohols studied. It was shown that substitution of hydrogen in the alcohols for the trichlorovinyl group takes place mainly at the carbon atom bound to the hydroxyl group, and as a result α-trichlorovinyl-substituted alcohols (Ia-f) are mainly formed

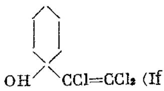
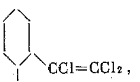
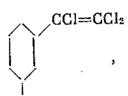
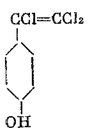
$$R^1CH(R^2)OH + CCl_2{=}CCl_2 \rightarrow \underset{\text{Ia-f}}{CCl_2{=}CCl{-}CR^1(R^2)OH} + HCl$$

$$R^1 = R^2 = H\ (a);\ Me\ (b);\quad R^1 = H,\ R^2 = n\text{-}Pr\ (c);\quad R^1 = H,\ R^2 = n\text{-}Am\ (d);\ R^1 = Me,\ R^2 = n\text{-}Bu\ (e);\ R^1 + R^2 = -(CH_2)_5-\ (f).$$

The position of the trichlorovinyl and hydroxyl groups in (Ic-e) can be inferred from the mass spectrum fragments $[CCl_2{=}CCl{-}CR^1OH]^+$ with m/z 159 (Ic, d) or m/z 173 (Ie), to which the maximal peaks correspond. It is probable that in these cases the fragmentation takes place at the branching point of the carbon chain of the alkanol, as the result of elimination of ions of C_3H_7, C_5H_{11}, and C_4H_9 groups, respectively.

An increase in the length of the carbon chain leads to a decrease in TCE conversion, but the yield of alcohols (I) practically does not change.

TABLE 1. Reaction between Tetrachloroethylene (TCE) and Alcohols (molar ratio alcohol : TCE = 3 : 1, [TBP] = 0.2 mole/liter, residence time in reactor 1.5-3.5 min, 50 atm, 180°C)

Alcohol	Conversion of TCE, %	Reaction products	Yield, based on converted TCE, %
CH_3OH	28	$CCl_2{=}CClCH_2OH$ (Ia)	85
$C_4H_9CH(CH_3)OH$	23–28	$CCl_2{=}CClCH(OH)(CH_3)_2$ (Ib)	90–95
n-C_4H_9OH	24	$CCl_2{=}CClCH(OH)C_3H_7$ (Ic)	73
		$CCl_2{=}CClCH(C_2H_5)CH_2OH$ (II)	Traces
		$CCl_2{=}CClCH(CH_3)CH_2CH_2OH$ (III)	7
		$CCl_2{=}CClCH_2(CH_2)_2CH_2OH$ (IV)	Traces
n-$C_6H_{13}OH$	11	$CCl_2{=}CClCH(OH)C_5H_{11}$ (Id)	75
$C_4H_9CH(CH_3)OH$	2,5	$CCl_2{=}CClC(OH)(CH_3)C_4H_9$ (Ie)	65
		$CCl_2{=}CClCH(CH_3)CH_2CH_2CH(OH)CH_3$ (V)	15
	14,5	 (If)	72
		 (VI)  (VII)  (VIII)	8

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1577-1582, July, 1982. Original article submitted November 12, 1981.

0568-5230/82/3107-1401$07.50

TABLE 2. ^{13}C NMR Spectra of Substituted Cyclohexanes ($CDCl_3$, 32°C)

Compound	δ ^{13}C, ppm[a]							
	C^1	C^2	C^3	C^4	C^5	C^6	CCl	CCl_2
I(f)	75,9	35,2	21,2	24,6	21,2	35,2	138,6	117,9
(VII)[b]	69,2 (68,3)	38,3 (37,8)	41,0 (39,8)	28,4 (27,9)	23,1 (22,5)	34,3 (33,4)	136,1[c] –	116,0 –
(VIII)[b]	69,2 (68,0)	34,3 (33,7)	27,8 (26,6)	41,6 (41,1)	27,8 (26,6)	34,3 (33,7)	136,5[c] –	116,0 –
(VII)[d]	91,3 or 92,0	46,3	44,3 or 44,7	31,6	26,0	41,5 or 41,0	–	–
(VIII)[d]	92,0 or 91,3	41,0 or 41,5	30,8	44,7 or 44,3	30,8	41,0 or 41,5	–	–
(IX)	43,0	29,8	25,7	25,4	25,7	29,8	137,8	115,4
cyclo-$C_6H_{11}OH$	65,9	34,9	23,7	25,0	23,7	34,9	–	–

---

a) Chemical shifts were measured with reference to $CDCl_3$ solvent (δ 76.9 ppm). In parentheses, the calculated values are given [4].

b) Assignment of CCl and CCl_2 was based on effects of Cl and Alk in substituted ethylenes [5].

c) A different assignment is also possible: 136.5 to (VII), and 136.1 to (VIII).

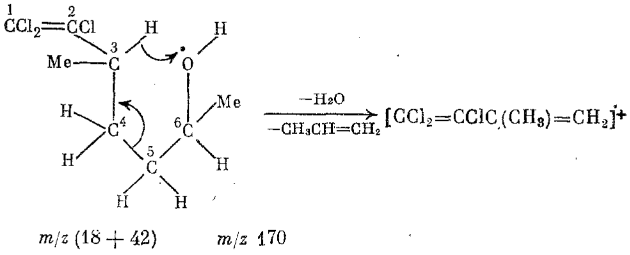
d) Spectrum was taken with addition of $Eu(dpm)_3$. Molar ratio: compound : $Eu(dpm)_3 = 2:1$.

It should be noted that alcohols with more than three C atoms in the chain react not only at α-C atoms, but also at other reaction centers with the formation of isomers (Table 1). In the reaction of TCE with n-butanol, not only 1,1,2-trichloro-1-hexen-3-ol (Ic), but also 1,1,2-trichloro-3-ethyl-1-buten-4-ol (II), 1,1,2-trichloro-3-methyl-1-penten-5-ol (III), and 1,1,2-trichloro-1-hexen-6-ol (IV) were identified. In the mass spectra of (Ic) and (II)-(IV), molecular ions with m/z 202 (204, 206) were observed with intensity ratios of the isotopic peaks that show that the molecules of these compounds contain three Cl atoms each. In the spectra of (II)-(IV), the maximal peak corresponds to the $CH_2=\overset{+}{\underset{\cdot\cdot}{O}}H$ (m/z 31); the last is characteristic of the fragmentation spectra of primary alcohols. Due to the presence in the spectrum of (III) of intense peaks with m/z 157, 121, 45, corresponding to the $[CCl_2=CClCH(CH_3)]^+$, $[M-CH_2CH_2OH-HCl]^+$, and $[CH_2CH_2OH]^+$ ions, we can determine the branching point of the allyl chain, and structure (III) is confirmed. Structure (III) is also confirmed by the data of IR spectroscopy. In the IR spectrum of isolated (III), bands are observed with a frequency of 3638 (ν OH), 1595 cm^{-1} ($\nu C=C$), and also bands of stretching (2980, 2885 cm^{-1}) and deformational (1380 cm^{-1}) vibrations of the methyl group.

As the result of the reaction of TCE with 2-hexanol, besides 1,1,2-trichloro-3-methyl-1-hepten-3-ol (Ie), its isomer (V) is also formed with the trichlorovinyl group attached to the δ-C atom. Compounds (Ie) and (V) were isolated by adsorption chromatography on a column.

In the IR spectrum of (V), intense absorption maxima are observed in the 3624, 2970, 2875, 1380, and 1595 cm^{-1} regions, corresponding to the OH and CH_2 groups and the double bond. In the electron-impact (EI) mass spectra of compound (Ie), there is a molecular ion peak (230 amu), while in the spectrum of (V) the highest mass number for the observed ions is 170. To find whether the latter is a molecular or a fragment ion, we used mass spectrometry with chemical ionization (CIM) by isobutane, at which fragmentation proceeds under milder conditions. The presence in the CIM spectrum of (V) of peaks with m/z 231 and 287 (of a protonated ion $[M+H]^+$ and a cluster ion $[M+57]^+$, respectively) shows that (V) has mol. wt. 230. The fragment ion with m/z 170 forms during the decomposition of (V) under EI, probably as the result of a synchronous elimination of water and olefin, as represented below, characteristic of the fragmentation of alcohols [2]. (See scheme, next page.) In the high mass numbers region, in the spectrum of (V) there is a peak of an ion with m/z 157, which is probably formed as the result of cleavage of the C^3-C^4 bond, and corresponds to the fragment $[CCl_2=CClCH(CH_3)]^+$. The most intense peak (100%, 45 amu) is characteristic of the fragment ion $[CH_3CH(OH)]^+$, which forms as the result of the cleavage of the C^5-C^6 bond in (V).

In the reaction of the TCE with cyclohexanol, not only 1-trichlorovinyl-1-cyclohexanol (If), but also 2-, 3-, and 4-trichlorovinyl-1-cyclohexanols (VI)-(VIII) are formed. By using the chromato-mass-spectrometry method,



it was found that in the spectra of each of the four mixture components, molecular ions with m/z 228 (230, 232) are observed, with intensity ratios of isotopic peaks characteristic of compounds with three Cl atoms. The structures of (If), (VII), and (VIII) were found by the ^{13}C NMR method. The results are shown in Table 2. For (If), the chemical shifts (CS) of symmetrically located (with respect to C^1) carbon atoms are equal in pairs (for C^2 and C^6, 35.2 ppm, and for C^3 and C^5, 21.2 ppm); for C^1 the CS is 75.9 ppm. For the interpretation, the spectra of (If), (VII), and (VIII) were compared with the ^{13}C spectra of cyclohexanol and trichlorovinylcyclohexane (IX) obtained from TCE and cyclohexane. The spectrum of the mixture of isomers VII and VIII isolated from the reaction mixture (δ: 21.3; 27.8; 28.4; 34.4; 38.3; 41.0; 41.6; 69.2; 116.0; 136.1; 136.5 ppm) shows that the mixture does not contain either 1- or 2-trichlorovinylcyclohexanol, since in the spectrum there is no C^1 signal with CS of 75.9 ppm, nor a signal in the 50 ppm region, whose CS could be determined by the α-effect of the $CCl=CCl_2$ group of 16.1 ppm in (IX) and the β-effect of the OH group of 8.0-8.5 ppm in cyclohexanol [3] (the CS were calculated with reference to C_6H_{12}, in which $\delta = 26.9$ ppm [4]). The above spectrum can be assigned either to a mixture of isomers (VII) and (VIII), or to a mixture of their conformers under the condition that the rate of conversion of the isomers on the NMR time scale is low.

By studying the spectra in the 30-100°C range and analyzing the literature data for alkyl-, halo-, and hydroxyl-substituted cyclohexanes [3-5], we could conclude that this is the spectrum of a mixture of isomers (VII) and (VIII). This was also confirmed by the CS calculation and ^{13}C spectra with the addition of $Eu(dpm)_3$. From the CS calculation, assuming additivity of the effects of the OH and $CCl=CCl_2$ groups, it follows that the signals at 27.8 and 28.4, and at 41.0 and 41.6 ppm correspond to different isomers and that the C^1 signals (and also C^6) in (VII) and (VIII) and C^2 and C^6 signals in (VIII) cannot be resolved because of the proximity of their CS values.

To prove this supposition, we measured the ^{13}C spectra with addition of the $Eu(dpm)_3$ shifting agent. Analysis of the spectra showed that at a molar ratio shifting agent : mixture of isomers = 1 : 10, the C^1 signals (69.2 ppm) are resolved, and at a 1 : 2 ratio, the signals at 34.3 ppm also become resolved. Thus, all the 10 signals of the ring C atoms were revealed: six signals for (VII) and four signals for (VIII). The spectra with $Eu(dpm)_3$ also confirmed the correctness of this assignment, since the maximum shift with reference to the signals position without the addition of the shifting agent is, as expected, observed for C^1 bound to an OH group (by 22.1 and 22.8 ppm); it is smaller for C^2 and C^6 (6.7 and 8.0 ppm), and still smaller (2.9-3.3 ppm) for the more distant C atoms. We should note that the calculated CS values agree well with the experimental if we assume the additivity of the substituent effects. For isomer (VII), the deviations for the five cyclic C atoms are equal to 0.5-0.9 ppm, and for (VIII) the deviations of the three values are equal to 0.5-0.6 ppm, while for the three others, they are 1.2 ppm. Table 2 shows that, in contrast to the strong descreening effect on the C^1 atom of the $CCl=CCl_2$ group in trichlorovinylcyclohexane (IX) (α-effect of 16.1 ppm), the β-effect is considerably smaller (2.9 ppm), and it is also smaller than the γ-effect of the OH (8.0 ppm [3]) and CH_3 groups (5.2-8.9 ppm [4]).

The value of CS for C^1 found in the spectrum of a mixture of (VII) and (VIII), equal to 69.2 ppm shows that the main contribution to the screening of C^1 is introduced by the conformer with an equatorial OH group, as in cyclohexanol ($\delta C^1 = 69.5$ ppm), which contains 70% of this conformer [5]. In alkylcyclohexanols with an axial OH group, the CS of C^1 is 65-67 ppm [3]. The $CCl=CCl_2$ group in isomers (VII) and (VIII) is oriented in the same way, probably equatorially, since the differences in the CS for the $-CCl=$carbon atom in the trichlorovinyl group are not high (0.4 ppm).

Thus, in the radical reactions of TCE with aliphatic alcohols, a cleavage of the H atom takes place not only at the α-C atom of the alcohol (the main reaction), but also at atoms present in the β-, γ-, and δ-positions with respect to the hydroxyl. The hydroxyalkyl radicals thus formed, by addition to TCE form adduct-radicals which split Cl atoms to form isomeric unsaturated alcohols. It should be noted that alcohols isomeric with the main product are formed preferably during an attack at the ω-1 C atom of the alcohol, probably because of the higher stability of the radicals thus formed.

EXPERIMENTAL

The reaction products were identified by the following physicochemical methods: elemental analysis, IR, PMR, ^{13}C NMR spectroscopy, and mass spectrometry. The IR spectra were run in CCl_4 solution and in KBr tablets on the UR-20 apparatus, the PMR spectra, on the Varian-60 apparatus, ^{13}C NMR, on the Bruker WP-60 apparatus; and mass spectra, on the Varian-MAT CH-6 and Varian-MAT-111 apparatus (SE-30 column, 160°C), and on the Riber quadrupole mass spectrograph (capillary column OV-17, 160°C).

The starting materials were AR grade.

The reaction of TCE with the alcohols (molar ratio 1 : 3) was studied at a pressure of 50 atm at 180°C, and at the initiator (TBP) concentration of 0.2 mole/liter in a continuous action type apparatus with titanium reactor, in an inert atmosphere [1]. The residence time of the reagents in the reactor was 1.5-3.5 min. The mixtures were analyzed by GLC [1]. The reaction products were isolated by vacuum distillation in an argon current, or by adsorption chromatography on a silica gel column brand L 100/160 μ, using benzene as eluent.

Reaction of Tetrachloroethylene with Methanol. Main reaction products – trichloroallyl alcohol (Ia), bp 83-86°C (10 mm), n_D^{20} 1.5200 (cf. [6]).

Reaction of Tetrachloroethylene with Isopropanol. Main reaction product – 1,1,2-trichloro-3-methyl-1-buten-3-ol (Ib), bp 80-82°C (11 mm), n_D^{18} 1.5110 (cf. [7]). PMR spectrum (δ, ppm, CCl_4): 1.5 s (CH_3), 3.0 s (OH) (shifts on addition of CF_3COOH), relative intensity of CS corresponds to theoretical (6 : 1).

Reaction of Tetrachloroethylene with 1-Butanol. Main reaction product – 1,1,2-trichloro-1-hexen-3-ol (Ic), bp 107-108°C (12 mm), n_D^{18} 1.5020 (cf. [8]). Found: C 35.85; H 4.69; Cl 51.05%. $C_6H_6Cl_3O$. Calculated C 35.45; H 4.64; Cl 52.27%. PMR spectrum (in CCl_4) is represented by an OH group singlet with δ 4.46 ppm, shifting to the weak-field region on addition of CF_3COOH, a triplet of the CH group adjacent to CH_2 and OH (δ 4.9 ppm), and a complex multiplet in the 1-1.5 ppm region of the C_3H_7 group, with a ratio of integral intensities of 1 : 1 : 7. Mass spectrum, m/z (relative intensity, %): 202, 204, 206 $[M]^{+\cdot}$ (10, 10, 3); 167, 169, 171 $[M-Cl]^+$ (15, 10, 2); 159, 161, 163 $[M-C_3H_7]^+$ (100, 97, 33); 149 $[M-Cl-H_2O]^+$ (4); 95 (17); 89 (7); 55 (15); 43 (19).

Side products of the reaction: 1,1,2-trichloro-3-ethyl-1-buten-4-ol (II), 1,1,2-trichloro-3-methyl-1-penten-5-ol (III), and 1,1,2-trichloro-1-hexen-6-ol (IV). Compounds (II) and (IV) were determined in the reaction mixture in trace amounts by chromato-mass-spectrometry. The molecular ions (II) and (VI) have m/z 202, 204, 206 amu. Compounds (II) and (IV) could not be unequivocally assigned from the mass spectra.

Compound (III) is formed in an amount of 1 : 10 with respect to (Ic) (GLC data); it was isolated by adsorption chromatography from the fraction with bp 107-120°C (10 mm), n_D^{21} 1.5030. Mass spectrum, m/z (%): 202, 204, 206 $[M]^{+\cdot}$ (12, 11, 3); 184, 186, 188 $[M-H_2O]^+$ (10, 10, 3); 166, 168 $[M-HCl]^+$ (6, 3); 157, 159, 161 $[M-CH_2CH_2OH]^+$ (36, 33, 12); 149, 151, 153 $[M-Cl-H_2O]^+$ (60, 38, 7); 125 (24); 123 (75); 121 (80); 113 (52); 95 (26); 89 (18); 87 (28); 85 (35); 45 $[CH_2CH_2OH]^+$ (40); 31 $[CH_2OH]^+$ (100).

Reaction of Tetrachloroethylene with 1-Hexanol. Main reaction product – 1,1,2-trichloro-1-octen-3-ol (Id), bp 88-92°C (1 mm), n_D^{18} 1.4960. PMR spectrum (δ, ppm, CCl_4): 4.75 t (J = 6.0 Hz, (CH), 4.65 s (OH), shifting on addition of CF_3COOH to the weak-field region, 0.7-2.0 m (11 H of C_5H_{11} group). Mass spectrum, m/z (%): 230, 232, 234 $[M]^{+\cdot}$ (5,5,1); 195, 197 $[M-Cl]^+$ (10, 5); 159, 161, 163 $[M-C_5H_{11}]^+$ (100, 96, 32); 97 (14); 95 (24); 71 (5).

Reaction of Tetrachloroethylene with 2-Hexanol. Main reaction product – 1,1,2-trichloro-3-methyl-1-hepten-3-ol (Ie), bp 92-93°C (1 mm), n_D^{20} 1.4955; isolated by adsorption chromatography on a column from a fraction, bp 74-80°C (0.4 mm), n_D^{22} 1.4880. PMR spectrum (δ, ppm CCl_4): 3.53 s (OH), shifting on addition of CF_3COOH to the weak-field region; 1.52 s (CH_3), and a multiplet in the 0.7-2.1 ppm region (C_4H_9). The intensity of the OH and $\rangle C(CH_3)C_4H_9$ groups proton signals corresponds to theoretical (1 : 12). Mass spectrum, m/z (%): 230, 232, 234 $[M]^{+\cdot}$ (0.5, 0.4, 0.1); 215, 217, 219 $[M-CH_3]^+$ (1, 1, 0.1); 195, 197 $[M-Cl]^+$ (2, 1); 173, 175, 177 $[M-C_4H_9]^+$ (100, 98, 30); 85 (8); 57 (4).

Side product of the reaction, 1,1,2-trichloro-3-methyl-1-hepten-6-ol (V), is formed in an amount of 25% with respect to (Ie). It was isolated by adsorption chromatography on a column from a fraction, bp 74-80°C (0.4 mm), n_D^{22} 1.4880. CIM spectrum (in $i\text{-}C_4H_{10}$) m/z (%): 287, 289 $[M+57]^+$ (0.5; 0.5), 231, 233, 235 $[M+H]^+$ (2.0; 1.8; 0.4); 213, 215, 217 $[M+H-H_2O]^+$ (5.0; 5.0; 1.5); 177, 179, 181 $[M+H-H_2O-HCl]^+$ (100, 70, 10); 159 (12). Mass spectrum: 170, 172, 174 $[M-H_2O-CH_3CH{=}CH_2]^+$ (26, 25, 9); 157, 159, 161 $[M-CH_2CH_2CH(OH)-CH_3]^+$ (9, 8, 2); 137 (14), 135 (18); 121 (9); 85 (9); 71 (21); 55 (18); 45 $[CH(OH)CH_3]^+$ (100).

Reaction of Tetrachloroethylene with Cyclohexanol. Main reaction product – 1-trichlorovinyl-1-cyclohexanol (If), bp 83-85°C (0.06 mm), n_D^{20} 1.5383, mp 35-39°C (cf. [9]) (bp 97.5°C (4 mm)), was isolated by adsorption chromatography on a column from a fraction, bp 87-90°C (0.1 mm), n_D^{17} 1.5360. Found: C 42.52; H 5.31; Cl 48.87%. $C_8H_{11}Cl_3O$. Calculated: C 41.85; H 4.83; Cl 46.34%. Mass spectrum m/z (%): 228, 230, 232 $[M]^{+\cdot}$ (6, 6, 2); 210 $[M - H_2O]^+$ (2); 193, 195, 197 $[M - Cl]^+$ (72, 48, 8); 185, 187, 189 $[M - C_3H_7]^+$ (23, 22, 8); 172, 174, 176 $[M - C_4H_8]^+$ (100, 100, 32); 166 (11); 164 (19); 161 (11); 159 (21); 157 (21); 151 (28); 149 (38); 137, 139, 141 $[M - Cl - C_4H_8]^+$ (70, 50, 10); 123 (30); 121 (30); 99 (34); 81 (50); 55 (53); 43 (32); 41 (36).

Side products of the reaction: 2-trichlorovinyl-1-cyclohexanol (VI), 3-trichlorovinyl-1-cyclohexanol (VII), and 4-trichlorovinyl-1-cyclohexanol (VIII) are formed in an amount of 1 : 10 with respect to (If). The mixture of (VII) and (VIII) was isolated by adsorption chromatography on a column from a fraction bp 90-100°C (0.1 mm), n_D^{17} 1.5390. Found: C 41.95; H 5.16; Cl 45.74. $C_8H_{11}Cl_3O$. Calculated: C 41.85; H 4.83; Cl 46.34%.

Reaction of Tetrachloroethylene with Cyclohexanol. A mixture of cyclohexane and TCE (molar ratio 3 : 1) and an initiator (TBP, 0.2 mole/liter) was passed through a reactor heated to 200°C at a rate of 17.5 h^{-1}, and under a pressure of 50 atm. The unreacted starting materials were evaporated in vacuo, and the residue was fractionated to yield trichlorovinylcyclohexane (IX), bp 116-118°C (22 mm), n_D^{21} 1.5145; yield, based on reacted TCE, 85%, conversion, calculated per initial TCE, 33%. Found: C 45.14; H 5.23; Cl 49.37%. $C_8H_{11}Cl_3$. Calculated: C 45.00; H 5.19; Cl 49.81%. Mass spectrum, m/z (%): 212, 214, 216 $[M]^{+\cdot}$ (28, 26, 9); 177, 179, 181 $[M - Cl]^+$ (36, 24, 6); 156, 158, 160 $[M - C_4H_8]^+$ (36, 34, 10); 143 (15); 141 (33); 123 (12); 121 (19); 113 (28); 105 (33); 83 (44); 69 (30); 67 (65); 55 (65); 43 (60); 41 (100).

CONCLUSIONS

As the result of a radical reaction between tetrachloroethylene and aliphatic alcohols in liquid phase, not only products of the substitution of hydrogen at the α-C atom of the alcohol for the trichlorovinyl group, but also isomers with a trichlorovinyl group at other C atoms, preferably in the ω-1 position, are formed.

LITERATURE CITED

1. L. K. Salamandra, Yu B. Vol'kenshtein, M. A. Besprozvannyi, L. P. Gudovich, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 2868 (1974).
2. R. M. Silverstein et al., Spectrometric Identification of Organic Compounds, Wiley (1974).
3. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, J. Am. Chem. Soc., 92, 1338 (1970).
4. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience (1972).
5. G. Migajima and K. Takahashi, J. Phys. Chem., 75, 331, 3766 (1971); Org. Magn. Reson., 6, 413 (1974).
6. G. I. Nikishin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1134 (1959).
7. Belgian Pat. No. 622421 (1961); Chem. Abstr., 59, 11255f (1963).
8. GFR Pat. No. 1188064 (1963); Chem. Abstr., 62, 13046f (1965).
9. Jap. Pat. No. 6309663 (1966); Chem. Abstr., 71, 60848h (1969).