STRUCTURE OF PRODUCTS AND STEREODIRECTION OF THE RADICAL TELOMERIZATION OF PROPYLENE WITH CHLOROFORM

B. A. Énglin, V. A. Valovoi,
L. G. Zelenskaya, T. A. Babushkina,
G. K. Semin, V. B. Bondarev,
B. N. Osipov, and R. Kh. Freidlina

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In our previous communication [1] we discussed the stereochemistry of the radical telomerization of propylene with CCl_4 within a broad range of temperatures (55-200°). The use of statistical methods of evaluating the distribution of diastereomeric racemic forms of 1,1,1,7-tetrachloro-3,5-dimethyloctane [telomer homolog $CCl_3[CH_2CH(CH_3)]_3Cl(T_3)$] permitted us to establish that both reactions determining the probability of the formation of isomers of T_3 (see Scheme A; asymmetrical carbon atoms are marked by asterisks):

$$CCl_3CH_2\overset{*}{C}H(CH_3)\,CH_2\dot{C}HCH_3 + C_3H_6 \rightarrow CCl_3[CH_2\overset{*}{C}H(CH_3)]_2CH_2CH(CH_3) \quad (1)$$

$$CCl_3[CH_2\overset{*}{C}H(CH_3)]_2\,CH_2\dot{C}HCH_3 + CCl_4 \rightarrow CCl_3]CH_2\overset{*}{C}H(CH_3)]_2\,CH_2\overset{*}{C}HClCH_3 + \dot{C}Cl_3 \quad (2)$$

Scheme A

obey the same (or close) statistical laws. Consequently, the directions of approach of the monomer and telogen to the radicals $CCl_3[CH_2CH(CH_3)]_n^{\cdot}$ (n = 2 and 3) coincide, ensuring minimum nonbonded interactions of the substitutents in the reagents.

An investigation of the diastereomeric composition of the products of telomerization of propylene with $CHCl_3$ permitted a verification of the coincidence of the stereochemical peculiarities of substitution and addition with the participation of the radicals $CCl_3[CH_2CH(CH_3)]_n^{\cdot}$. As is evident from Scheme B, asymmetrical centers arise in telomerization with $CHCl_3$ only at the step of chain propagation

$$CCl_3[CH_2\overset{*}{C}H(CH_3)]_{n-1}\,CH_2\dot{C}HCH_3 + C_3H_6 \rightarrow CCl_3[CH_2\overset{*}{C}H(CH_3)]_nCH_2CH(CH_3) \quad (1)$$

$$CCl_3[CH_2\overset{*}{C}H(CH_3)]_{n-1}CH_2\dot{C}HCH_3 + HCCl_3 \rightarrow CCl_3[CH_2\overset{*}{C}H(CH_3)]_{n-1}CH_2CH_2CH_3 + \dot{C}Cl_3 \quad (2)$$

Scheme B

and the ratio of the diastereomeric racemic modifications of the telomer homologs $CCl_3[CH_2CH(CH_3)]_nH$ ($n \geq 3$), in contrast to the products of telomerization with CCl_4, should characterize the stereochemistry of only one reaction of addition to propylene. Therefore, by comparing the distribution of diastereomeric forms of $CCl_3[CH_2CH(CH_3)]_nH$ and the telomer homologs $CCl_3[CH_2CH(CH_3)]_{n-1}Cl$ corresponding in number of asymmetrical centers, it is easy to establish the stereochemical differences of the processes of substitution and addition of aliphatic radicals $CCl_3[CH_2CH(CH_3)]_n^{\cdot}$. Such a comparison is one of the purposes of this work.

A determination of the structure of the products of telomerization of propylene with $CHCl_3$ was also of interest for another reason. Since $CHCl_3$ is capable of entering into a reaction of homolytic substitution with cleavage of the C – H and C – Cl bonds [2], the kinetic chain in telomerization with a telogen can be carried by two radicals: $\dot{C}Cl_3$ and $\dot{C}HCl_2$. Consequently, four types of telomer homologs are probable (for propylene: $CCl_3[CH_2CH(CH_3)]_nH$, $CCl_3[CH_2CH(CH_3)]_nCl$, $HCCl_2[CH_2CH(CH_3)]_nH$, and $CHCl_2[CH_2CH(CH_3)]_nCl$),

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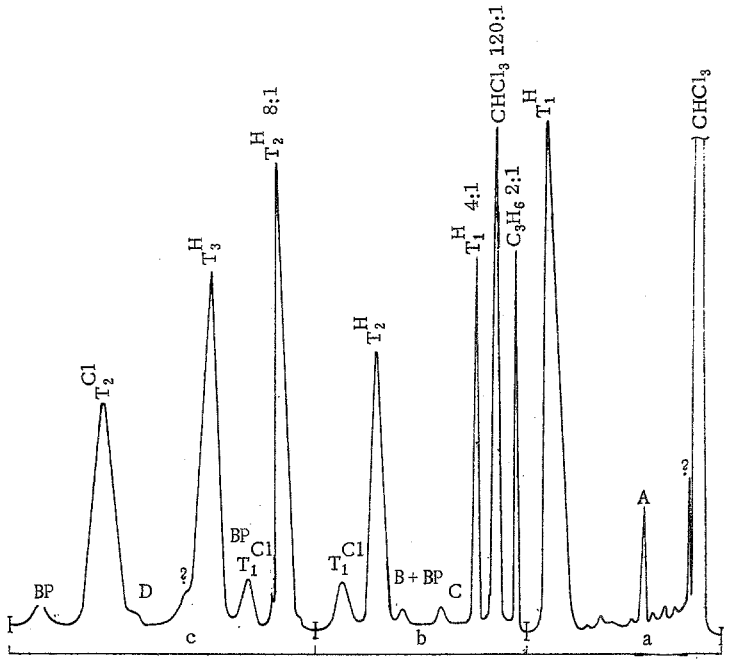

Fig. 1. Chromatogram of the products of telomerization of propylene with $CHCl_3$, initiated by benzoyl peroxide at 140°. T_1^H, T_2^H, and T_3^H) telomer homologs $CCl_3[CH_2CH(CH_3)]_nH$ with n = 1-3; T_1^{Cl}, T_2^{Cl}) telomer homologs $CCl_3[CH_2CH \cdot (CH_3)]_nCl$ with n = 1, 2; A and B) telomer homologs $CHCl_2 \cdot [CH_2CH(CH_3)]_nCl$ with n = 1, 2; C and D) telomer homologs $CHCl_2[CH_2CH(CH_3)]_nH$ with n = 1, 2; BP) products of decomposition of benzoyl peroxide. a) Glass column 3.5 × 2000 mm; 6% silicone elastomer on Chromosorb-W, fraction 0.25-0.50 mm; 50-60 ml/min He; katharometer; temperature of analysis 30°. b) Glass column 3.5 × 950 mm; 8.5% polyethylene glycol-4000 on Chromosorb-W, fraction 0.15-0.20 mm; carrier gas He; katharometer; temperature 75°. c) The same conditions (see b) but at 120°.

and the possibility of a kinetic investigation of the sensitivity of radical substitution at the C – H and C – Cl bonds to polar effects under strictly identical conditions emerges [3].

Gas – liquid chromatographic analysis of the products of peroxide initiated telomerization of propylene with $CHCl_3$ (Fig. 1) indicated that the reaction actually is more complex than with CCl_4 [4] and leads to a large number of close-boiling substances, the synthesis, isolation, and identification of which are described below.

EXPERIMENTAL

The compounds T_1^H to T_3^H and T_2^{Cl}, corresponding to the basic peaks in Fig. 1, were isolated from the products of telomerization by distillation on a fractional distillation column (~20 theoretical plates), followed by purification by preparative gas – liquid chromatography (70-120°; stainless steel column 28 × 1000 mm; 20% PEG-4000 on Chromosorb-P; carrier gas N_2; pressure at the entrance ~1.5 kg/cm^2). The synthesis was conducted in a stainless steel autoclave with a capacity of ~1 liter in the presence of benzoyl peroxide (or tert-butyl peroxide), 2% of the total of reagents, at 140-150° and a mole ratio $[C_3H_6]/[CHCl_3] \approx 0.4$-0.8 (70-150 g C_3H_6 and 450-550 g $CHCl_3$ were loaded; the conversion of the monomer in 4 h reached 20%).

Some properties of T_1^H to T_3^H, cited in Table 1, as well as an investigation of their PMR, IR, NQR, and mass spectra (Tables 2-4), permitted these compounds to be classed as telomers $CCl_3[CH_2CH(CH_3)]_nH$ with n = 1-3. The compound T_2^{Cl}, according to the data of elemental analysis and the PMR spectra, corresponded to the telomer homolog $CCl_3[CH_2CH(CH_3)]_2Cl$ – the product of telomerization of propylene with

TABLE 1. Properties of Certain Products of Telomerization of Propylene with $CHCl_3$

Compound	Bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	Found, %			Calculated, %		
				C	H	Cl	C	H	Cl
T_1^H	23 (4)	1,2182	1,4510	29,9	4,3	65,8	29,8	4,4	65,8
T_2^H	76 (15)	1,1261	1,4606	41,6	6,6	51,8	41,4	6,4	52,2
T_3^H	94 (4)	1,0492	1,4649	49,2	7,8	43,0	48,8	7,8	43,4
A	64 (25)	1,2572	1,4600	29,8	4,3	65,9	29,8	4,4	65,8
B	56 (2)	1,1593	1,4711	41,7	6,5	51,8	41,4	6,4	52,2

CCl_4 (for the characteristics of T_2^{Cl}, see [4]). The compound T_1^{Cl} ($CCl_3CH_2CHClCH_3$) was identified according to the retention time on two phases of opposite polarity (PEG-4000 and silicone elastomer).

The formation of the telomers T_1^H to T_3^H and T_1^{Cl}, T_2^{Cl} on account of chain transfer by the radicals $CCl_3[CH_2CH(CH_3)]_n^{\cdot}$ at the C – H and C – Cl bonds in $CHCl_3$ presupposes the presence of the homologs $HCCl_2$ ·$[CH_2CH(CH_3)]_nCl$ in the reaction mixture (A, B with n = 1, 2 in Fig. 1) and $CHCl_2[CH_2CH(CH_3)]_nH$ (C, D with n = 1, 2, see Fig. 1). Since the isolation of these substances from the products of the telomerization of propylene with $CHCl_3$ presented considerable difficulties, we synthesized the compounds A to D by other methods and identified them in the telomer mixture according to the retention time (on PEG-4000 and silicone elastomer).

The adduct A was produced by telomerization of propylene with chloroform at 150° with the catalytic systems: $FeCl_2 \cdot 4H_2O$ or $Fe(CO)_5$ + CH_3OH, which, as is well known [5], promote activation of the C – Cl bond in $CHCl_3$ and predominant formation of adducts with a terminal dichloromethyl group. In a stainless steel autoclave (volume ~1 liter) we loaded 10 g $FeCl_2 \cdot 4H_2O$ in 100 ml CH_3OH (80 g), 740 g $CHCl_3$, and 200 g propylene ($[C_3H_6]/[CHCl_3]$ ~0.8) or 500 g $CHCl_3$ and 350 g C_3H_6 ($[C_3H_6]/[CHCl_3]$ ~2.0); after 12-15 h, the conversion with respect to the monomer reached 70%, yield of A ~60%. At high ratios of the reagents we noted the formation of up to 15% (of the content of A) of telomer B.

The homologs C and D were synthesized by selective reduction [6] with the system: $Fe(CO)_5$ + $(C_2H_5)_3$ ·SiH of the trichloromethyl group in T_1^H and T_2^H to $CHCl_2$.

Since according to the data of [6] the reduction with silicon hydride, catalyzed by $Fe(CO)_5$ practically does not affect the CH_2Cl– and –CHCl– groups, we used this method to obtain the telomer B from the corresponding product of the telomerization of propylene with CCl_4 (T_2^{Cl} = $CCl_3CH_2CH(CH_3)CH_2CHClCH_3$, for conditions of synthesis see [4]). The reaction was carried out in an autoclave (0.5 liter) at 150° in the presence of 1.0% $Fe(CO)_5$ and triethylsilane, 50% of the weight of T_2^{Cl} (in 5 h the conversion of T_2^{Cl} was ~50%). $CHCl_2CH_2CH(CH_3)CH_2CHClCH_3$ was isolated by preparative gas – liquid chromatography (the properties are are cited in Table 1) and used subsequently for structural analysis (see Tables 2-4) and a gas – liquid chromatographic evaluation of the distribution of diastereomeric racemic modifications of the dl – dd-type. It should be mentioned that even with a less selective [6] system $H_2PtCl_6 \cdot 6H_2O$ + $HCl_2Si(CH_3)$, the reduction of T_2^{Cl} at 150° proceeded chiefly to compound B, which practically did not enter into further conversions (the yield of $CH_2ClCH_2CH(CH_3)CH_2CHClCH_3$, see the PMR spectrum in Table 4, did not exceed several percent of the initial T_2^{Cl}).

We studied the structure of the telomer homologs T_1^H to T_3^H and A, B, of special interest for evaluating the stereochemical peculiarities of the telomerization of propylene with $CHCl_3$ and CCl_4, by the methods of NQR, PMR, IR, and mass spectrometry.

In the mass spectra of T_1^H to T_3^H (MKh-1303 spectrometer; temperature of the feed system 100°, ionization chamber 120°; emission current 2 mA, energy of ionizing electrons 50 eV), just as for the structurally close $CCl_3[CH_2CH(CH_3)]_nCl$ [4] and $CCl_3(CH_2CH_2)_nCl$ [7], no molecular ions were detected (evidently as a result of the low stability of polychloroalkanes to electron impact [7]). However, the presence of isotopic peaks of the ions $[M - Cl]^+$ with mass numbers 125/127/129 (T_1^H), 167/169/171 (T_2^H), 209/211/213 (T_3^H) and relative intensities close to those expected [8] for ions with two chlorine atoms (see Table 2), permits us to propose the following empirical formulas for T_1^H to T_3^H: $C_4H_7Cl_3$, $C_7H_{13}Cl_3$, $C_{10}H_{19}Cl_3$. The mass spectra of all three homologs contain isotopic lines with m/e 117/119/121 and a distribution of intensities characteristic of ions with three chlorine atoms [8], which is evidence of a terminal trichloromethyl group (for the compound T_3^H, the isotopic picture is somewhat disturbed by the ions $C_6H_8Cl^{37}$ with

TABLE 2. Relative Intensities* of the Characteristic Lines in the Mass Spectra of the Compounds T_1 to T_3, A, and B

Compound	F†	m/e																					
		43	63	65	109	111	117	119	121	125	127	129	131	133	167	169	171	209	241	213
T_1^H	43	100,0	2,9	8,6	13,4	7,5	4,0	4,2	1,67	36,8	21,2	4,0	0,3	0,3	—	—	—	—	—	—
T_2^H	70	57,9	8,8	4,4	6,8	4,4	2,5	2,4	0,93	4,9	0,9	0,72	3,5	1,1	0,29	0,43	0,03	—	—	—
T_3^H	69	15,9	9,9	9,8	0,8	0,9	1,4	0,8	0,18	0,6	0,1	0,94	0,1	2,3	0,70	0,16	0,08	0,03	0,01	0,01
A	89	0,1	24,2	3,6	3,3	2,0	—	—	—	1,0	0,4	0,04	—	—	—	—	—	—	—	—
B	41	9,6	31,2	8,6	0,5	0,4	1,0	0,5	0,18	0,2	0,1	0,21	2,9	4,3	0,99	0,60	0,1	—	—	—
‡	—	—	1	0,33	1	0,65	1	0,98	0,32	1	0,6	0,11	1	0,33	1	0,65	0,11	1	0,65	0,11

* The intensities are cited in % of the maximum peak.

† The line of the spectrum with maximum intensity.

‡ The expected relative occurrences of isotopes in the ions with number of Cl atoms from 1 to 3 [8].

m/e 117). The presence of this group in T_1^H to T_3^H is confirmed [7] by the peaks 109/111 (the ions $[CCl_2 = CH - CH_2]^+$), especially intense for T_1^H and T_2^H.

A comparison with the data for linear polychloroalkanes $CCl_3(CH_2CH_2)_nCl$ [7] indicates the possibility of branching of the carbon skeleton of the telomers $CCl_3[CH_2CH(CH_3)]_nH$. The increased content of hydrocarbon ions $[C_3H_7]^+$ with mass 43 (in $CCl_3CH_2CH_2CH_3$ the maximum line of the spectrum corresponds to this mass, see Table 2) and the increase in the intensity of the peaks 131-133 (ions $[CCl_3CH_2]^+$) for T_2^H and T_3^H are probably explained by substituents at C-3 in T_2^H or at C-3 and C-5 in T_3^H (in accord with the empirical rule of predominant decomposition at the more substituted carbon atom [8]). The ease of stripping of the side methyl groups evidently determines the appearance of lines with ion masses $[M - HCl - CH_3]^+$ and $[M - 2HCl - CH_3]^+$ in the spectra of T_2^H and T_3^H (compare with the telomers $CCl_3[CH_2 \cdot CH(CH_3)]_nCl$ in [4]).

In the mass spectra of compounds A and B, the fragment ions $[M - Cl]^+$ (125/127/129 and 167/169/171, i.e., the molecular formulas of T_1^H and A, as well as T_2^H and B, coincide) are observed; the intensities of all the lines characterizing the CCl_3 and $CH_3CH_2CH_2$ groups are appreciably lowered (m/e 43, 109, 111, 117, 119, 121), and the content of peaks with masses 63/65 (CH_3CHCl group [4]) increases sharply. Branching at the C-3 atom is possible for compound B (see the ions with m/e 131 and 133 for T_1^H to T_3^H, A, and B).

In the NQR spectra of the compounds T_1^H to T_3^H, A, and B (IS-2 pulsed spectrometer of the Central Design Office of the Institute of Radioengineering and Electronics of the Academy of Sciences of the USSR), signals were noted in the region of ~32, 36, and 38 MHz (seeTable 3), corresponding [4, 9] to the resonance of Cl^{35} in the $CH_3CHClCH_2$, $CHCl_2$, and CCl_3 groups. The elevation of all the frequencies for A, close to that calculated [9], is apparently due to the mutual influence of electron-acceptor substituents in the β-position to one another (for more details, see [4]).

Analogous results on the identification of the functional groups were obtained in an investigation of the IR spectra of the compounds under consideration. As can be seen from Fig. 2, T_1^H to T_3^H are characterized by intense absorption bands around 582-592, 696-700, and 760-776 cm^{-1}, which, in the opinion of the authors of [10], are determined by the C – Cl vibrations in the CCl_3 and CCl_3CH_2 groups. In the spectra of A and B, the first two frequencies are entirely absent; however, absorption is observed at 625 and 664-669 cm^{-1}, due [10] to the C – Cl vibrations in the $CHCl_2$ (660-670 and 745-754 cm^{-1} [10]) and CHCl groups (617-640 cm^{-1} [10]).

The hydrocarbon portion of T_1^H to T_3^H, A, B, and a number of structurally close model compounds was studied by the PMR method (35-45% in CCl_4, Hitachi-60 and Perkin – Elmer R-12 spectrometers with working frequency 60 MHz, ~34°, internal standard hexamethyldisiloxane). The complex structure of the spectra of T_1^H to T_3^H (even for T_1^H, rotational isomerism and the low values of of δ/I lead to a spectrum that does not obey the simple multiplicity

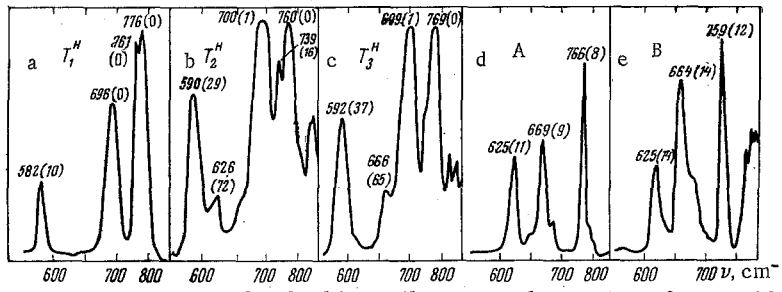

Fig. 2. IR spectra of polychloroalkanes in the region of 500-800 cm^{-1}, +25°; UR-10; the frequencies were verified according to the spectrum of indene (the error in the determination does not exceed ±1 cm^{-1}); the percent transmission (for T_1H to T_3H) or width of the band $\Delta\nu_{1/2}$ in cm^{-1} (A and B) are indicated in parentheses; KBr prism; b, c) l 0.03 mm. a, d, e) In cyclohexane solution: a) l 0.067 cm, C 0.48 M; d) l 0.012 cm, C 0.22 M; e) l 0.012 cm, C 0.30 M.

TABLE 3. NQR Frequencies of Certain Polychloroalkanes* (MHz, Cl^{35}, 77°K)

Group	Compound			Calculated data [9]	
	T_1H	T_2H	T_3H		
CCl_3	38,0 (0,5)	38,0 (0,45)	38,0 (0,45)	38,0	
	A		B	A	B
$CHCl_2$- $CH_3CHClCH_2$-	35,8 (1,0) 32,7 (0,7)		35,5 (0,6) 32,5 (0,8)	35,9 32,7	35,5 32,2

* The frequencies are cited for substances in the "vitrified" state (for the possibility of comparing these frequencies with the data for crystals, see [4]; the width of the signals $\Delta\nu_{1/2}$ at half the height of the peak is indicated in parentheses).

rules, Fig. 3) permitted us to make assignments only according to the chemical shifts and relative integral intensities of certain signals. Three multiplets with centers at 2.68, 1.83, and 1.08 ppm (Table 4) and intensity ratio 1:1:1.5 confirm the structural formula of T_1H (considering the coincidence of $\delta_{CCl_3CH_2}$ = 2.68 ppm with the literature data [4]). The signals around 2.6 ppm are also preserved for T_2H, and the expected [4] strong field shift of the signals of the protons of the terminal CH_3CH_2 group is observed (as a result of a decrease in the deshielding influence of the CCl_3 group). In addition, a doublet appears in the spectrum of T_2H with the chemical shift characteristic of the methyl groups in the fragment $CCl_3CH_2CH(CH_3)$ and a signal in the region of ~2.0 ppm (hydrogen at a tertiary carbon atom). From this it follows that the structure cited in Table 4 (addition "head to tail") is most probable for the isomer T_2H, and we might expect an analogous structure for the telomer T_3H (in particular, for the latter the corresponding values of δ are close to the chemical shifts of T_2H, which indicates the same first unit $CCl_3CH_2CH(CH_3)$ for these compounds).

The PMR spectra of A and B differ significantly from those considered above, but are easily interpreted by a comparison with the chemical shifts of the $CHCl_2$ and $CHCl_2CH_2$ groups in the model compounds 6-8 and with the literature data [4, 11] on δ for the CH_3CCl, $(CH_3)CH$, and CHCl groups (see Table 4, as well as the distribution of integral intensities in Fig. 3).

Thus, an investigation of the mass, IR, NQR, and PMR spectra of T_1H to T_3H, A, and B indicated that the structure of these compounds corresponds to the telomer homologs $CCl_3[CH_2CH(CH_3)]_nH$ with n = 1-3 and $CHCl_2[CH_2CH(CH_3)]_nCl$ with n = 1, 2. Consequently, in the radical telomerization of propylene with $CHCl_3$, chain transfer is accomplished at the C – H and C – Cl bonds, with the formation of at least two different radicals carrying the kinetic chain, $\dot{C}Cl_3$– and $\dot{C}HCl_2$–.

TABLE 4. Chemical Shifts of the Protons of Certain Groups in Polychloroalkanes (δ, ppm)

Number	Compound	Groups				
		CCl_3CH_2	CH	$CH_3(CH_2)$	$(CH_3)CH$	$(CH_3)CH_2$
1	$CCl_3CH(CH_3)CH_3$ (T_1^H)	2,68	—	1,83	—	1,08
2	$CCl_3CH_2CH(CH_3)CH_2CH_3$ (T_2^H)	2,62	1,98	1,39	1,14	0,96
3	$CCl_3(CH_2CH)_2CH_2CH_3$ (T_3^H)	2,60	1,99	—	1,08	—
	Data of [4]	2,62—2,77	—	—	1,06 [11]	0,95

Number	Compound	$CHCl_2$	CHCl	CH_2Cl	$CHCl_2(CH_2)$	CH_3CCl	$(CH_3)CH$	$(CH_3)CH_2$
4	$CHCl_2CH(CH_3)CHClCH_3$ (A)	5,92	4,20	—	2,49	1,56	—	—
5	$CHCl_2CH_2CH(CH_3)CHClCH_3$ (B)	5,86	4,10	—	2,17	1,52	1,01	—
6	$CHCl_2CH_2CH_2CH_2CH_3$	5,78	—	—	2,25	—	—	0,96
7	$CHCl_2CH_2CH(CH_3)_2$	5,71	—	—	2,03	—	0,97	—
8	$CHCl_2CH_2CH_2Cl$	5,98	—	3,71	2,63	—	—	—
9	$ClCH_2CH_2CH(CH_3)CHClCH_3$	—	4,14	3,55	—	1,55	0,97	—
	Data of [4]	—	3,95—4,22	3,47—3,87	—	1,49—1,56	1,06 [11]	0,95

* The chemical shifts were determined from 2 to 4 spectra according to the center of gravity of the multiplets, followed by recalculation to tetramethylsilane (considering δ = 0.06 ppm for hexamethyldisiloxane).

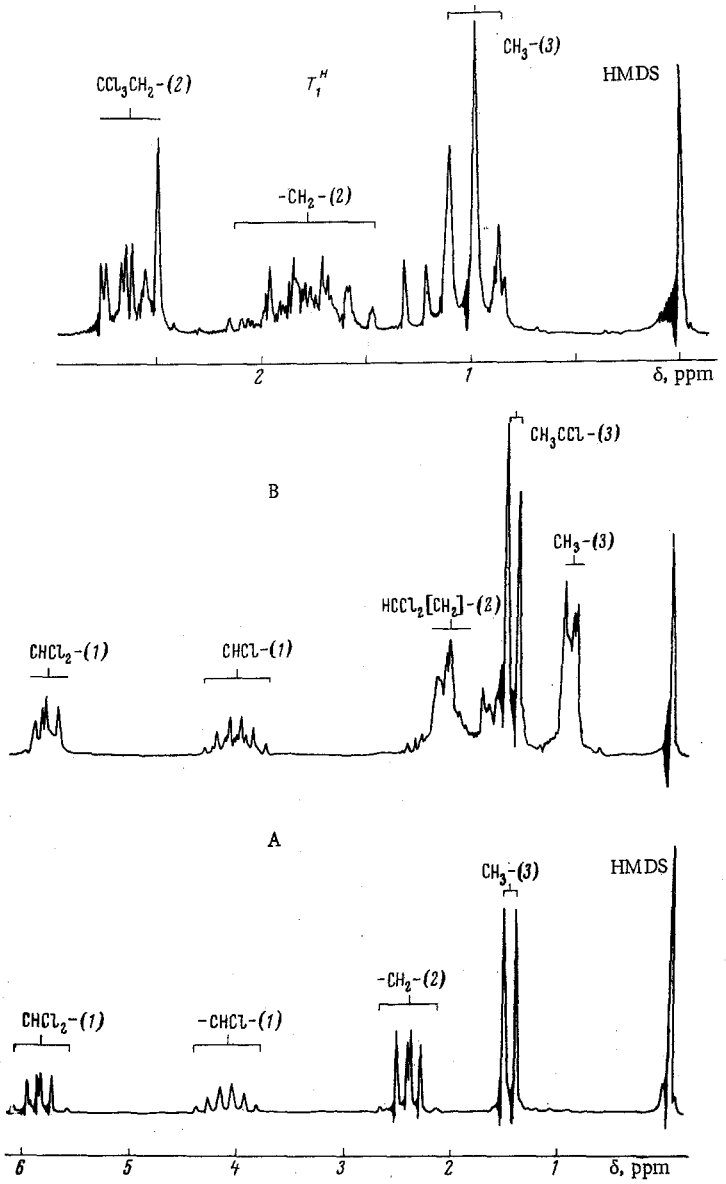

Fig. 3. PMR spectra of certain products of radical telomerization with $CHCl_3$ (60 MHz, standard hexamethyldisiloxane, 34°, 34-45% in CCl_4; the relative integral intensities of the multiplets are indicated in parentheses).

DISCUSSION OF EXPERIMENTAL RESULTS

The establishment of the structure of the products of radical telomerization of propylene with $CHCl_3$ permitted an investigation of the kinetics of this process (the corresponding data are cited in [3]) and a consideration of the stereochemistry of the reaction of addition and substitution of aliphatic radicals $CCl_3 \cdot [CH_2CH(CH_3)]_n$.

To evaluate the stereodirection of the addition to propylene, we attempted to determine the ratio of diastereomeric racemic modifications of the telomer homolog T_3^H (for T_3^H with two asymmetrical centers, only two racemic forms of the dl- and dd-types are probable), using the method of capillary gas – liquid chromatography, just as in [4]. The analysis was conducted on columns with an efficiency of ~26,000 theoretical plates (stainless steel, 0.25 mm × 15 m, SCOTC; meta-bis-polyphenyl ether; 130°; pressure at the entrance ~1.2 kg/cm^2) or 200,000 theoretical plates (stainless steel, 0.25 mm × 90 m; propylene glycol-1500; linear programing of the temperature from 140 to 200° at a rate of 2 deg/min; pressure at the entrance ~1.5 kg/cm^2). In both cases splitting of the peak of T_3^H into two components with relative contents

of 65 and 35% was observed on the chromatograms. This result permits us to assert that the addition of the radical $CCl_3[CH_2CH(CH_3)]_2^{\cdot}$ to propylene (step 1, Schemes A and B) proceeds with some stereodirectiveness; moreover, as was shown in [1], chiefly the *dl*-modification of T_3^H is formed (the authors of [1] established a syndio-direction of steps 1 and 2 of Scheme A and step 1 of Scheme B). From this, in accord with the scheme

$$CCl_3CH_2CH(CH_3)CH_2\dot{C}HCH_3 + C_3H_6 \xrightarrow{K_p^s} CCl_3[CH_2CH(CH_3)]_3^{\cdot} + CHCl_3 \rightarrow dl\text{-}T_3^H + \dot{C}Cl_3$$
$$CCl_3CH_2CH(CH_3)CH_2\dot{C}HCH_3 + C_3H_6 \xrightarrow{K_p^i} CCl_3[CH_2CH(CH_3)]_3^{\cdot} + CHCl_3 \rightarrow dd\text{-}T_3^H + \dot{C}Cl_3$$

Scheme C

we can find the ratio of the rate constants of addition to propylene according to iso- and syndio-mechanisms at an equilibrium state of the process

$$\frac{d\,(dl\text{-}T_3^H)}{d\,(dd\text{-}T_3^H)} = \frac{K_p^s\,[T_2^{\cdot}]\,[C_3H_6]}{K_p^i\,[T_2^{\cdot}]\,[C_3H_6]} = \frac{K_p^s}{K_p^i} = 1.86 \qquad (I)$$

To compare the stereochemical peculiarities of reactions (1) and (2) of Scheme A, we investigated the diastereomeric composition of the telomer homolog T_2Cl. The ratio of the d*l*- and dd-forms of this compound was determined, in contrast to T_3^H, by the step of chain transfer with CCl_4 (Scheme D):

$$CCl_3CH_2CH(CH_3)CH_2\dot{C}HCH_3 + CCl_4 \xrightarrow{K_{tr}^s} dl\text{-}T_2^{Cl} + \dot{C}Cl_3$$
$$CCl_3CH_2CH(CH_3)CH_2\dot{C}HCH_3 + CCl_4 \xrightarrow{K_{tr}^i} dd\text{-}T_2^{Cl} + \dot{C}Cl_3$$

Scheme D

According to the data of gas – liquid chromatographic analysis (for the conditions, see above), the content of the d*l*- and dd-modifications in T_2Cl is 58 and 42%.* Calculation according to the equation

$$\frac{d\,(dl\text{-}T_2^{Cl})}{d\,(dd\text{-}T_2^{Cl})} = \frac{K_{tr}^s\,[T_2^{\cdot}]\,[CCl_4]}{K_{tr}^i\,[T_2^{\cdot}]\,[CCl_4]} = \frac{K_{tr}^s}{K_{tr}^i} = 1.38 \qquad (II)$$

leads to a ratio of the rate constants of iso- and syndio-chain transfer K_{tr}^s/K_{tr}^i almost coinciding with K_p^s/K_p^i thereby confirming the identical (or close) stereochemical principles of the reactions of addition to propylene and substitution with CCl_4 for the radicals $CCl_3[CH_2CH(CH_3)]_n$ with $n \geq 2$ (see Schemes A and B).

The data on the distribution of diastereomeric forms in T_2Cl and T_3^H also permit us to evaluate the possible influence of the cumbersome terminal CCl_3 group on the stereodirectiveness of the addition or substitution reactions of the radical $CCl_3CH_2CH(CH_3)CH_2\dot{C}HCH_3$.

As was established in [1], the total probability P_i of isotatic development of the chain in the telomerization of propylene with CCl_4 for the temperatures 100-145° (compare with the conditions of synthesis of T_2Cl and T_3^H) is equal to 0.26-0.28. In the calculation of P_i, the authors of [1] proceeded on the basis of a distribution of the i-, h-, and s-racemic diastereomeric forms of the telomer homolog $CCl_3[CH_2CH\cdot(CH_3)]_3Cl$, the relative configurations of which are determined (see Scheme A) by the stereochemistry of the addition of the radical $CCl_3CH_2CH(CH_3)CH_2\dot{C}HCH_3$ and chain transfer with the radical $CCl_3CH_2CH(CH_3)\cdot CH_2CH(CH_3)CH_2\dot{C}HCH_3$ (in the latter the CCl_3 group is farther from the reaction center).

The value $P_i \sim 0.27$ corresponds to a yield of the dd-form of T_2Cl in the telomerization of propylene with CCl_4 less than 30% at 100-145° and a ratio $K_{tr}^s/K_{tr}^i \sim 2.7$, which is twice as great as that observed experimentally, for example, for T_2Cl [see Eq. (II)]. Consequently, the stereodirectivness of the step of transfer with the participation of the radical $CCl_3CH_2CH(CH_3)CH_2^{\cdot}CHCH_3$ (Scheme D, Eq.(II)), approximately coinciding with the stereoselectivity of the addition of this radical to propylene (see Eq. (I) and Scheme C) differs substantially from the stereodirectiveness of substitution with the longer chain radical (step 2, Scheme A). Possibly such differences in the stereoregularity are due chiefly to a change in the stereochemical influence of the terminal CCl_3 group in the telomer radicals considered.

* Under the same conditions of analysis, a diastereomeric composition entirely identical with T_2Cl was obtained for compound B (58% d*l*- and 42% dd-form).

CONCLUSIONS

1. Four types of telomer homologs, corresponding to cleavage of the C – H and C – Cl bonds in the telogen during chain transfer and the formation of the radicals $\dot{C}Cl_3$– and $\dot{C}HCl_2$–, carrying the kinetic chain, were identified in the products of radical telomerization of propylene with $CHCl_3$ by the methods of gas – liquid chromatography, mass, IR, NQR, and PMR spectroscopy.

2. The addition of the radicals $CCl_3[CH_2CH(\dot{C}H_3)]_n$ with $n \geq 2$ to propylene proceeds with some stereoregularity and obeys close stereochemical principles with chain transfer by these radicals to CCl_4.

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