RADICAL TELOMERIZATION OF 1-HEXENE WITH BUTYRALDEHYDE

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The telomerization of unsaturated compounds with aldehydes is a promising method for synthesizing polyfunctional carbonyl compounds of various structures. At the same time, the possible decarbonylation of acyl radicals $R\dot{C}O$ [1] and also a certain lack of regioselectivity in their addition to α-olefins [2] probably account for the fact that the behavior of aldehydes in radical telomerization has been comparatively little studied previously [3, 4]. The present work is devoted to studying the telomerization of 1-hexene with butyraldehyde, which is accompanied by partial decarbonylation of the acyl radicals at the initiation stage and by rearrangement of the growing radicals, and also to a comparative kinetic study of the parallel telomerization processes involving acyl and alkyl radicals.

An analysis of the reaction mixture showed that it contained the telomer homologs T_n (n = 1-3), which were formed according to a general scheme involving cleavage of the C–H bond of the telogen, growth, and chain transfer of growing radicals to the aldehyde

$$CH_3CH_2CH_2C(O)H\,(S) \xrightarrow{RO^{\cdot}} CH_3CH_2CH_2\dot{C}O\quad (A)$$
$$A + nCH_2{=}CHC_4H_9\,(M) \rightarrow CH_3(CH_2)_2CO(CH_2CHC_4H_9)_n^{\cdot}\ (B_n)$$
$$B_n + S \rightarrow CH_3CH_2CH_2\dot{C}O + CH_3(CH_2)_2CO(CH_2CHC_4H_9)_nH$$
$$(T_n,\ n = 1\text{—}3);$$

Among the telomers with three monomer units, compound T_3' (isomer of T_3) was identified by ^{13}C NMR; its formation may be due to rearrangement of growing radicals B_2 with 1,6-migration of a hydrogen atom followed by addition of radical C to a 1-hexene molecule

$$\underset{(B_2)}{CH_3(CH_2)_2CO(CH_2CHC_4H_9)_2^{\cdot}} \xrightarrow{1,6\text{-}H} \underset{(C)}{CH_3CH_2\dot{C}HCO(CH_2CHC_4H_9)_2H} \xrightarrow[S]{C_6H_{12}}$$
$$\rightarrow \underset{(T_3')}{CH_3CH_2CH(C_6H_{13})COCH_2CH(C_4H_9)C_6H_{13}}$$

It was also possible to identify telomer homologs Y_m, formed according to the scheme

$$C_3H_7C(O)H \xrightarrow{RO^{\cdot}} C_3H\,\dot{C}O \xrightarrow{-CO} C_3H\text{-}^{\cdot} \xrightarrow[DH]{m\text{-}C_4H_9CH{=}CH_2} C_3H_7(CH_2CHC_4H_9)_mH$$
$$(Y_m,\ m = 1 - 3)$$

The reaction pathway resulting from cleavage of an α-C–H bond in the aldehyde molecule is not present in this case.

Telomers T_1, T_2, and T_3' were isolated in a pure form, while telomer T_3 was mixed with T_3'. The structures of T_n were confirmed by the ^{13}C NMR spectroscopy data (Table 1). The signals from the CO and $^{13}CH_2CO$ groups are characteristic. Moreover, in the spectra of T_2 and T_3 signals from CH groups appear, and there is a signal due to $CH{-}^{13}CH_2{-}CH$ for T_3. In the spectrum of T_3' there are signals from $^{13}CH_3CH_2CH$, $^{13}CHCO$, $^{13}CH_2CO$, and CH groups, which taken in combination constitute evidence for the presence of a C_6H_{13} substituent on the carbon atom adjacent to the CO group, namely, in the propyl section of the molecule and not on the side of the longer chain. The ^{13}C NMR spectra of the hydrocarbon telomers are also consistent with the structure proposed for them (Table 1). The signals from the CH, $CH{-}^{13}CH_2{-}CH$, and $CH{-}CH_2{-}^{13}CH_2$ groups are characteristic.

When the experiments were carried under strictly controlled conditions (Table 2) it was possible to determine the specific chain-transfer constants for the primary radicals $C_3H_7C(O)CH_2\dot{C}HC_4H_9$ (B_1) $(C_1^T = 1.7)$ and $C_3H_7CH_2\dot{C}HC_4H_9$ (D) $(C_1^Y = 4.3)$; by correlating the results obtained $(C_1^T < C_1^Y)$ it was possible to assume that although radicals B_1 are apparently nucleo-

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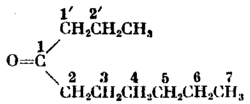
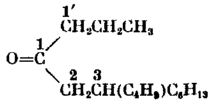
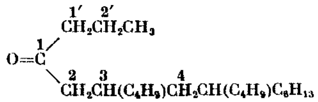
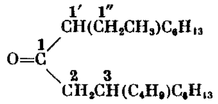
TABLE 1. ^{13}C NMR Spectra of Telomers

Compound	Formula	δ, ppm from TMS					
		C=O	CH_3	$\underline{CH}$–CO	CH	$\underline{CH_2}CO$	–CH_2*–
T_1		206,9	13,7; 14,0	–	–	44,2(1′); 42,3(2)	16,9(2′); 23,3; 28,8; 31,5; 22,3
T_2		207,1	13,7; 14,0	–	33,2	44,8(1′); 47,3(2)	16,9(2′); C_4H_9: 34,0; 28,7; 22,5; C_6H_{13}: 33,6; 26,5; 29,4; 31,7; 22,5
T_3 (mixed with T_3′)		207,2	14,0	–	30,8; 34,6	44,9(1′); 47,7(2)	16,9(2′); 39,1(4); C_6H_{13}: 33,7; 26,5; 29,4; 31,7; 22,8
T_3′		210,6	11,8 (C_2H_5); 14,0	53,5	32,5	47,1(2)	24,3(1″); C_6H_{13}: 27,3; 26,5; 31,0; 31,5; 22,5; C_4H_9: 33,8; 28,7; 22,5; C_6H_{13}: 33,5; 26,5; 29,4; 31,7; 28,8
Y_1	$(CH_3CH_2CH_2CH_2)_2CH_2$	–	13,9	–	–	–	22,5; 31,8; 29,2; 29,5
Y_2	$(CH_3CH_2CH_2CH_2)_2CHC_6H_{13}$	–	14,1	–	37,3	–	23,0; 28,8; 33.3; 33,6; 26,6; 29,0; 31,8; 22.6
Y_3	$(CH_3CH_2CH_2CH_2)_2CHCH_2CH(C_4H_9)C_6H_{13}$	–	14,0	–	34,6	–	23,0; 28,6; 33,5 C_4H_9; 38,8 (CH–CH_2–CH); 33,5; 26,3; 29,7; 31,8; 22,6 (C_6H_{13})

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*Given in the order shown in the formula.

TABLE 2. Telomerization of 1-Hexene (M) with Butyraldehyde (S) (140°C, τ = 1 h, t-butyl peroxide (TBP) 0.5% of S)

Experiment No.	Batch, mmole		Conversion, %		M/S_{av}	Distribution of telomers, mole %					C_1^T/C_1^Y	$\Sigma T_n/\Sigma Y_m$
	M	S	M	S		T_1/Y_1	T_2/Y_2	$T_3/Y_{>2}$	T_3'	$\Sigma T_{>3}$		
1	1,13	11,3	43	19	0.1	95/98	5/2	–	–	–	1.7/3.8	0.4
2	3,4	11,3	13	20	0.3	86/93	12/7	1	1	–	1.9/4.1	0.7
3	5,7	11,3	11	14	0.5	77/89	18/11	2	3	–	1.7/4.1	0.9
4	7,9	11,3	9	31	0.8	66/85	18/13	3/2	9	4	1.6/4.5	0.9
5	5,7	5,7	12	12	1.0	62/83	24/14	4/3	7	3	1.6/4.7	1.2
6	7,4	5,7	11	31	1.5	51/76	26/18	5/6	11	7	1.5/4.6	1.1
7	8,5	5,7	16	34	1.7	52/72	26/20	6/8	10	6	1.8/4.2	0.8
8	9,6	5,7	5	9	1.7	45/70	27/21	6/9	13	9	1.4/4.0	1.3
9	11,3	5,7	2	5	2.1	47/68	26/22	8/10	10	9	1.9/4.5 C_1= =1,7/4.3	1.2
10*	3,4	11,3	15	20	0.3	–*	–*	29(29)	7(7)	–*	–*	

*Calculation made for T_3 and T_3' combined; experiment carried out in a similar manner to No. 2, but with T_2 added (3 wt. % based on S) (calculation for No. 2 given in brackets).

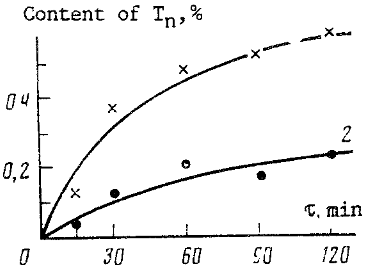

Fig. 1. Dependence of content of T_n in reaction mixture on time of reaction (140°C, TBP at 0.5 mole % of S, M/S = 1): 1) T_2; 2) T_3'.

philic [5, 6], at the stage involving chain transfer to the aldehyde polar factors are more favorable for alkyl radicals D than for radicals B_1.

A possible alternative route for the formation of T_3' is a secondary reaction of T_2 with 1-hexene. The following experimental results are evidence against this proposal: a) the absence of a compound that is analogous in structure to T_3' for telomers with two monomer units; b) the high selectivity of the process leading only to the formation of a compound with a C_6H_{13} substituent on one of the equivalent methylene groups adjacent to CO, namely, on the side of the short chain (this indicates at the same time that there is no 1,4-migration of hydrogen in radical B_2); c) the similarity in the pathway of the kinetic curves for formation of compounds T_2 and T_3' (Fig. 1); d) the lack of change in the ratio T_3'/T_3 when a known sample of T_2 is added to the initial compounds (Table 2, No. 10). Thus, in the present work we have revealed one of the few cases of rearrangement of radicals with a 1,6-migration of hydrogen along a chain of atoms containing a CO group, when there are no hydrogen atoms at the 5-position (relative to the radical site) which could participate in 1,5-migration. It also is of interest to point out the high degree of 1,6-rearrangement of the B_2 radical ($T_3'/(T_3' + T_3) \approx 0.7$) when the rate of the competing chain-transfer reaction is apparently quite high because the aldehyde is a very effective chain-transfer agent for the reaction.

EXPERIMENTAL

NMR spectra were recorded on a Bruker WP-200 spectrometer using the DEPT method, with CCl_4 as the internal standard and the chemical shifts of the signals calculated relative to TMS. PMR spectra were obtained on a Bruker WP-200 spectrometer, with TMS as internal standard GLC analysis of the reaction products was conducted on an LKhM-80 chromatograph, with helium, katharometer, and columns: 1) 1000 × 3 mm, 20% SKTFT-50 on Chromatone N-AW-HMDS, 0.16-0.20 mm; 2) 2000 × 3 mm, 15% Carbowax-20 M on Chromatone N-AW-HMDS, 0.16-0.20 mm, with temperature programming (from 50°C, 4°C/min). Preparative GLC was carried out on a Tsvet instrument with columns: 1) 1200 × 9 mm; 2) 1800 × 9 mm; 3) 2500 × 9 mm; 20% SKTFT-50 on Chromatone N-AW-HMDS, 0.16-0.20 mm; 150-230°C. The weight content of the reaction products was calculated from the areas of the peaks using standards and also by internal normalization without corrections.

Telomerization of 1-Hexene with Butyraldehyde. a) Preparative Experiments. A mixture of 34 mmoles of butyraldehyde, 34 mmoles of 1-hexene, and 1.7 mmoles of TBP was added to glass ampuls (30 cm^3), and traces of air were removed by means of freezing—evacuation—thawing out. The ampuls were filled with nitrogen, sealed, placed in metal casings, and heated for 2 h at 140°C, while being rotated in a silicone bath. The initial compounds were distilled off and the residue separated by distillation of narrow fractions, from which the telomers were isolated by means of preparative GLC (Table 1). Their structures were confirmed from their ^1H and ^{13}C NMR spectra. Additive calculations gave good agreement with experiment [7]: 4-decanone, d_4^{20} 0.8268, n_D^{20} 1.4238, MR (calc) = 48.39, MR (found) = 48.17 (cf. [8]); nonane, d_4^{20} 0.7197, n_D^{20} = 1.4039, MR (calc) = 43.76, MR (found) = 43.50. The yield of the mixture of telomers based on the initial batch of telogen was 7.5 g (59%), of which 31% was made up by ketone telomers and 28% by hydrocarbon telomers. The conversion of monomer was 56% and that of telogen 77%. Two hydrocarbons were identified in small quantities in the reaction mixture (10-15% of all the products combined), with structures that were not investigated. b) Analytical experiments Nos. 1-15 were carried out in ampuls of capacity 3 cm^3 according to the method described above. The conditions of the analytical experiments, the results of GLC analysis, and the values of C_1 (calculated from the equation of Mayo [9]) are given in Table 2.

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CONCLUSIONS

1. Telomerization of 1-hexene with butyraldehyde results in the formation of two main series of telomers — ketones and hydrocarbons.

2. In the reaction studied, radical rearrangement with 1,6-migration of a hydrogen atom along the chain containing a carbonyl group occurs to a significant extent.

LITERATURE CITED

1. H. Fisher and H. Paul, Acc. Chem. Res., 20, No. 5, 200 (1987).
2. G. N. Nikishin, M. G. Vinogradov, and R. V. Kereselidze, Zh. Org. Chem., 2, No. 11, 1918 (1966).
3. K. Hirota, S. Iizuka, H. Ochi, and M. Hatada, Bull. Chem. Soc. Jpn., 36, No. 1, 115 (1963).
4. V. V. Fedorov, A. G. Shostenko, and P. A. Zagorets, "The chemistry and technology of organic and high molecular weight compounds," Tr. Mosk. Khim.-Tekh. Inst., No. 86, 3 (1975).
5. B. Giese and H. Horler, Chem. Ber., 119, No. 2, 444 (1986).
6. I. Tabbaa, M. Cazaux, and R. Lalade, Bull. Soc. Chim. Belg., 92, Nos. 11, 12, 1011 (1983).
7. L. P. Lindemann and J. Q. Adams, Anal. Chem., 43, No. 10, 1245 (1971).
8. M. S. Kharasch, W. H. Urry, and B. M. Kuderna, J. Org. Chem., 14, No. 2, 251 (1949).
9. F. Mayo, J. Am. Chem. Soc., 70, No. 11, 3689 (1948).