1,5- AND 1,9-MIGRATION OF HYDROGEN DURING TELOMERIZATION OF PROPYLENE WITH DIMETHYL ACETAL

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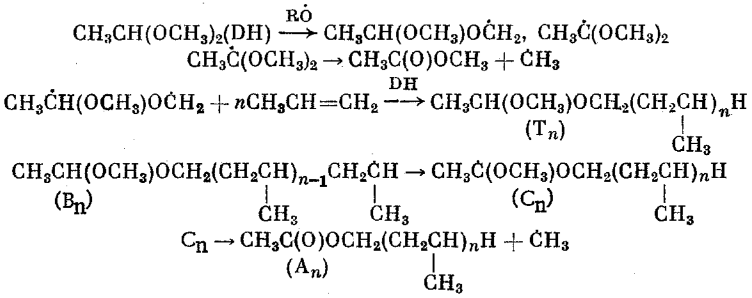
The telomerization of ethylene with dimethyl acetal goes mainly via cleavage of the C—H bond in the methoxyl group to give two series of telomers, and specifically unsymmetrical acetals and acetates [1]. Here the formation of the acetates is related to rearrangement of the growing radicals, with 1,5- and 1,9-migration of the H atom and fragmentation of the rearranged radicals. Taking into consideration the substantial effect of the nature of the monomer on the course of the telomerization [2] and, in particular, on the rearrangement of the radicals with a 1,5- and 1,9-migration of hydrogen in the telomerization process, we studied the telomerization of propylene with dimethyl acetal in the present paper. The reaction was run in the presence of tert-butyl peroxide at 140-150°C (Table 1). Telomers were isolated from the reaction mixture, and specifically acetals and acetates, the formation of which can be depicted by the scheme



$$CH_3CH(OCH_3)_2(DH) \xrightarrow{R\dot{O}} CH_3CH(OCH_3)O\dot{C}H_2,\ CH_3\dot{C}(OCH_3)_2$$
$$CH_3\dot{C}(OCH_3)_2 \rightarrow CH_3C(O)OCH_3 + \dot{C}H_3$$
$$CH_3\dot{C}H(OCH_3)O\dot{C}H_2 + nCH_3CH{=}CH_2 \xrightarrow{DH} \underset{(T_n)}{CH_3CH(OCH_3)OCH_2}(CH_2\underset{CH_3}{CH})_nH$$
$$\underset{(B_n)}{CH_3CH(OCH_3)OCH_2}(CH_2\underset{CH_3}{CH})_{n-1}CH_2\underset{CH_3}{\dot{C}H} \rightarrow CH_3\dot{C}(OCH_3)\underset{(C_n)}{OCH_2}(CH_2\underset{CH_3}{CH})_nH$$
$$C_n \rightarrow \underset{(A_n)}{CH_3C(O)OCH_2}(CH_2\underset{CH_3}{CH})_nH + \dot{C}H_3$$

It should be mentioned that among the compounds containing up to three monomeric units in the molecule (n = 1-3), both series of T_n and A_n telomers were not represented equally. Thus, the unsymmetrical T_n acetals, with n = 1, 2, were isolated from the reaction mixture by preparative GLC, and it was shown that the T_3 telomer is absent. At the same time, among the acetates only the A_n telomers with n = 1 and 3 were isolated (Tables 1 and 2), and it was shown that the A_2 acetate is practically absent.

The fragmentation of the B_n radical can occur with the elimination of either the $\dot{C}H_3$ or $\dot{C}H_2(CH_2\underset{CH_3}{CH})_nH$ radicals and the respective formation of either A_n compounds or methyl acetate. As the result of growth, recombination, and disproportionation reactions the cleaved radicals are converted to a mixture of hydrocarbons (H_n), whose yield reaches 65% of the sum of the products (see Table 1).

As in the case of the telomerization of ethylene with dimethyl acetal, the absence of the A_2 acetate among the reaction products is explained by the fact that the B_2 radical (see Scheme) does not isomerize with a 1,7-migration of the H atom, but instead is fixed via chain transfer to the telogen, as a result of which only the T_2 acetal is formed among the telomers with n = 2. At the same time, the B_1 and B_3 radicals rearrange with respectively 1,5- and 1,9-migration of H. A comparison of the ratios of the $A_n/(A_n + T_n)$ telomers in the case of ethylene and propylene permits mentioning some of the traits and general directions of each reaction. With close M/S_{av} values (0.33-0.43) for the first telomers (n = 1, 1,5-shift of H) these ratios are close (0.66 for ethylene and 0.64 for propylene).

In both reactions only the unsymmetrical T_2 acetal was detected among the telomers with n = 2. A substantial difference is observed in the case of the third group of telomers:

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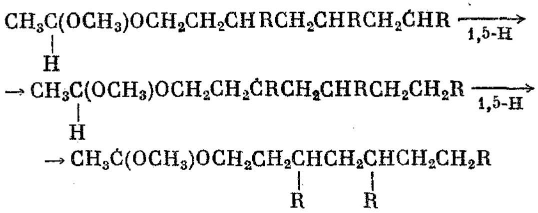
TABLE 1. Telomerization of Propylene (M) with Dimethyl Acetal (S) (150°C, 0.2 mole % of tert-butyl peroxide, 45 min)

S_H	M_H	Conversion, mole %	$\frac{M}{S}$ av	Amt. of telomer homologs with n monomeric units, mole %				Yield, % ($n \leqslant 3$)	
mmoles				T_1	A_1	T_2	A_3	$\Sigma T_n + A_n$	ΣH_n
63,5	8,6	60	0,09	37,1	56,2	6,7	–	35,6	64,4
65,0	10,7	36	0.14	35,7	51,6	8,7	4,0	33,6	66.4
53,3	20,5	27	0,33	32,2	56,1	7,1	4,6	37,8	62,2
54,2	26,4	24	0,43	28,8	49,7	9,1	12,4	31,4	68,6

TABLE 2. Characteristics of Isolated Telomers

Compound	n_D^{20}	d_4^{20}	Empirical formula	Found/calc.		
				MR	C, %	H, %
$CH_3CH(OCH_3)OCH_2CH_2CH_2CH_3$	1,3930	0,8409	$C_7H_{16}O_2$	37,46 / 37,61	63,68 / 63,64	12,04 / 12,12
$CH_3CH(OCH_3)OCH_2(CH_2\underset{CH_3}{\underset{\mid}{C}H})_2H$	1,4140	0,8438	$C_{10}H_{22}O_2$	51,52 / 51,46	70,12 / 68,97	12,72 / 12,63
$CH_3C(O)OCH_2(CH_2\underset{CH_3}{\underset{\mid}{C}H})_3H$	1,4275	0,8788	$C_{12}H_{24}O_2$	58,51 / 59,17	72,81 / 72,00	12,04 / 12,00

for ethylene $A_3/(A_3 + T_3) \approx 0.27$, whereas in the reaction with propylene this ratio is equal to one (the unrearranged T_3 acetal is practically absent). As a result, the transition from ethylene to propylene had little effect on the degree of 1,5-H-migration, but it led to a substantial increase in the degree of rearrangement of the radicals with a 1,9-migration of H. A similar phenomenon was also observed in the case of carboxylic acid esters [2]. The transition from ethylene to propylene had little effect on the facile 1,5-transition of H, but it led to the appearance of a rarely encountered, and unfavorable from the standpoint of the transition state, rearrangement of the radicals with 1,3-H-migration. This "cooperation" is explained by the favorable (in the case of propylene) coupling of the polar factors in the chain transfer step, where the nucleophilic growing $CH_2\dot{C}HCH_3$ radical attacks the electrophilic portion of the radical in the transition state, from which the migrating H atom leaves. This cooperation has little effect on the facile 1,5-H-migration, but it does exert a substantial facilitating effect on the course of the less favorable rearrangement processes. At the same time, an increase in only the degree of 1,9-H-migration can be explained if the "cascade" mechanism is assumed for 1,9-H-migration in the G radical (two consecutive 1,5-H-transitions).

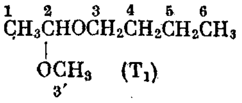
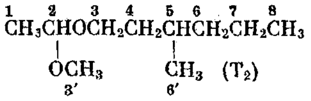
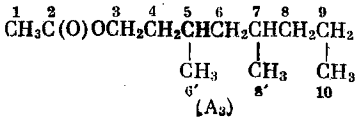


$$CH_3\underset{H}{\underset{\mid}{C}}(OCH_3)OCH_2CH_2CHRCH_2CHRCH_2\dot{C}HR \xrightarrow[1,5\text{-}H]{} CH_3\underset{H}{\underset{\mid}{C}}(OCH_3)OCH_2CH_2\dot{C}RCH_2CHRCH_2CH_2R \xrightarrow[1,5\text{-}H]{} CH_3\dot{C}(OCH_3)OCH_2CH_2\underset{R}{\underset{\mid}{C}H}CH_2\underset{R}{\underset{\mid}{C}H}CH_2CH_2R$$

When going from ethylene (R = H) to propylene ($R = CH_3$) the hydrogen in position 5 (from the radical center) becomes tertiary and should migrate more easily to the radical center than when R = H. A similar mechanism was proposed earlier for the 1,10- and 1,11-transitions of H in hydrocarbon radicals [3].

The structure of the isolated telomers was confirmed by the ^1H and ^{13}C NMR spectral data. The PMR spectra of the T_1 and T_2 acetals (Table 3) have the characteristic signals of the OCH_3 and OCH_2 groups, and also a doublet from $\underline{CH_3}CH$ and a quadruplet of the acetal hydrogen in $CH_3\underline{CH}$. In the spectra of the A_1 and A_3 acetates were observed the characteristic singlet of CH_3CO_2 in a region free of other signals (∿2 ppm), a triplet from OCH_2CH_2 (4.13 ppm), and the sum of the signals of the hydrocarbon portion of the molecule. The

TABLE 3. ^1H and ^{13}C NMR Spectral Data for Isolated Compounds

Compound	Type of spectrum	δ, ppm from TMS					
		C(O)O, OCHO	CH_3O	CH_2O	$\underline{CH_3}CH_n$, $\underline{CH_3}C\lt$	CH	CH_2
 $CH_3CH(OCH_3)OCH_2CH_2CH_2CH_3$ (T_1)	^1H	4,60 q (2)	3,27 s (3′)	3,42 t (3)	1,20d (1), 0,93 t (6)	–	1,27–1,62 m
	^{13}C	99,5 (2)	50,9 (3′)	64,2 (3)	18,7 (1), 13,6 (6)	–	31,9 (4), 19,3 (5)
$CH_3C(O)OCH_2CH_2CH_2CH_3$ (A_1)	^1H	–		4,13 t (3)	2,02 s (1), 0,96 t (6)	–	1,16–1,64 m
 $CH_3CH(OCH_3)OCH_2CH_2CH(CH_3)CH_2CH_2CH_3$ (T_2)	^1H	4,56 q (2)	3,18 s (3)	3,40 t (3)	1,22 d (1), 0,76–0,98m (8, 6′)	–	1,17–1,64 m
	^{13}C	99,4 (2)	50,8 (3)	62,5 (3)	18,7 (1), 14,1 (8), 19,8 (6)	29,3 (5)	36,7 (4), 39,3 (6), 19,4 (7)
 $CH_3C(O)OCH_2CH_2CH(CH_3)CH_2CH(CH_3)CH_2CH_2CH_3$ (A_3)	^1H			4,13 t (3)	1,96 s (1), 0,78–0,99 m (6′, 8′, 10)		1,08–1,60 m
	^{13}C	168,7 (2)		61,9 (3)	14,3 (10), 19,8 (6′, 8′), 19,3 (1)	29,6 (5,7)	35,4 (4), 44,5 (6), 40,0 (8), 19,9 (9)

ratio of the integral intensities and the multiplicity of the signals correspond to the made assignments. Butyl acetate (A_1) was also identified by GLC via an authentic sample.

The ^{13}C NMR spectra of the acetals also have the characteristic signals of the $CH(OR)_2$ (99 ppm), CH_3O, and CH_2O groups. The signals 168.7 ($CH_3{}^{13}COO$) and 61.9 ppm (OCH_2) are characteristic for the A_3 acetate. The signals of the hydrocarbon portion of the molecule were assigned on the basis of the spectral data for the previously studied standard compounds with an analogous structure of the hydrocarbon skeleton [4].

The PMR spectra of the hydrocarbons disclosed the absence of any signals of protons attached to functional groups (signals are present only in the 0.77-1.56 ppm region).

EXPERIMENTAL

The PMR spectra were taken on a Perkin–Elmer R-20 instrument (60 MHz), while the ^{13}C NMR spectra were taken on a Bruker–Physic HX-90 instrument (22.6 MHz). The reaction products were isolated by preparative GLC on a PAKhV-0.2 instrument (using a katharometer, He as the carrier gas, and a 2200 × 9 mm column packed with 15% Carbowax 20M deposited on Chromaton N-AW (0.2-0.25 mm). A quantitative analysis of the reaction mixtures was made by GLC on a LKhM-8M chromatograph, using a katharometer, He as the carrier gas (3 liters/h), and the columns: 1) 5000 × 4 mm, packed with 15% Carbowax 20M deposited on Chromaton N-AW (0.2-0.25 mm); 2) 3000 × 4 mm, packed with 20% SKTPT-50X deposited on Chromaton N-AW (0.2-0.25 mm).

Telomerization of Propylene with Dimethyl Acetal. The experiments (see Table 1) were run in a 10-ml stainless-steel autoclave. Prior to experiment the telogen was freed of traces of oxygen by the freezing–evacuation–thawing method. The autoclaves plus reactants, rotated at a speed of 8 rpm, were heated in a silicone oil bath. The experimental conditions and GLC analysis results are given in Table 1.

To isolate the reaction products the experiments were run in a rotated 500-ml steel autoclave. Prior to experiment the autoclave was cooled with liquid N_2, 200 g of chilled dimethyl acetal, and 10 g of TBP were charged into the autoclave, followed by the addition of 60 ml of liquid propylene, and the experiment was run at 140° for 4 h. We ran seven experiments in a similar manner, which were combined. After distilling off the starting dimethyl acetal the weight of the mixed telomers was 155.7 g; this mixture was fractionally distilled into the fractions: I) 30° (38 mm)-45° (7 mm), weight 24.5 g; II) 45° (7 mm)-62° (2 mm), weight 18.1 g; III) 62° (2 mm)-90° (1 mm), weight 18.8 g, and residue 68 g. Fractions I, II, and III were fractionally distilled through a packed column. The telomers, and specifically acetals and acetates, were isolated from the obtained narrow fractions by preparative GLC (see Tables 1 and 2).

CONCLUSIONS

1. The telomerization of propylene with dimethyl acetal leads to the formation of two series of telomers, and specifically acetals and acetates.

2. The formation of the acetates is due to rearrangement of the growing radicals with a 1,5- and 1,9-migration of hydrogen. The transition from ethylene to propylene leads to a substantial increase in the degree of 1,9-migration of hydrogen.

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