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TELOMERIZATION OF ETHYLENE WITH DIMETHYLACETAL

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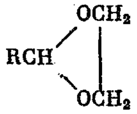
A comparison of the results of a study of ethylene telomerization with cyclic and linear acetals shows interesting features in the behavior of the latter.

The cyclic acetals  react in radical telomerization mainly through the C —H bond in the OCHRO group, even with R = H [1, 2]; linear $CH_2(OCH_2R^1)_2$ acetals react principally at the C —H bond of the alkoxyl group, even dimethylacetals with R^1 = H [3]. It is shown in the present study that acetaldehyde dimethylacetal, besides reaction at the mobile acetal hydrogen, reacts to a considerable extent in radical telomerization also by rupturing the C —H bond of the CH_3O group.

The telomerization of ethylene with acetaldehyde dimethylacetal was carried out in the presence of tert-butyl peroxide (TBP) at 140°C. From the reaction mixture, by a combination of fractionation and preparative gas —liquid chromatography (GLC), three series of telomers were isolated: the acetals $CH_3CH(OCH_3)OCH_2(CH_2CH_2)_nH$ (T_n, n = 1-3), the ketones $CH_3CO(O)-(CH_2CH_2)_nH$ (K_n, n = 1-3), and the acetates $CH_3C(O)OCH_2(CH_2CH_2)_nH$ (A_n, n = 1 and 3) (Table 1). The structure of the compounds isolated was confirmed by their PMR spectra. Each series of telomers has a characteristic type of proton enabling their reliable identification: the ketones from the acetyl group singlet, the acetals from the CH_3O and $\underline{CH_3}CH$ group signals, the acetates from the CH_3CO_2 group singlet. Amyl acetate (A_n, n = 2) was practically absent in the reaction mixture (GLC and PMR data). Besides eight telomers (total yield 75-80%), 11 hydrocarbons with a total yield of 15-25% were isolated from the mixture (Table 2). Signals from protons screened by the functional groups were missing from their PMR spectra.

The formation of acetals (T_n) takes place by the normal telomerization arrangement with chain transfer at the OCH_3 group:

$$CH_3CH(OCH_3)_2 + RO^\cdot \rightarrow CH_3CH(OCH_3)O\dot{C}H_2 \quad (I)$$

$$(I) + nCH_2{=}CH_2 \xrightarrow{DH} CH_3CH(OCH_3)OCH_2(CH_2CH_2)_nH$$

The T_1-T_3 acetals were isolated as narrow fractions (90-95%). The PMR spectra showed the presence of typical signals from $\underline{CH_3}CH$ (d), $CH_3\underline{CH}$ (q), OCH_3 (s), and $O\underline{CH_2}CH_2$ (t) groups. No ketal telomers were detected in the reaction mixture. It can be supposed that one way of forming K_n ketones is the telomerization of existing acetaldehyde in the reaction mixture (expts. 6 and 7) according to the scheme

$$CH_3CHO + nCH_2{=}CH_2 \xrightarrow[CH_3CHO]{RO^\cdot} CH_3C(O)(CH_2CH_2)_nH,\ K_n,\quad n = 1\text{—}3$$

or thermal breakdown of the ketals [4].

Methyl ethyl ketone (K_1) was identified by GLC with an authentic specimen; the ketone K_2 was isolated individually, and K_3 as a narrow fraction (90%). Their structure was confirmed by the PMR spectra (see Table 1), which contain signals from the CH_3CO groups (singlet, 3H) and CH_2CH_2CO (triplet, 2H). According to expts. 6 and 7, the reaction mixture contains about 0.5% of acetaldehyde.

In the reaction mixture, in the T_1-T_3 range, besides the telomers T_n and K_n we identified propyl acetate (A_1) and heptyl acetate (A_3) with the A_2 acetate absent (see Table 2).

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TABLE 1. PMR Spectral Data for the Telomers Isolated

Ketones	δ, ppm, relative to TMS				Acetals	δ, ppm, relative to TMS					Acetates	δ, ppm, relative to TMS		
	1	2	3	4		1	2	3	4	5		1	2	3
$\overset{1}{CH_3}C(O)\overset{2}{CH_2}\overset{4}{CH_3}$ *	2,10	2,42	—	0,87	$\overset{1}{CH_3}\overset{2}{CH}(\overset{3}{O}CH)_3\overset{4}{O}CH_2CH_2\overset{5}{CH_3}$ †	1,17	4,55	3,22	3,34	0,86	$\overset{1}{CH_3}C(O)O\overset{2}{CH_2}CH_2\overset{3}{CH_3}$	1,96	3,97	0,86
$\overset{1}{CH_3}C(O)\overset{2}{CH_2}(\overset{3}{CH_2})_2\overset{4}{CH_3}$	2,11	2,49	1,24	0,87	$\overset{1}{CH_3}\overset{2}{CH}(\overset{3}{O}CH_3)O\overset{4}{CH_2}(CH_2)_3\overset{5}{CH_3}$ ‡	1,17	4,60	3,23	3,40	0,86	–	—	—	—
$\overset{1}{CH_3}C(O)\overset{2}{CH_2}(\overset{3}{CH_2})_4\overset{4}{CH_3}$	2,06	2,35	1,20	0,86	$\overset{1}{CH_3}\overset{2}{CH}(\overset{3}{O}CH_3)O\overset{4}{CH_2}(CH_2)_5\overset{5}{CH_3}$ **	1,16	4,58	3,22	3,34	0,86	$\overset{1}{CH_3}C(O)O\overset{2}{CH_2}(CH_2)_5\overset{3}{CH_3}$	1,85	4,04	0,87

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*Standard.

†n_D^{20} 1.3868; d_4^{20} 0.8303.

‡n_D^{20} 1.3995; d_4^{20} 0.8305.

**d_D^{20} 1.4092; d_4^{20} 0.8308.

TABLE 2. Telomerization of Ethylene (M) with Dimethylacetal (S) (150°, 0.3 mole % TBP, 40 min)

Expt.	$\left(\frac{M}{S}\right)_{av}$	Telomer-homolog content with n monomer units, %									Yield, %*	
		Acetals $CH_3CH(OCH_3)OCH_2(CH_2CH_2)_nH$			Acetates $CH_3C(O)CH_2(CH_2CH_2)_nH$			Ketones $CH_3C(O)(CH_2CH_2)_nH$			telomers	hydrocarbons
		1	2	3	1	2†	3	1‡	2	3		
2	0,09	19,3	12,8	5,3	24,9	–	3,2	7,6	21,7	5,2	83,2	16,8
3	0,29	14,2	12,8	14,7	19,3	–	4,4	6,5	20,7	7,4	82,0	18,0
4	0,37	10,7	8,1	15,2	20	–	4,4	5,7	27,2	8,7	72,0	28,0
5	0,41	8,22	10,4	12,6	17,6	–	6,1	5,12	26,3	13,7	75,5	24,5

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*Yield of telomers and hydrocarbons is quoted per total of identified products up to T_3 inclusive.

†Yield of acetates < 1%.

‡Analysis made with distillation of original, resulting in reduced yield of methyl ethyl ketone.

This selective formation of acetates may be due to a rearrangement of the first and third growing radicals $CH_3CH(OCH_3)OCH_2(CH_2CH_2)_n^{\cdot}$ with 1,5- and 1,9-migration of H respectively:

$$CH_3CH(OCH_3)O\dot{C}H_2 + nCH_2 = CH_2 \rightarrow CH_3CH(OCH_3)OCH_2(CH_2CH_2)_n^{\cdot}$$

$$CH_3CH(OCH_3)OCH_2CH_2\dot{C}H_2 \xrightarrow{1,\,5\text{-H}} CH_3\dot{C}(OCH_3)OCH_2CH_2CH_3$$

$$CH_3CH(OCH_3)OCH_2(CH_2CH_2)_3^{\cdot} \xrightarrow{1,\,9\text{-H}} CH_3\dot{C}(OCH_3)OCH_2(CH_2CH_2)_3H$$

$$CH_3\dot{C}(OCH_3)OCH_2(CH_2CH_2)_nH \xrightarrow[n=1,\,3]{-CH_3^{\cdot}} CH_3C(O)OCH_2(CH_2CH_2)_nH$$

Propyl acetate was isolated individually and its structure was confirmed by the PMR spectra (see Table 1). Heptyl acetate was identified by GLC with an authentic specimen and also from the PMR data on a fraction consisting of heptyl acetate (60%) and methylheptylacetal (T_3, 40%) (see Table 1). The absence of amyl acetate (A_2) is connected with the fact that the $CH_3CH(OCH_3)OCH_2(CH_2CH_2)_2^{\cdot}$ radical does not undergo rearrangement with 1,7-migration of H.

With primary alkyl radicals, 1,10- and 1,11-migration of H was observed in [5]. It is suggested that these rearrangements can also take place as two successive 1,5- or 1,5- and 1,6-hydrogen transfers. For the 1,9-migration of H, conformations can exist in the transition state which provide a sufficiently close approach of the radical center to the migrating H atom. Nevertheless, even in the case under consideration, two successive H migrations can occur.

The formation of methyl acetate, up to 5% of the original acetal, can be attributed to the β breakdown of $CH_3C(OCH_3)OCH_2(CH_2CH_2)_nH$ (n = 0, 1, 3) radicals. Methyl acetate is also formed directly when dimethylacetal is heated with TBP (expts. 6 and 7).

The hypothesis that the A_n acetates are formed by the telomerization of methyl acetate does not accord with the following experimental results: a) the absence of amyl acetate A_2; b) the absence of methyl butyrate in the reaction mixture (GLC on an authentic specimen), although it is known from [6, 7] that, under similar conditions, methyl acetate reacts mainly at the acyl group (by 70-80%) to form methyl esters of higher acids; c) even when telomerization is carried out with pure methyl acetate, its conversion does not exceed 2-3%. As its content in the reaction mixture is up to 5 or 6% (expts. 6 and 7), the formation of propyl acetate in a yield of 13% (on total of propyl acetate + methyl acetate) cannot be ensured.

EXPERIMENTAL

The PMR spectra were recorded on Hitachi – Perkin – Elmer R-20 (60 MHz) and Perkin – Elmer R-12 (60 MHz) instruments. The reaction products were separated by preparative GLC in a PAKhV-0.2 apparatus and catharometer with helium as the carrier gas. The column was 2600 × 9 mm with 20% SKTFT-50 on Chromaton N-AW (0.2-0.25 mm). Quantitative analyses of the reaction mixtures were made by GLC in an LKhM-8M chromatograph and catharometer. The carrier gas was helium (3 liters/h); the columns were: 1) 3000 × 4 mm with 15% Carbowax-20 m on N-AW Chromaton (0.2-0.25 mm); 2) 2000 × 4 mm with 15% Apiezon L on Chromaton N-AW (0.2-0.25 mm).

Telomerization of Ethylene with Dimethylacetal

Experiment 1. A rotating steel autoclave of 0.5-liter capacity was loaded with 168.1 g of dimethylacetal and 7.9 g of tert-butyl peroxide (TBP), and ethylene was blown in. The experiment was carried out at 140° for 4 h with an ethylene pressure of 40-45 atm, maintained by pumping in according to its absorption. After distilling off the initial dimethylacetal the mixture of products (16.2 g) was distilled into fractions: I) 46° (60 mm)-36° (30 mm), 6.2 g; II) 36° (30 mm)-37° (3 mm), 4.4 g; residue 3 g. Fractions I and II were distilled in a packed tower. The corresponding narrow fractions from four similar experiments were combined and the telomers were isolated with additional purification by preparative GLC. Their structure was confirmed by the PMR spectra (see Table 1). The hydrocarbons and ethylene oligomers were similarly isolated.

Experiments 2-5. These experiments were made in stainless-steel autoclaves of 10-cm^3 capacity. Before an experiment the telogen was purified from traces of oxygen by the well-known procedure of "freezing – vacuum – nitrogen – thawing." Control experiments showed that practically no telogen was entrained during evacuation. After filling with the reactants, the amount of which was determined with an accuracy of up to 0.02 g, the autoclaves were heated in a bath of silicone oil with rotation at 8 rpm. The experimental conditions and the GLC analyses are given in Table 2.

Experiments 6 and 7. These experiments were conducted similarly to expts. 2-5; a 2.2% solution of TBP in dimethylacetal was used; 150°, 60 min.

From 6.5 g of TBP solution in dimethylacetal and 0.32 g of ethylene, according to GLC there was obtained (calculated on the original acetal): methyl acetate — 5.6%, acetaldehyde — 0.6%, propyl acetate — 0.8%. In expt. 7, without ethylene, 5% of methyl acetate and 0.3% of acetaldehyde were obtained.

CONCLUSIONS

1. Telomerization of ethylene with acetaldehyde dimethylacetal gives three series of products: acetals $CH_3CH(OCH_3)OCH_2(CH_2CH_2)_nH$ (n = 1-3), acetates $CH_2CO_2CH_2(CH_2CH_2)_nH$ (n = 1 and 3), and ketones $CH_2CO(CH_2CH_2)_nH$ (n = 1-3).

2. To account for the formation of propyl and heptyl acetates a scheme has been proposed which includes the rearrangement of the growing radicals with 1,5- and 1,9-migration of hydrogen, respectively.

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