FREE-RADICAL ADDITION OF METHYL DIBROMOACETATE TO ETHYLENE AND 1-HEXENE

R. Kh. Freidlina and A. A. Kamyshova

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Methyl dibromoacetate does not undergo addition to methyl acrylate in the presence of peroxides, but this reaction does proceed in the presence of iron pentacarbonyl [1]. The negative result which is obtained when a peroxide is used is apparently related to the fact that both the unsaturated compound and the addend are electrophilic compounds. It is assumed that stage (3) of the reaction (scheme) proceeds with difficulty, viz., the chain transfer, requiring the reaction of electrophilic radical A ($R' = CO_2CH_3$) and the electrophilic methyl dibromoacetate molecule

Scheme

$$\text{initiator} \longrightarrow 2R^{\bullet}$$

$$R^{\bullet} + CHBr_2CO_2CH_3 \longrightarrow RBr + \dot{C}HBrCO_2CH_3 \quad (1)$$

$$\dot{C}HBrCO_2CH_3 + CH_2 = CHR' \longrightarrow CH_3O_2CCHBrCH_2\dot{C}HR'\,(A) \quad (2)$$

$$A + CHBr_2CO_2CH_3 \longrightarrow CH_3O_2CCHBrCH_2CHBrR' + \dot{C}HBrCO_2CH_3 \quad (3)$$

$$R' = CO_2CH_3;\ H;\ C_4H_9$$

In this paper, it is shown that when methyl acrylate is replaced with nucleophilic compounds, i.e., ethylene and 1-hexene ($R' = H$, C_4H_9), the reaction with methyl dibromoacetate proceeds smoothly in the presence of peroxides because of rupture of the C–Br bond, just as in the case of methyl bromoacetate [2, 3], according to the equation

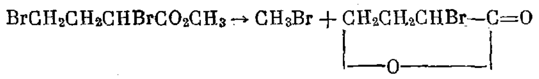
$$CHBr_2CO_2CH_3 + CH_2 = CHR' \xrightarrow{\text{peroxide}} CH_3O_2CCHBr\,(CH_2CHR')_n\,Br$$

$$R' = H,\quad n = 1,\ 2;\ R' = C_4H_9,\quad n = 0$$

Ethylene reacted with methyl dibromoacetate with the formation of telomers. The reaction proceeded both at 55°C in the presence of dicyclohexyl peroxydicarbonate and at 100°C with benzoyl peroxide, and telomer homologs were isolated with n = 1, 2. The structure of the obtained telomers was confirmed by PMR spectra and by certain chemical transformations. Table 1 shows the proton chemical shifts (δ, ppm) for the obtained telomers. NMR spectra were taken on a Perkin–Elmer instrument at a frequency of 60 MHz, the internal standard was hexamethyldisiloxane, and $\delta = 0.05$ ppm.

The structure of the telomers was also confirmed by IR spectra. Thus, the spectrum of the telomer with n = 1 contained frequencies of 566 and 640 cm^{-1}, and that of the telomer with n = 2 contained frequencies of 565 and 649 cm^{-1}, characteristic of the CH_2Br group [4-6].

Methyl 1,3-dibromobutyrate formed a lactone easily when heated with a catalytic amount of $Fe(CO)_5$ according to the method of [7]



$$BrCH_2CH_2CHBrCO_2CH_3 \rightarrow CH_3Br + \underbrace{CH_2CH_2CHBr-C{=}O}_{O}$$

Under the same conditions, methyl 1,5-dibromocaproate does not undergo closure to a lactone.

Data on the effect of the reaction temperature and the ratio $C_2H_4/CHBr_2CO_2CH_3$ (M/S) on the composition of the telomer mixture which was formed are given in Table 2 (the experiments were carried out in assay

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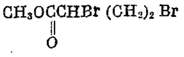
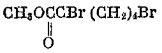
TABLE 1*

Compound	Groups			
	—CHBr—	—CH₂Br	—CH₂—	CH₃O—
 $CH_3O\underset{\underset{O}{\|}}{C}CHBr\,(CH_2)_2\,Br$	4,54t	3,56t	2,58q	3,76s
 $CH_3O\underset{\underset{O}{\|}}{C}CBr\,(CH_2)_4Br$	4,26t	3,42t	1,87q	3,72s

* s, singlet; t, triplet; q, quadruplet; m, multiplet. Integral intensities for telomer with n = 1, 1:2:2:3; and for telomer with n = 2, 1:2:6:3.

autoclaves with a capacity of 0.01 liter). As shown in Table 2, the increase of the reaction temperature did not significantly influence the conversion and the distribution of the telomer homologs, nor did the threefold increase of the ratio M/S; the telomer with n = 1 remained the principal reaction product (its content in the mixture was not less than 70%).

The addition of methyl dibromoacetate to 1-hexene was carried out in the presence of various peroxides (dicyclohexyl peroxydicarbonate, benzoyl peroxide, and tert-butyl peroxide) at temperatures of 55, 100, and 145°C, respectively. As a result of the reaction, a mixture of racemic forms of 1-carbomethoxy-1,3-dibromoheptane was formed. By gas–liquid chromatography, it was established that the ratio of the two forms between 55 and 140°C did not depend on the temperature and was equal to ~45 : 55. By repeated distillation in a column with 20 theoretical plates, we were able to obtain both racemic forms of the diastereomers individually and to analyze each by PMR and IR spectroscopy. The indicated structure of 1-carbomethoxy-1,3-dibromoheptane was hereby confirmed. The stereochemistry of this compound is being studied.

EXPERIMENTAL

Telomerization of Ethylene with Methyl Dibromoacetate. The experiments were carried out in a rotating stainless-steel autoclave with a capacity of 0.25 liter. Methyl dibromoacetate (42.5 g) and 2 g benzoyl peroxide were placed in the autoclave, and, after the air was replaced with N_2, ethylene was introduced up to a pressure of 100 atm. The autoclave was heated at 95-100°C for 7 h, with the pressure falling from 320 to 240 atm. From 46.3 g of the reaction mixture, loaded in a Vigre column, 14.6 g (66% conversion) of the unreacted starting compound was distilled. According to gas–liquid chromatographic analysis (glass column, 2 m in length and 4 mm in diameter; Chromosorb W, 0.25-0.5 mm; stationary phase, 6% silicone elastomer; temperature, 150°C; carrier gas, N_2; flame-ionization detection), the telomer mixture (28.5 g) contained telomers with n = 1, 35%; n = 2, 42%; and n = 3, 23%.* The telomer mixture which was obtained from several experimental runs was subjected to fractionation in a column. Adsorption chromatography on silica gel was used to obtain analytically pure substances. Methyl 1,3-dibromobutyrate was isolated, with bp 71°C (5 mm); n_D^{20} 1.5084; d_4^{20} 1.8446. Found: C 23.30; 23.18; H 3.15; 3.12; Br 61.32; 61.07%: MR 42.03. $C_5H_8Br_2O_2$. Calculated: C 23.10; H 3.10; Br 61.49%; MR 42.47. Methyl 1,5-dibromocaproate was similarly prepared, with bp 113°C (2 mm); n_D^{20} 1.5056; d_4^{20} 1.6555. Found: C 29.33; 29.37; H 4.25; 4.17; Br 54.92; 55.16%; MR 51.65. $C_7H_{12}Br_2O_2$. Calculated: C 29.19; H 4.20; Br 55.50%; MR 51.71.

Preparation of α-Bromobutyrolactone. Methyl 1,3-dibromobutyrate (7.3 g) and 0.3 g $Fe(CO)_5$ were refluxed in a flask at 135-137°C for 8 h. After distillation in a Vigre column, 3.9 g (83% of theor.) of the lactone was obtained with bp 96-97°C (5 mm); n_D^{20} 1.5088; d_4^{20} 1.7640. Found: C 29.58; 29.43; H 3.01; 3.09%; MR 27.92. $C_4H_5BrO_2$. Calculated: C 29.12; H 3.06%; MR 27.89.

Addition of Methyl Dibromoacetate to 1-Hexene. The experiments were carried out in glass ampuls in a thermostat with stirring. 1-Hexene (8.4 g), 20 g methyl dibromoacetate, and 1.4 g dicyclohexyl peroxydicarbonate were placed in two ampuls, the ampuls were filled with argon by the "freezing–evacuation–thawing" method, sealed, and heated at 55°C for 7 h. As a result of distillation in a column, two fractions were isolated: a) 2.3 g with bp 98°C (50 mm) (80% conversion of methyl dibromoacetate); b) 23.8 g with bp 97-104°C (3 mm); residue 3.6 g. By repeated distillation of fraction b), 22.3 g (70.6%) 1,3-dibromo-1-carbomethoxyheptane was obtained, with bp 117-118°C (4 mm); n_D^{20} 1.4928; d_4^{20} 1.5002. Found: C 34.35; 34.52; H 5.22; 5.14; Br 50.13; 50.18%; MR 61.21. $C_9H_{16}O_2Br_2$. Calculated: C 34.20; H 5.10; Br 50.57%; MR 61.05.

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*The compound was identified from the linear relation of the logarithms of the retention times of the homologs to the number of carbon atoms in the molecule.

TABLE 2

T, °C	M/S	Time, h	Conversion of telogen*, %	Correlation of telomer homologs†		
				$n = 1$	$n = 2$	$n = 3$
55	1,96	5	73	93	7	—
55	6,83	5	100	74	23	3
95	1,95	5	84,3	92	8	—
95	6,16	5	100	68	28	4

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* Conversion of the starting methyl dibromoacetate was determined by gas–liquid chromatography (methyl bromoacetate indicator) with calibration mixtures.

†The sum of the telomers which were formed was taken as 100%.

To separate individually the racemic forms of the diastereomers, the reaction mixtures of several experimental runs were combined and subjected to fractionation in a column with a packing of 20 theoretical plates. The following constants were obtained for the first racemic form of 1,3-dibromo-1-carbomethoxyheptane: bp 113°C (3 mm); n_D^{20} 1.4913; d_4^{20} 1.4894; MR 61.49; for the second one: bp 117°C (3 mm); n_D^{20} 1.4930; d_4^{20} 1.4980; MR 61.32.

CONCLUSIONS

1. Telomerization of ethylene with methyl dibromoacetate was carried out with peroxide initiation. Telomers with n = 1, 2 were isolated, and their structure was confirmed.

2. Addition of methyl dibromoacetate to 1-hexene was carried out in the presence of peroxides, and the racemic forms of the diastereomers of 1,3-dibromo-1-carbomethoxyheptane were isolated.

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