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Abstract

Full Text

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TELOMERIZATION OF METHACRYLIC ACID WITH TRIALKYL PHOSPHITES

(Presented by Academician B. A. Arbuzov, 13 XI 1957)

In previously published works ([1]), Gilm Kamai and V. A. Kukhtin showed that trialkyl phosphites can undergo the Arbuzov rearrangement under the action of α, β-unsaturated aldehydes and acids; in the case of acids the reaction proceeds according to the scheme:

$$\text{I.}\quad (RO)_3P: + {}^{\delta+}CH_2{=}CR_1{-}C\begin{matrix}\overset{\delta-}{O}\\ OH\end{matrix} \longrightarrow (RO)_3P^+\ \begin{matrix} O{-}C{=}O \\ | \\ CHR_1 \\ | \\ CH_2 \end{matrix}$$

$$\text{or}\quad \left[(RO)_3P^+\quad \begin{matrix} {-}O{-}C{=}O \\ | \\ CHR_1 \\ | \\ CH_2 \end{matrix}\right],$$

$$\text{II.}\quad (RO)_3P\ \begin{matrix} O{-}C{=}O \\ | \\ CHR_1 \\ | \\ CH_2 \end{matrix} \longrightarrow (RO)_2P({=}\,O)CH_2CHR'COOR.$$

Continuing investigations in this field, we established that, under certain conditions, not one but several molecules of methacrylic acid can add to a molecule of trialkyl phosphite; in this case the reaction assumes the character of telomerization.

Carefully purified triethyl phosphite (purified with sodium and carefully distilled) can telomerize with methacrylic acid without a catalyst. Formation of the telomer occurs both at room temperature and on heating.

Phosphite purified by simple distillation with methacrylic acid does not telomerize.

However, even when telomerization without a catalyst does occur, the amount of telomer is insignificant. Therefore it was first necessary to find a suitable catalyst for carrying out the telomerization of phosphites with methacrylic acid.

Connell and Coover ([2]), who recently described the telomerization of trialkyl phosphites with lactones, used triethylamine and sodium methylate as catalysts.

The experiments we carried out showed that although these two catalysts do induce telomerization of trialkyl phosphites with methacrylic acid, their use as catalysts is difficult, since it is hard to achieve good reproducibility of the experiment; moreover, the yields of telomers are usually not high.

The most suitable catalyst for the telomerization reaction of trialkyl phosphites with methacrylic acid proved to be benzoyl peroxide. We studied telomerization in the presence of various amounts of benzoyl peroxide and at different ratios of the starting components. Telomers with different average molecular weights were obtained.

All the telomers obtained are white powdery products that have no definite melting point; upon heating they soften and char, and are practically insoluble at room temperature in acetone, dioxane, benzene, nitrobenzene, carbon tetrachloride, ethyl alcohol, hexane, aniline, and chloroform. They dissolve upon heating in methanol and acetic acid.

The results of our experiments are summarized in Table 1.

Table 1

Effect of the experimental conditions on the average molecular weight and degree of polymerization (n) of telomers
$(RO)_2P[CH_2C(CH_3)COO]_nR$
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O
(the experiments were carried out at 20°)

Experiment no.	Initial reagents	Molar ratio of reagents	Catalyst	Amount of catalyst, wt. %	Phosphorus content, %	n	Mol. wt. (avg.), calc.	Mol. wt. (avg.), found (by phosphorus)	Mol. wt. (avg.), determined cryoscopically	Telomer yield, %
1	$(C_2H_5O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 2	CH_3ONa	0.2	5.5	5	596	558	–	26.8
2	$(C_2H_5O)_3P$ $(CH_2=C-COOH)$ | CH_3	1 : 2	$(C_2H_5)_2N$	0.4	5.4	5	596	582	–	25.2

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Experiment no.	Initial reagents	Molar ratio of reagents	Catalyst	Amount of catalyst, wt. %	Phosphorus content, %	n	Mol. wt. (avg.), calc.	Mol. wt. (avg.), found (by phosphorus)	Mol. wt. (avg.), determined cryoscopically	Telomer yield, %
3	$(C_2H_5O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 1	$(C_6H_5COO)_2$	0.01	6.1	4	510	504	–	47.3
4	$(C_2H_5O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 5	Same	0.01	3.9	7	768	752	665	44.4
5	$(C_2H_5O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 10	””	0.01	2.4	14	1371	1410	–	30.2
6	$(C_2H_5O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 5	””	0.001	5.9	4	510	515	–	14.3
7	$(C_2H_5O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 5	””	0.1	1.34	23	2144	2109	–	89.2
8	—O— C = O \ $(C_2H_5O)_3P^+$ $CHCH_3$ \ CH_2CH_2 = C— COOH | CH_3	1 : 4	””	0.01	4.6	6	682	680	–	51.2
9	$(C_7H_7O)_3P$ $CH_2=C-COOH$ | CH_3	1 : 5	””	0.2	3.4	8	896	930	855	34.5

If one proceeds from our previously published works ([1]), it may be assumed that telomerization proceeds according to the following scheme.

1. **Chain initiation:**

$$(R)_3P\colon + \overset{\delta+}{CH_2} = C(CH_3) - \overset{\delta-}{C}\underset{OH}{\overset{=O}{|}} \longrightarrow (RO)_3P^+ - CH_2 - C(CH_3) = C\underset{OH}{\overset{O^-}{|}}$$

2. Chain growth:

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$$(RO)_3\overset{+}{P}{-}CH_2CH(CH_3)C(=O)\,O^- + n\left[\overset{\delta+}{CH_2} = C(CH_3){-}C(=O)\,OH\right]^{\delta-} \longrightarrow$$

$$\longrightarrow (RO)_3\overset{+}{P}{-}\left[CH_2CH(CH_3)COO\right]_n CH_2CH(CH_3)C(=O)\,O^-$$

3. Chain termination:

$$(RO)_3\overset{+}{P}{-}\left[CH_2CH(CH_3)COO\right]_n CH_2CH(CH_3)C(=O)\,O^- \longrightarrow (RO)_2P(=O)\left[CH_2CH(CH_3)COO\right]_{n+1} R$$

It is possible that the telomer has another structure if chain growth proceeds by addition in the 1-2 position, as occurs in the polymerization of acrylates, and not in the 1-4 position, as in the interaction of α,β-unsaturated acids with phosphites. We did not study the structure of the telomer.

To verify the proposed reaction scheme, the following experiment was carried out. A mixture of equimolecular amounts of triethyl phosphite and methacrylic acid was left at room temperature until the phosphite in the mixture had completely disappeared. It was assumed that this produced an intermediate product of the Arbuzov rearrangement corresponding to the first stage of the reaction. Then a fourfold excess of methacrylic acid was added to the reaction mass, with benzoyl peroxide added as catalyst. Intensive formation of the telomer began immediately. The telomer was obtained in good yield and was analogous in its properties to that obtained in the experiment in which the components were mixed at once in the same ratio (see experiments Nos. 4 and 9).

The result obtained, first, confirms the formation of an intermediate product in the interaction of trialkyl phosphites with α,β-unsaturated acids and, second, confirms the probability of the proposed telomerization mechanism. The role of the catalyst, the mechanism of its influence on telomerization, remains unclear.

The experiments carried out showed that with an increase in the concentration of methacrylic acid in the initial mixture, the average molecular weight of the telomer increases. Thus, under otherwise identical conditions, at a molar ratio of phosphite to methacrylic acid of 1 : 1, the average molecular weight of the telomer is 504; at a ratio of 1 : 5, the molecular weight is 752, and at a ratio of 1 : 10 it becomes equal to 1410 (see Table 1, experiments Nos. 3, 4, 5).

As our experiments show, with an increase in the concentration of benzoyl peroxide the average molecular weight of the telomer increases (within the range of experiments carried out). In the telomerization of triethyl phosphite with methacrylic acid in a molar ratio of 1 : 5, the influence of the concentration of benzoyl peroxide on the average molecular weight of the telomer is expressed as follows:

Benzoyl peroxide concentration	Average molecular weight
0.1	2109
0.01%	752
0.001%	515

It is known that in the polymerization of acrylates an inverse dependence is usually observed. Evidently, in the case of telomerization, a decrease in the percentage of benzoyl peroxide leads to a weakening of the intensity of telomerization; chain termination occurs more rapidly, and the reaction is directed mainly toward the Arbuzov rearrangement.

The ability of the intermediate product of the addition of triethyl phosphite to methacrylic acid to enter into the telomerization reaction compels us

one to suppose that the P–O bond in the ring is ionic in character. If the dipolar ion initially formed in the course of the Arbuzov rearrangement were stabilized into a cyclic intermediate with a covalent P–O bond, then it could hardly serve as the beginning of a chain in telomerization; in any case, telomerization would proceed less intensively than in a mixture of the starting components. Our experiments showed that, in the interaction of methacrylic acid with the intermediate product, telomerization proceeds more intensively and is completed more rapidly than in a mixture of phosphite and acid. It should therefore be assumed that the intermediate product has the structure

–O–C=O

CHR′

CH_2

$(RO)_3P^+$

It should be noted that Connel and Coover [(2)] also assume the formation of an intermediate dipolar ion upon addition of phosphite to a lactone; subsequently the reaction proceeds in two directions: either an Arbuzov rearrangement occurs, leading to the formation of a phosphonocarboxylic ester, or, under certain conditions, chain growth occurs with formation of a telomer.

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Note: Figure translations are in progress. See original paper for figures.

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