Preparation of 1 : 1- and 2 : 1-Telomers of Allyl Acetate Using the Azeotropic Mixture with Carbon Tetrachloride[1]

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(Received June 15, 1967)

Recently, several relations were observed between the structure and the reactivity of carboxylic acid esters of allylic alcohols in their γ-ray induced telomerization with carbon tetrachloride.[2-4]

In this paper, the results will be reported on an investigation to confirm the effect of temperature, the elevation of which caused an increase in the yield of 1 : 1-telomer as had been observed in the preliminary experiment.[2] In consequence, an apparatus was devised to increase the yields of 1 : 1- and 2 : 1-telomers and to decrease simultaneously the yield of the 3 : 1-telomer of allyl acetate.

Experimental

Irradiation at an Elevated Temperature. By modifying the Soxhlet's extractor, an apparatus was constructed as shown in Fig. 1. A solvent of a suitable boiling point in the Flask 2 was heated to boiling by the Heating Mantle 1, and the temperature inside the Glass Mantle 4 could be maintained to be constant. A sample solution was introduced into the Ampoule 5, on the top of which is connected the U-Tube 6 containing a suitable amount of carbon tetrachloride to prevent the sample solvent from its escaping and, at the same time, to avoid the danger of an unexpected violent reaction. This apparatus was placed at a given distance from the γ-ray source 8. Methanol, bp 65°C, was used as the heating solvent, and the Flask is protected from γ-ray by the Pb-Block 9.

By this device, the strength of γ-ray falls only slightly, and the Ampoule can be placed, if necessary, at the least distance from the γ-ray source.

Irradiation of Circulated Sample. Again by modifying the Soxhlet's extractor, the other apparatus was constructed as shown in Fig. 2. A mixture of allyl acetate and carbon tetrachloride in the Flask 2 is heated to boiling by the Heating Mantle 1. The vapor of the azeotropic mixture goes through the Side

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[1] γ-Ray Induced Telomerization Reactions between Allylic Compounds and Carbon Tetrachloride. V; Part IV: M. Ōkubo, This Bulletin, **40**, 1672 (1967).

[2] M. Ōkubo, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 1191 (1966).

[3] M. Ōkubo, *ibid.*, **87**, 1196 (1966).

[4] M. Ōkubo, *ibid.*, **88**, 212 (1967).

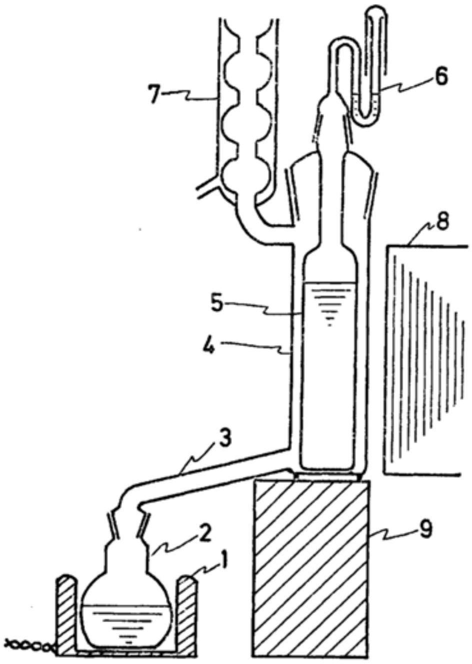


Fig. 1. The apparatus for irradiation at an elevated temperature.

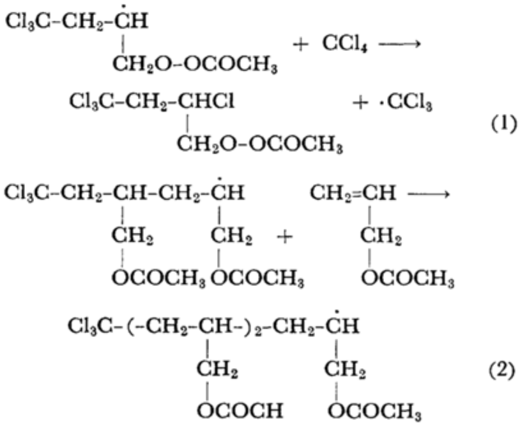
1 Heating mantle
2 Flask
3 Side tube
4 Glass mantle
5 Ampoule
6 U-tube
7 Condenser
8 γ-Ray source
9 Pb-block

Tube 3 and the Glass Mantle 4, and then to the Condenser 7. The liquefied azeotrope comes down through the Long Funnel 6 and fills up the Reaction Tube 5 and is irradiated. The produced telomers and the unreacted materials run over the top of 5, passing through 3, and comes back to 2. The telomers are stored in 2, and protected from γ-ray by the Pb-Block 9. The unreacted azeotrope is brought to 5 and is irradiated again. So, this method is named the circulation technique in this paper.

The concentration of allyl acetate in the Reaction Tube 5 changes gradually, and it was determined by the titration with a KBr-$KBrO_3$ aqueous solution before and after the irradiation. Then, the remaining solution in 5 was put back into 2, and the resulting total solution was titrated to determine the overall consumption of ally acetate.

Results and Discussion

Effect of Temperature. Using the apparatus of Fig. 1, a solution of the molar ratio of 1/5 (allyl acetate, 0.0667 mol, and CCl_4, 0.333 mol) was irradiated at the dose rate of 5.5×10^4 R/hr, at 65°C. Table 1 lists this result together with the results of the preceding experiments at 25°C.[1] From these data, it can be seen that the elevation of the temperature makes the reaction faster, and the lowering of the initial concentration of the allyl ester causes an increase in % consumption of C=C bond. Furthermore, both of these changes of the reaction condition favor the yields of 1 : 1- and 2 : 1-telomers. Since these changes of the reaction condition may accelerate the chain transfer of the propagating radical to CCl_4, the above result is ascribed to the acceleration of the step (1) and, at the same time, to the relative retardation of the step (2).



$$\mathrm{Cl_3C{-}CH_2{-}\dot{C}H(CH_2O{-}OCOCH_3) + CCl_4 \longrightarrow Cl_3C{-}CH_2{-}CHCl(CH_2O{-}OCOCH_3) + \cdot CCl_3} \qquad (1)$$

$$\mathrm{Cl_3C{-}CH_2{-}CH(CH_2OCOCH_3){-}CH_2{-}\dot{C}H(CH_2OCOCH_3) + CH_2{=}CH(CH_2OCOCH_3) \longrightarrow Cl_3C{-}({-}CH_2{-}CH(CH_2OCOCH){-})_2{-}CH_2{-}\dot{C}H(CH_2OCOCH_3)} \qquad (2)$$

From the above observation, the increase in the yields of 1 : 1- and 2 : 1-telomers is expected when the irradiation is carried out at higher temperatures and lower concentrations.*1 However, the apparatus of Fig. 1 does not seem to fit for this purpose, since, besides the necessity of an heating solvent, a voluminous reaction tube is required to contain the large volume of a diluted solution of CCl_4. To avoid these inconveniences, the circulation technique was adopted and the apparatus of Fig. 2 was devised.

Results of Circulation Technique. Allyl acetate, 80 g, and CCl_4, 246 g (molar ratio of 1/2), were introduced into the Flask 2 in Fig. 2. The voltage applied on the Heating Mantle was controlled so that the azeotropic mixture came down from the Condenser at a rate of *ca.* two drops per second. In this condition, the molar ratio of the solution inside the Reaction Tube was found to be 1/7.5. After irradiation for 170 hr, it came down to 1/19. The results are shown in Table 2.

The reaction temperature was nearly the boiling point of CCl_4, 76°C. The production ratios of 3 : 1-telomer in Table 2 resemble the ratio obtained in the experiment of 1/5 molar ratio at 65°C, but are slightly higher than that obtained in the experiment of 1/10 molar ratio at 25°C in Table 1. Therefore, the concentration lowering by half is considered to be more effective than the temperature elevation by 40 or 50 degrees for the increase in the

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*1 Both of 1 : 1- and 2 : 1-telomers can be isolated easily by distillation under the reduced pressure, and the 2 : 1-telomers of allyl carboxylates have been shown to give a trichloroethyl derivative of tetrahydrofurfuryl alcohol in good yields.[3]

Table 1. Effects of temperature and concentration in the telomerization of allyl acetate

Molar ratio[a]	Irradn. temp. °C	Irradn. hours hr	C=C consumption %	Telomer production ratios[b]		
				1 : 1	2 : 1	3 : 1
1/2	25	120	74	1	10.0	7.5
1/5	25	72	85	1	5.7	2.6
1/10	25	48	87	1	2.9	0.74
1/5	65	43—48	85—90	1	3.4	0.93

a) The molar ratio of allyl acetate to CCl$_4$.

b) Telomer production ratios were calculated by dividing the moles consumed for 2 : 1- and 3 : 1-telomers with those for 1 : 1-telomers, respectively.[2)]

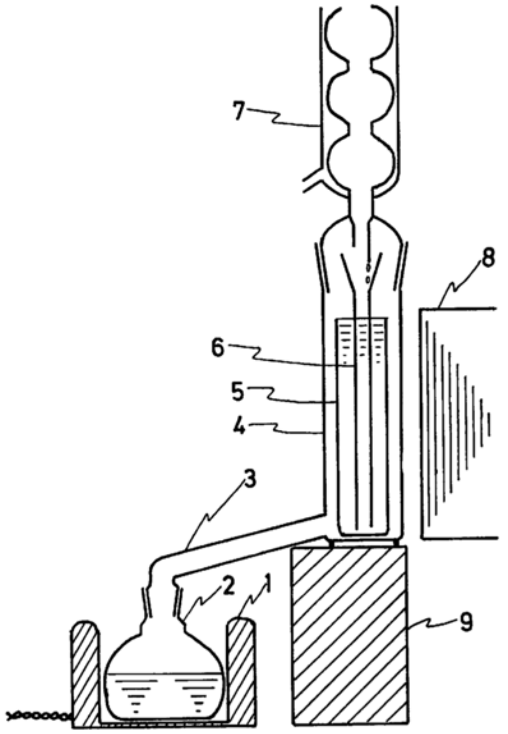

Fig. 2. The apparatus for irradiation of circulated sample

1 Heating mantle
2 Flask
3 Side tube
4 Glass mantle
5 Reaction tube
6 Long funnel
7 Condenser
8 γ-Ray source
9 Pb-block

Table 2. Irradiation of the circulated mixture allyl acetate, 80 g; CCl$_4$, 246 g

Irradn. hours hr	C=C consumption %	Telomer production ratios		
		1 : 1	2 : 1	3 : 1
120	40	1	3.3	1.3
170	82	1	3.9	1.3

yields of 1 : 1- and 2 : 1-telomers. But, it is remarkable that, notwithstanding the use of the mixture as high molar ratio as 1/2, the content of 1 : 1- and 2 : 1-telomers reached 80.3% by weight of the total products, and therefore, this technique was shown to be useful for preparing these telomers.

The advantages of this method are: that the concentrated solutions can be used and, therefore, a large quantity of the allyl ester can be treated at once; and that, as mentioned already, the heating of the reacting sample can be performed automatically without the heating solvent.

A disadvantage, the slightly higher yield of the 3 : 1-telomer than that obtained in the case of the molar ratio of 1/5 at 65°C, may be partly due to the fact that the concentrated solution of the allyl ester in the Flask 2 is irradiated continuously during the experiment with scattered γ-rays and, moreover, with weak γ-rays which have passed through the Pb-Block.

One of the well-known undesirable features of the telomerization reaction in general is that the telomer of a particular molecular weight cannot be prepared exclusively when a concentrated solution of taxogen is used. The present method suggests one of the directions to overcome this difficulty.

The author is indebted to Mr. Keichi Nunome of the present institute for operating the γ-ray irradiator. He also offers his gratitude to Professor Ryozo Goto of Kyoto University for his encouragement throughout the work.