[CONTRIBUTION FROM THE POLYMER LABORATORY, H. D. JUSTI & SON, INC.]

THE PREPARATION OF THE CYCLOPENTYL ESTERS OF ACRYLIC, METHACRYLIC, AND CROTONIC ACIDS

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A very large number of esters of methacrylic and acrylic acids have been reported in the literature. However, cyclopentyl methacrylate and cyclopentyl crotonate have not been reported. Cyclopentyl acrylate has been synthesized earlier by Ipatov (1) by the esterification of α,β-dibromopropionic acid with cyclopentanol followed by debromination. The isolated product was impure. The preparation of the cyclopentyl esters of acrylic, methacrylic, and crotonic acids was considered desirable in view of the influence of the planar character of the cyclopentyl group on the properties of the corresponding esters as well as the polymers and copolymers obtained from these esters of the unsaturated acids.

When a monomer undergoes polymerization, a reduction in volume takes place. Crawford (2) reported a shrinkage of 20.6 per cent during the polymerization of methyl methacrylate at 25°. Similar values have been reported by Nichols and Flowers (3). The per cent shrinkage decreases as the size of the alcohol substituent in the methacrylate ester increases (2, 3). Cyclohexyl methacrylate undergoes shrinkage during polymerization to the extent of 12.5 per cent (4) and has been investigated extensively from the standpoint of utility in optical applications. Although cast cyclohexyl methacrylate polymers were used during World War II for military optical instruments, *e.g.* with polystyrene in achromats, the brittleness and lower degree of surface hardness of cyclohexyl methacrylate polymers have limited their usefulness. Cyclopentyl methacrylate should undergo polymerization shrinkage only slightly greater than that reported for cyclohexyl methacrylate. The low theoretical shrinkage expected during the polymerization of cyclopentyl methacrylate and the influence of planar cyclopentyl groups in contrast to the non-planar nature of cyclohexyl groups, on the properties of the polymer may lead to desirable optical properties for precision casting in relatively thick sections of lenses, prisms, and other optical devices.

EXPERIMENTAL[1]

1. Preparation of cyclopentyl methacrylate. A. From glacial methacrylic acid. A mixture of 47.3 g. (0.55 mole) of glacial methacrylic acid, 43 g. (0.5 mole) of cyclopentanol, 2 g. of hydroquinone, 2 g. of *p*-toluenesulfonic acid, and 80 ml. of benzene was refluxed gently in a 500-ml. flask fitted with a trap and a reflux condenser. Refluxing was continued until no more benzene-water azeotrope distilled over. In all, 9.5 ml. of water was collected in the trap. After cooling, the reaction mixture was washed thoroughly with dilute sodium hydroxide solution and then with water. It was dried over calcium chloride. To the clear liquid was added 0.5 g. of di-β-naphthyl-*p*-phenylenediamine and benzene was removed under reduced pressure. The residual liquid was fractionally distilled through a 10-plate column

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[1] Microanalyses by Doctors G. Weiler and F. P. Strauss, Oxford, England.

packed with glass helices to give 67 g. of a pleasant-smelling colorless liquid, yield 72%, b.p. 84–85°/27 mm., n_D^{25} 1.4504, d_4^{25} 0.9640.

Anal. Calc'd for $C_9H_{14}O_2$: C, 70.09; H, 9.15.

Found: C, 70.03; H, 8.98.

B. From methyl methacrylate. A mixture of 86 g. (1 mole) of cyclopentanol, 250 g. (2.5 moles) of methyl methacrylate, 3 g. of *p*-toluenesulfonic acid and 3 g. of hydroquinone was placed in a 1-l. flask and connected to a one-meter column packed with glass helices. The mixture was gently refluxed and the azeotrope of methyl alcohol and methyl methacrylate, boiling at 64.2°, was removed periodically until no more azeotrope came over. After cooling, the reaction mixture was washed thoroughly with dilute sodium hydroxide solution and then with water. It was dried over calcium chloride. To the clear liquid was added 0.5 g. of di-β-naphthyl-*p*-phenylenediamine and methyl methacrylate was removed under reduced pressure. The residual liquid was fractionally distilled through a 10-plate column to give 100 g. of cyclopentyl methacrylate, yield 65%, b.p. 71–73°/23 mm; n_D^{25} 1.4486. Cyclopentyl methacrylate obtained in this manner contained traces of cyclopentanol.

C. From methacrylyl chloride. Methacrylyl chloride, b.p. 98–99°/772 mm., n_D^{25} 1.4405, used for this reaction was obtained by the action of thionyl chloride on glacial methacrylic acid. In a 500-ml. three-necked flask fitted with a thermometer, a stirrer, and a dropping-funnel was added 20 g. (0.5 mole) of sodium hydroxide and 100 ml. of water. The alkali solution was cooled to 5° by immersion of the flask in methanol to which Dry Ice was added occasionally. Cyclopentanol, 43 g. (0.5 mole) was added to the flask. Methacrylyl chloride, 52.25 g. (0.5 mole) then was added dropwise to the reaction mixture taking care that the temperature of the reaction mixture did not rise above 5°. During this addition, the contents of the flask were stirred well. When all the acid chloride had been added, stirring was continued for half an hour. The reaction mixture was diluted with 100 ml. of ether and the ethereal solution washed with dilute sodium hydroxide solution and finally with water. It was dried over fused calcium chloride. To the dry ether solution 0.5 g. of di-β-naphthyl-*p*-phenylenediamine was added. After the removal of ether, the residual liquid was fractionally distilled through a 10-plate column to give 50 g. of cyclopentyl methacrylate, yield 58%, b.p. 70–72°/22 mm., n_D^{25} 1.4472. Cyclopentyl methacrylate obtained by this method also contained traces of cyclopentanol.

2. Preparation of cyclopentyl acrylate. A. From glacial acrylic acid. A mixture of 79.2 g. (1.1 moles) of glacial acrylic acid, 86 g. (1 mole) of cyclopentanol, 2 g. of hydroquinone, 2 g. of *p*-toluenesulfonic acid, and 200 ml. of benzene was refluxed gently in a 1-l. flask fitted with a trap and a reflux condenser. In all 19.3 ml. of water was collected in the trap. The reaction mixture was treated in the manner described previously to give 114 g. of a sweet smelling colorless liquid, yield 81.4%, b.p. 75–76°/31 mm., n_D^{25} 1.4500, d_4^{25} 0.9801. Ipatov (1) prepared it by the esterification of α,β-dibromopropionic acid with cyclopentanol followed by debromination. He reported b.p. 166–170°/750 mm., n_D^{20} 1.4653, d_4^{20} 1.0230.

Anal. Calc'd for $C_8H_{12}O_2$: C, 68.54; H, 8.63.

Found: C, 68.35; H, 8.66.

B. From ethyl acrylate. A mixture of 86 g. (1 mole) of cyclopentanol, 250 g. (2.5 moles) of ethyl acrylate, 3 g. of dry sodium ethoxide, and 3 g. of hydroquinone was refluxed gently in a 1-l. flask and connected to a one-meter column packed with glass helices. The azeotrope of ethanol and ethyl acrylate, boiling at 77.5°, was removed periodically until no more azeotrope came over. The reaction mixture was treated in the manner described previously to give 85 g. of cyclopentyl acrylate, yield 60.7%, b.p. 71–73°/23 mm., n_D^{25} 1.4470. Cyclopentyl acrylate obtained by this method contained traces of cyclopentanol.

3. Preparation of cyclopentyl crotonate. A. From crotonic acid. A mixture of 47.5 g. (0.55 mole) of crotonic acid, 43 g. (0.5 mole) of cyclopentanol, 3 g. of hydroquinone, 3 g. of alkanesulfonic acid mixture, and 100 ml. of benzene was refluxed to remove 9.5 ml. of water in the trap. The reaction mixture was treated in the manner described previously to give 52 g. of a colorless liquid, yield 67.5%, b.p. 84–85°/15 mm., n_D^{25} 1.4562, d_4^{25} 0.9699.

Anal. Calc'd for $C_9H_{14}O_2$: C, 70.09; H, 9.15.

Found: C, 70.33; H, 9.22.

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SUMMARY

Cyclopentyl esters of acrylic, methacrylic, and crotonic acid have been synthesized. Direct esterification was found to be the preferred procedure for obtaining these esters of high purity.

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