[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE COLLEGE OF ST. THOMAS]

THE ACRYLATE ESTERS OF ETHYLENE GLYCOL

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In the course of a series of experiments involving polymerizable compounds it became desirable for us to investigate the glycol esters of acrylic acid. Perusal of the literature disclosed the surprising fact that very little information on such compounds is available. It is true that glycol acrylates (1–4) and derivatives of these esters (5–7) as well as acrylic esters of other polyhydroxy compounds (8–11) are mentioned, especially in the patent literature, but with the exception of Caldwell's work (1) no specific directions for the preparation of ethylene glycol mono- or di-acrylate could be found.

The method of Caldwell (1) for the preparation of ethylene glycol monoacrylate from acrylic acid and ethylene oxide was not well suited to the equipment of our laboratory. Furthermore, we were prompted to wonder why more straight-forward synthetic methods had never been used in these preparations. Accordingly attempts were made to prepare the glycol acrylates by several procedures. The first efforts were not highly successful because attempts at purification by fractionation led to polymerization. It was finally observed that if the distillations were conducted at low pressures (20 mm. or less) and if light were rigorously excluded from the apparatus, purifications could be accomplished readily. It was then found possible to prepare ethylene glycol monoacrylate by the following schemes:

a. $CH_2{=}CHCOCl + HOCH_2CH_2OH \rightarrow CH_2{=}CHCO{-}OCH_2CH_2OH + HCl$
b. $CH_2{=}CHCOONa + BrCH_2CH_2OH \rightarrow CH_2{=}CHCO{-}OCH_2CH_2OH + NaBr$
c. $CH_2{=}CHCOOH + HOCH_2CH_2OH \rightarrow CH_2{=}CHCO{-}OCH_2CH_2OH + H_2O$

Contrary to our original ideas on the subject, ethylene glycol diacrylate proved more difficult to prepare than did the monoacrylate. Successful preparation of this ester was accomplished, however, by a modification of reaction c above.

EXPERIMENTAL

I. PREPARATION OF ETHYLENE GLYCOL MONOACRYLATE

(*a*). *From acrylic acid chloride.* The acid chloride was prepared according to the procedure of Stemple, Cross, and Mariella (12). A 2000-ml., 3-necked flask was charged with chloroform (500 ml.), ethylene glycol (83 g.), anhydrous sodium sulfate (189 g.), sodium sulfite (154 g.), and cuprous chloride (1 g.). The copper salt was included as an inhibitor, the sulfite to react with the HCl produced and to provide a reducing atmosphere of SO_2, and the sulfate to take up the water released by the decomposition of the sulfite. To the mixture in the reaction flask a sample of 100 g. of acrylic acid chloride in the form of a 50% (volume) solution in chloroform was added dropwise over a period of 1 hour. The reaction mixture was vigorously stirred during the addition period and for 1 hour after the chloride had been introduced. The temperature of the reaction was maintained at 35–40° throughout by means of an ice-bath. After the stirring period the salts were filtered off, dissolved in water, and the solution extracted with 50-ml. portions of chloroform. The combined filtrate and ex-

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tracts were then dried, inhibited with pyrogallol, and evaporated at room temperature under reduced pressure to 115 g. of an oil. Vacuum-fractionation of this material in a copper fractionating column with total exclusion of light gave 80–86 g. (63–68%) of a water-white liquid, b.p. 61–65° (1 mm.); d^{23}_{4} 1.011; n_{D}^{23} 1.4460; M_D (calc'd) 28.0, M_D (obs.) 28.1.

(*b*). *From sodium acrylate.* Sodium acrylate was prepared by charging a 1000-ml. beaker with glacial acrylic acid (79 g., m.p. 13.4°), hydroquinone (5 g.), and 500 ml. of methanol. To this mixture was added a solution of sodium hydroxide (40 g.) in 50 ml. of water. The caustic solution was added dropwise over a period of about 30 minutes while the reaction mixture was stirred continuously. The solid sodium acrylate was filtered off and dried in a vacuum oven at 80° and 50 mm. for 36 hours. The yield was 74.5 g. (70%).

A 250-ml. 3-necked flask was charged with ethylene bromohydrin (50 g.), sodium acrylate (64 g., a 50% excess), pyrogallol (2 g.), cuprous chloride (1 g.), and 115 ml. of water. The flask and contents were heated on a steam-bath for 1½ hours with constant stirring. The reaction mixture was cooled and then extracted with several small portions of chloroform. Vacuum evaporation of the chloroform gave 32.5 g. of an oil which on fractional distillation gave 24.4 g. (53%) of ester, b.p. 75–77° (2 mm.); n_{D}^{23} 1.4460.

(*c*). *From acrylic acid.* An 8-oz. brown bottle, previously cleaned and dried, was charged with glacial acrylic acid (133 g., m.p. 13.4°), ethylene glycol (68 g., a 10% excess), pyrogallol (0.8 g.), and *p*-toluenesulfonic acid (0.1 g.). The bottle was then loosely capped, placed on the steam coil of a steam drying-cabinet and allowed to heat for 24 to 48 hours at 80°. The reaction vessel was then removed and the contents were cooled and transferred to a fractionating apparatus which was protected from all light. The mixture was separated into several fractions by distillation. The fraction boiling between 57 and 60° at 0.5 mm. (about 91 g.) was collected. This was then dissolved in 250 ml. of benzene, extracted twice with 20-ml. portions of water, and then dried over calcium chloride in the presence of copper powder. Refractionation gave 65.5 g. (30%) of the ester, b.p. 57–60° (0.5 mm.); n_{D}^{20} 1.4464. Purity by the bromate titration method of Albertson and MacGregor (13), 98.4%.

It is evident that method (*a*) gave the best results in our hands from the standpoint of yield. It should be noted that aside from the physical constants reported above, the only values given for ethylene glycol monoacrylate in the literature are those of Caldwell (1): b.p. 77–80° (4 mm.); n_{D}^{20} 1.4415.

II. PREPARATION OF ETHYLENE GLYCOL DIACRYLATE

A 500-ml. round bottom flask was charged with ethylene glycol (32 g.), glacial acrylic acid (133 g.), *p*-toluenesulfonic acid (2 g.), pyrogallol (1 g.), copper powder (1 g.), and 150 ml. of benzene. The flask, suitably covered to exclude all light, was attached to an azeotropic phase separator and the cyclic distillation of the benzene entraining liquid was begun. When about 90% of the theoretical amount of water of esterification had been removed heating was discontinued. In these experiments it was found advantageous to allow the reaction mixture to heat during one afternoon, then to sit overnight and to continue the azeotropic distillation the next day. Under these conditions more water was obtained than when continuous heating periods were employed even when these continuous periods were very long.

After removal of the water the residual benzene was taken off under a vacuum with gentle heat. The mixture was then subjected to vacuum fractionation as described under the monoacrylate. Yield of pure ester, 33.5 g. (40%). Purity by bromate titration (13), 97.7%. Constants: b.p. 53–57° (0.6 mm.), 56–58° (0.7 mm.), 62–65° (0.9 mm.); n_{D}^{20} 1.4545–1.4547; d^{26}_{20} 1.0935; M_D (calc'd) 41.5, (obs.) 41.9.

SUMMARY

Methods for the preparation of ethylene glycol mono- and di-acrylates are presented and the properties of these compounds are described. The effect of light on the polymerization characteristics of these esters is pointed out.

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