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VINYL ETHERS OF ALKYL HYDROXYACETATES AND THEIR POLYMERS

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A variety of products result from the reaction of acetylene with hydroxyl-containing organic compounds, depending upon the reactants and conditions. In the presence of alkaline catalysts, acetylene reacts with monohydric alcohols to form vinyl ethers (1), while with neutral mercuric salts or acidic catalysts, acetals are formed, presumably through the intermediate vinyl ether (2). In extending this reaction to hydroxycarboxylic acids, Nieuwland obtained cyclic acetals from lactic acid and higher homologs, while hydroxyacetic acid did not react (3).

It has been found that in the presence of acidic catalysts, alkyl hydroxyacetates react with acetylene, giving good yields of acetaldehyde di(carbalkoxymethyl) acetals. The acetals can be pyrolyzed to the corresponding vinyl ethers.

The acetaldehyde di(carbalkoxymethyl) acetals were prepared readily from methyl hydroxyacetate and isobutyl hydroxyacetate in 70–80% yields, by passing acetylene at atmospheric pressure over the ester containing mercuric oxide and a boron trifluoride/methanol complex (4) as catalyst. This method is superior in simplicity and performance to the use of mercuric phosphate catalyst and acetylene under pressure, which gives about 56% yields.

The vinyl ether was obtained conveniently by pyrolysis of the acetal at 300° over a silver-on-asbestos catalyst. In this way, carbomethoxymethyl vinyl ether was obtained in 70–82% yields, based on the acetal consumed (5). The conversions ranged from 45–70% per pass.

Carbomethoxymethyl vinyl ether polymerized rapidly and nearly quantitatively at −78° with boron trifluoride catalyst in methylene chloride solution, forming plastic, rubber-like polymers which resembled polyisobutylene and were soluble in the common halogenated and oxygenated organic solvents (6). The polymers underwent reactions typical of the carbomethoxy group. Hydrolysis gave water-soluble polycarboxylic acids. Reaction with ammonia gave low-melting, water-soluble amides, insolubilized by treatment with formaldehyde.

Carbomethoxymethyl vinyl ether copolymerized with isobutylene using boron trifluoride catalyst in methylene dichloride, yielding rubber-like products. Copolymers containing 5–9% of combined ether were soluble plastics somewhat more rubbery than the polyisobutylene control. Copolymerization of carbomethoxymethyl vinyl ether with propylene and with isobutyl vinyl ether gave viscous polymers containing 20–25% of combined carbomethoxymethyl vinyl ether.

EXPERIMENTAL

Acetaldehyde di(carbomethoxymethyl)acetal. A mixture of 15 g. of boron trifluoride/methanol (1:1 mole ratio) complex and 3 g. of mercuric oxide was introduced into a

1-liter, 3-necked flask, equipped with stirrer, thermometer, and an acetylene inlet tube. The mixture was heated until about one-half the mercuric oxide had dissolved. After cooling, 540 g. (6 moles) of methyl hydroxyacetate was added. The flask was cooled externally to maintain the temperature at 25–30°. Acetylene, purified by scrubbing with water, by passing over sodium hydroxide pellets, and by drying over calcium chloride and phosphorus pentoxide, was passed at atmospheric pressure over the surface of the vigorously stirred mixture. The acetylene was absorbed very rapidly (about 1 liter/min.), and the reaction was exothermic. The introduction of acetylene was stopped after 68 g. (2.6 moles) of acetylene had been absorbed.

The water cooling-bath was replaced with an ice-bath, and 20 g. of solid sodium carbonate was added to the well-stirred mixture. After 10 minutes, 50 cc. of saturated sodium carbonate solution was added. The dark-colored reaction mixture became light yellow in color. After 10 minutes, an equal volume (500 cc.) of ether was added. The aqueous phase was separated, and the ethereal solution was dried over anhydrous potassium carbonate. After filtration, the ether was evaporated, and the residue was distilled from a 1-liter modified Claisen flask equipped with a 15-inch column. A fraction of 308 g. (81% yield based on the acetylene absorbed) distilling at 115–120°/2–3 mm. was collected as acetaldehyde di(carbomethoxymethyl) acetal. A sample fractionated through a 15-inch Fenske column had the following properties: b.p. 114–116°/2 mm.; n_D^{25} 1.4308; d_4^{25} 1.1652.

Anal. Calc'd for $C_8H_{14}O_6$: C, 46.60; H, 6.85; M_R, 45.74.
Found: C, 46.72; H, 7.12; M_R, 45.72.

Acetaldehyde di(carbomethoxymethyl) acetal was also obtained by reacting methyl hydroxyacetate with acetylene under 250 lb./sq.in. pressure at 70° using 10% mercuric phosphate catalyst (Eimer and Amend). During reaction the temperature in the bomb increased to 95°. After acetylene adsorption had ceased (1.5 hours), the reaction product was removed, the mercuric phosphate was filtered from the liquid portion, and the filtrate was dried over anhydrous potassium carbonate. Distillation at reduced pressure gave a 56% yield of acetal which had physical properties in agreement with those listed previously.

Acetaldehyde di(carbisobutoxymethyl) acetal. Two grams of mercuric oxide was dissolved in 10 g. of boron trifluoride/methanol complex. To this was added 528 g. (4 moles) of isobutyl hydroxyacetate. The reaction was carried out in the same manner as in the case of the methyl ester and was stopped when the theoretical amount of acetylene (52 g. or 2 moles) had been absorbed. The reaction mixture was worked up in a similar manner. On fractionation a 400-g. sample of acetaldehyde di(carbisobutoxymethyl) acetal, distilling at 128–134°/2–3 mm., was collected. The yield was 70%. Refractionation through a 15-inch Fenske column gave a sample which had the following properties: b.p. 130–131°/2 mm.; n_D^{25} 1.4308; d_4^{25} 1.0204.

Anal. Calc'd for $C_{14}H_{26}O_6$: C, 57.86; H, 8.97; M_R, 73.32.
Found: C, 57.73; H, 9.10; M_R, 73.5.

Pyrolysis of acetaldehyde di(carbomethoxymethyl) acetal. Acetaldehyde di(carbomethoxymethyl) acetal (748 g.) was pyrolyzed over an asbestos-supported silver catalyst (7) at 260–300° at the rate of 1.45 g./min. Distillation of the condensate through a 24-inch Fenske column gave a fraction (482 g.) boiling at 71.5–73.5°/47–49 mm. along with 235 g. of recovered acetal. The 482 g. fraction, consisting of a mixture of methyl hydroxyacetate and the vinyl ether, was washed with an equal volume of water. Before separating the layers, a volume of diethyl ether equal to the volume of the aqueous layer was added. After extraction, the aqueous layer was separated and again extracted with a small amount of diethyl ether. The combined ethereal solution was repeatedly washed with equal volumes of water and was then dried over anhydrous potassium carbonate and sodium sulfate. After filtering off the solid material and evaporation of the diethyl ether, the residue was fractionated. A 222-g. fraction (yield 82% based on acetal consumed) distilling at 76.7°/49.5 mm. was obtained as the vinyl ether of methyl hydroxyacetate. Carbomethoxymethyl vinyl ether prepared in this way had the following properties: b.p. 76.7°/49.5 mm.; n_D^{25} 1.4232; d_4^{25} 1.0531.

Anal. Calc'd for $C_5H_8O_3$: C, 51.72; H, 6.90; sap. no., 116; M_R, 28.11.
Found: C, 51.96; H, 7.13; sap. no. 116.8; M_R, 28.06.

Polymerization of carbomethoxymethyl vinyl ether. A solution of 10 g. of vinyl ether in 70 g. of methylene chloride, contained in a reaction tube fitted with a sealed stirrer and gas inlet and outlet vents, was cooled in a bath at −78°. After the air had been displaced with dry nitrogen, 0.1 g. of anhydrous boron trifluoride gas was introduced over the well-stirred solution. Vigorous polymerization occurred almost immediately as evidenced by the evolution of heat. After 2 hours at −78°, the catalyst was destroyed by the addition of 2 g. of anhydrous ammonia. The reaction mixture was warmed to room temperature, and the colorless viscous solution was filtered to remove inorganic salts. After concentration of the polymer solution by distilling off about one-half the methylene chloride, the polymer was thrown out of solution by dilution with diethyl ether. The carbomethoxymethyl vinyl ether polymer (10 g.) so obtained was plastic and rubbery. It had an intrinsic viscosity of 4.9 (determined at 25° in chloroform at a concentration of 1 g./1000 cc. of solution) as calculated from the equation $N_i = \frac{(N_r - 1)}{C}$, in which N_i is intrinsic viscosity, N_r is relative viscosity, and C is moles of solute per liter of solution.

The carbomethoxy group in the polymer undergoes normal transformations. Hydrolysis occurred when a methanol/benzene solution of the polymer was refluxed with excess potassium hydroxide. The hydrolysis product was isolated by the addition of acetone to the concentrated, acidified aqueous solution. The polycarboxylic acid obtained corresponded to a conversion of 59% of the carbomethoxyl groups to carboxyl groups. The light brown acid was soluble in water, insoluble in common organic solvents, and became tacky when heated on a copper block at 150°.

Treatment of the polymer in benzene/ethanol solution with liquid ammonia gave a product corresponding to the conversion of 70% of the carbomethoxyl groups to amide groups. The dark colored product was soft and tacky. It was soluble in water and insoluble in acetone and benzene. It was insolubilized by reaction with aqueous formaldehyde in the presence of alkali followed by heating at 100°.

Copolymerization of carbomethoxymethyl vinyl ether and isobutylene. A solution of 1 g. of the carbomethoxymethyl vinyl ether, 35 g. of trichloroethylene, 11 g. of isobutylene, and 33 g. of propane was placed in the polymerization vessel and cooled to −78°. To the stirred solution was added 0.9 g. of anhydrous boron trifluoride in 0.3-g. portions. Very vigorous polymerization ensued, giving a viscous solution. After 3 hours, 5 g. of anhydrous ammonia was added to destroy the catalyst. The cooling bath was removed, and the solution was warmed to room temperature. Dilution of the solution with diethyl ether gave 12 g. of a colorless, plastic, rubbery copolymer of intrinsic viscosity 4.4 as determined on a 0.1% solution in tetralin. The copolymer carbon content of 83.46% and hydrogen content of 13.99% indicated a composition corresponding to a 94:6 weight ratio of isobutylene to carbomethoxymethyl vinyl ether.

Copolymerization of carbomethoxymethyl vinyl ether and propylene. A solution of 2.5 g. of vinyl ether, 25 g. of propylene, and 35 g. of methylene chloride, contained in a polymerization vessel under an atmosphere of dry nitrogen, was cooled to −78°. Above the well-stirred solution was introduced 3 g. of anhydrous boron trifluoride. After 72 hours at −78°, 5 g. of anhydrous ammonia was added to destroy the catalyst, and the mixture was warmed to room temperature. The solvent was removed from the filtered solution by evaporation at reduced pressure. The tan-colored, viscous polymer (13 g.) obtained had a saponification equivalent of 504, indicating a propylene/carbomethoxymethyl vinyl ether weight ratio of 79/21.

Copolymerization of carbomethoxymethyl vinyl ether and isobutyl vinyl ether. A solution of 1 g. of carbomethoxymethyl vinyl ether and 15 g. of isobutyl vinyl ether in 70 g. of methylene chloride, contained in a polymerization vessel under an atmosphere of dry nitrogen, was cooled to −78°. Polymerization was induced by adding 0.3 g. of anhydrous boron trifluoride. After an induction period of about 10 minutes, rapid polymerization occurred.

After 16 hours at −78°, the catalyst was destroyed by the addition of 2 g. of ammonia. The solution was warmed to room temperature, and the solvent was removed from the filtered solution by evaporation at reduced pressure. There was obtained 10 g. of a viscous copolymer having a saponification equivalent of 456, indicating an isobutyl vinyl ether/carbomethoxymethyl vinyl ether weight ratio of 75/25. The copolymer was soluble in ether, acetone, ethyl acetate, ethyl alcohol, and toluene but was insoluble in aliphatic hydrocarbons and water.

SUMMARY

A convenient method for the preparation of the acetals of methyl hydroxyacetate and isobutyl hydroxyacetate has been described. Pyrolysis of acetaldehyde di(carbomethoxymethyl) acetal gives the polymerizable vinyl ether of methyl hydroxyacetate.

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