[Contribution from the Rohm and Haas Company, Redstone Arsenal Research Division]

THE ACTION OF MINERAL ACID ON DIETHYL BIS(HYDROXYMETHYL)MALONATE[1]

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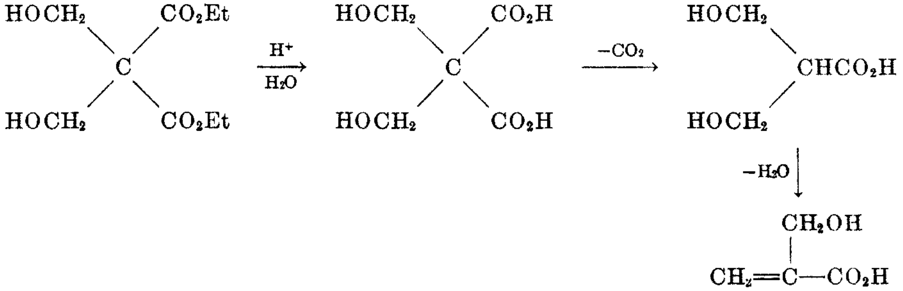
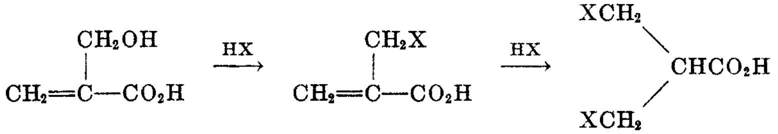
In a continuing study of methods for synthesizing α-(halomethyl)acrylic derivatives,[3] the action of mineral acid on diethyl bis(hydroxymethyl)malonate has been examined. From the results obtained, it seems reasonable to conclude that when diethyl bis(hydroxymethyl)malonate is heated with concentrated mineral acid, α-(hydroxymethyl)acrylic acid is obtained as the first isolable product. If the mineral acid is a halogen acid, displacement of the allylic hydroxyl by halide ion may occur, and this may be followed by addition of the halogen acid to the double bond. The extent to which these reactions take place depends on the nature of the halogen acid and on the experimental conditions. The action of mineral acid on diethyl bis(hydroxymethyl)malonate has been investigated twice previously in cursory fashion. Welch (1), who first showed that diethyl bis(hydroxymethyl)malonate could be prepared by condensation of formaldehyde and diethyl malonate at *p*H 8.5, found that the action of concentrated hydriodic acid gave α-(iodomethyl)acrylic acid in about 70% yield. Thus displacement of the allylic hydroxyl occurred, but there was no addition to the double bond. Work in this laboratory has shown that α-(iodomethyl)-acrylic acid decomposes very readily to liberate free iodine. This instability, typical of allyl iodides, severely limits its usefulness as a synthetic intermediate. Later Gault and Roesch (2) studied the action of both dilute and concentrated





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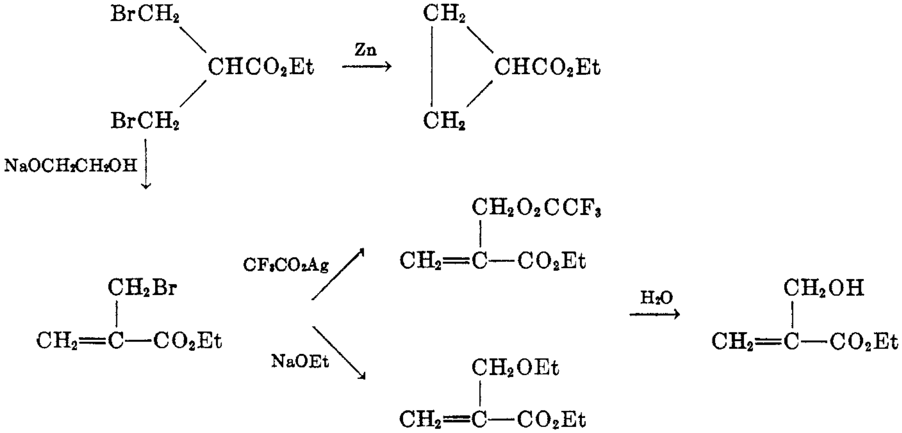
[3] For the previous paper in this series, see Ferris and Marks, *J. Org. Chem.*, **19**, 1971 (1954).

hydrochloric acid on diethyl bis(hydroxymethyl)malonate and obtained a mixture of products. The only component of the mixture which they were able to identify was a small amount of polymeric diethyl methylenemalonate.

By taking advantage of the tendency of hydrobromic acid to both displace the allylic hydroxyl and add to the double bond of the intermediate α-(hydroxymethyl)acrylic acid, a useful method for the synthesis of esters of β,β′-dibromoisobutyric acid and α-(bromomethyl)acrylic acid has been developed. When diethyl bis(hydroxymethyl)malonate was heated with a 15:1 excess of 48% hydrobromic acid, a 66% yield of crude β,β′-dibromoisobutyric acid could be crystallized from the reaction mixture. Recrystallization from hot water gave the pure acid, but hydrolysis was rapid and recovery low. The same tendency to rapid hydrolysis has been noted with β,β′-diiodoisobutyric acid (3). A better procedure was to esterify the crude acid directly with ethanol. Fractionation of the product from this reaction gave a small amount of ethyl α-(bromomethyl)-acrylate and a 57% yield of ethyl β,β′-dibromoisobutyrate. This previously unknown ester is a useful synthetic intermediate. It was cyclized by zinc in ethanol to give ethyl cyclopropanecarboxylate, a reaction which constitutes both a proof of structure for the dibromo ester and a new synthesis of a cyclopropanecarboxylic ester. Treatment of the dibromo ester with base readily effected elimination of hydrogen bromide to give ethyl α-(bromomethyl)acrylate. Neither sodium methoxide, sodium ethoxide, nor sodium hydroxide was a satisfactory agent for carrying out this reaction. The secondary displacement of the allylic bromine, which always accompanied the elimination reaction to a small extent, gave an ether or an alcohol which could not be separated from the bromo compound. This difficulty was avoided by the use of sodium ethylene glycolate in tetrahydrofuran. With this base, the by-product was much higher boiling than the product, and pure ethyl α-(bromomethyl)acrylate was obtained in 61% yield. Ethyl α-(bromomethyl)acrylate was converted to ethyl α-(hydroxymethyl)acrylate by a two step synthesis. The bromo ester reacted very rapidly with silver trifluoroacetate in ether to give a material which, on the basis of its infrared spectrum, was the expected ethyl α-(trifluoroacetoxymethyl)-



acrylate. The ease with which this metathetical reaction proceeded was a good indication that the bromine in ethyl α-(bromomethyl)acrylate was indeed allylic. The trifluoroacetate was converted without purification to ethyl α-(hydroxymethyl)acrylate by either ethanolysis or hydrolysis with saturated aqueous sodium bicarbonate. The yield was poor, but a pure sample of the hydroxy compound was obtained. The product from both methods of cleavage of the trifluoroacetate contained a small amount of lower-boiling by-product, easily removed by fractionation. It was suspected that this was ethyl α-(ethoxymethyl)-acrylate, and this was confirmed when the compound was prepared by the action of sodium ethoxide on ethyl α-(bromomethyl)acrylate (75% yield). The infrared spectra of the two materials were identical. It seems probable that the by-product was formed in the course of the preparation of ethyl α-(trifluoroacetoxymethyl)-acrylate, possibly by attack of the intermediate carbonium ion on the ether solvent.

Reactions of diethyl bis(hydroxymethyl)malonate with other acids, and with a smaller excess of hydrobromic acid, were not useful as preparative methods, either because yields were low or because complex mixtures of products, difficult to separate, were obtained. Such reactions were useful, however, in indicating that α-(hydroxymethyl)acrylic acid was probably an intermediate whenever diethyl bis(hydroxymethyl)malonate was acted on by concentrated mineral acid. Thus the action of a 7.5:1 excess of concentrated hydrobromic acid on diethyl bis(hydroxymethyl)malonate gave a very complex mixture of products. From esterification of the acid product with ethanol, low yields of ethyl α-(hydroxymethyl)acrylate, ethyl α-(bromomethyl)acrylate, ethyl β,β'-dibromoisobutyrate, and some unidentified higher-boiling material were obtained. Because of fractionation difficulties, none of these compounds was obtained in as pure a state as in the experiments described previously. All were positively identified, however, by comparison of physical constants and spectra with those of pure samples.

When diethyl bis(hydroxymethyl)malonate was heated with 50% sulfuric acid, and the reaction mixture was extracted continuously with ether, a viscous syrup was obtained. The infrared spectrum of this material contained the bands to be expected of α-(hydroxymethyl)acrylic acid, that is, hydroxyl, carbonyl, and olefin bands. Esterification with methanol indicated that most of the syrup was polymer, since only a 20% yield of distillable methyl α-(hydroxymethyl)-acrylate was obtained. This was, however, identical with the methyl α-(hydroxymethyl)acrylate prepared by an entirely different method by Jones, Shen, and Whiting (4). When diethyl bis(hydroxymethyl)malonate was heated with concentrated hydrochloric acid, a similar syrupy product was obtained. Esterification, this time with ethanol, again indicated that most of the product was polymer, but low yields of ethyl α-(chloromethyl)acrylate (2%) and ethyl α-(hydroxymethyl)acrylate (11%) were obtained. These esters were very difficult to separate by fractional distillation. Several distillations were necessary to obtain a good sample of ethyl α-(chloromethyl)acrylate, and the ethyl α-(hydroxymethyl)acrylate never gave a completely satisfactory analysis. The infrared spectrum of the latter was identical, however, with that of a pure sample of ethyl α-(hydroxymethyl)acrylate prepared as described previously. Thus in the case of hydrochloric acid there was little tendency for displacement of the allylic hydroxyl and none for addition to the double bond.

An attempt was made to prepare β,β′-dichloroisobutyric acid by reacting diethyl bis(hydroxymethyl)malonate with thionyl chloride and pyridine and hydrolyzing the product. Diethyl bis(chloromethyl)malonate was obtained in 38% yield, but it proved to be resistant to acid hydrolysis and to be degraded by base.

In the course of these experiments it was observed that esters of α-(hydroxymethyl)acrylic acid and α-(ethoxymethyl)acrylic acid frequently polymerized spontaneously during reaction or distillation at elevated temperature, and even on long standing in the cold. Esters of the α-(halomethyl)acrylic acids showed no tendency to polymerize.

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EXPERIMENTAL[4]

Action of concentrated hydrobromic acid on diethyl bis(hydroxymethyl)malonate (15:1 ratio). A mixture of 220 g. (1.0 mole) of diethyl bis(hydroxymethyl)malonate and 1675 ml. (14.8 moles) of 48% hydrobromic acid was heated until liquid began to distill from the mixture, and then was distilled vigorously for 2 hours. During this time 197.5 g. (90%) of ethyl bromide came over with the aqueous distillate. The material remaining was heated under reflux for 6 hours, and then the solution was chilled in ice for an hour. The crystals which separated were recovered on a sintered glass funnel, washed with a little ice-cold water, sucked as dry as possible, and further dried in a vacuum desiccator. Another 500 ml. of liquid was distilled from filtrate, and the crystallization process was repeated. The first crop amounted to 112.8 g. of brownish crystals, and the second crop, 50.7 g. of darker material. The combined yield of crude β,β′-dibromoisobutyric acid was 163.5 g. (66%). Two recrystallizations from boiling water gave about a 20% recovery of pure β,β′-dibromoisobutyric acid, white crystals melting at 100–102°. Its infrared spectrum showed an intense carbonyl band at 1697 cm.$^{-1}$. When the crystallization liquor was acidified with 5 *N* nitric acid and treated with aqueous silver nitrate, a heavy precipitate of silver bromide formed.

Anal. Calc'd for $C_4H_6Br_2O_2$: C, 19.56; H, 2.46; Br, 64.99.

Found: C, 19.95; H, 2.39; Br, 64.25.

Ethyl β,β′-dibromoisobutyrate. To 1000 ml. of benzene was added 242.5 g. (0.987 mole) of crude β,β′-dibromoisobutyric acid, 264 g. (6.0 moles) of ethanol, and 3 ml. of concentrated sulfuric acid. The resulting solution was heated under reflux for 20 hours, the condensate being passed through 100 g. of anhydrous magnesium sulfate before being returned to the reaction flask. Then 500 ml. of a mixture of benzene and ethanol was removed by distillation, 400 ml. of benzene was added, and another 500 ml. of distillate was removed. The residue was poured into 500 ml. of water, and the resulting mixture was neutralized with solid sodium bicarbonate and extracted with four 100-ml. portions of ether. After drying, the solvent was evaporated under reduced pressure, and the residue was fractionated through a 1.5 x 12 cm. packed column. There was obtained 4.7 g. of slightly impure ethyl α-(bromomethyl)acrylate, b.p. 59–65° (3.9 mm.), n_D^{20} 1.4720; 7.9 g. of an intermediate cut; and 154.1 g. (57%) of ethyl β,β′-dibromoisobutyrate, b.p. 84–86° (2.5 mm.), n_D^{20} 1.4970. The infrared spectrum of this material showed no hydroxyl and no olefin band, and an intense carbonyl band at 1733 cm.$^{-1}$.

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[4] All melting points are corrected, and all boiling points are uncorrected.

Anal. Calc'd for $C_6H_{10}Br_2O_2$: C, 26.30; H, 3.67; Br, 58.34.
Found: C, 26.61; H, 3.61; Br, 58.38.

Ethyl cyclopropanecarboxylate from ethyl β,β'-dibromoisobutyrate. A suspension of 28.0 g. (0.40 mole) of 90% zinc dust in 100 ml. of absolute ethanol was heated to gentle reflux, and 27.4 g. (0.10 mole) of ethyl β,β'-dibromoisobutyrate was added over 40 minutes. The mixture was heated under reflux for 48 hours, then was cooled and filtered. The filtrate was poured into 250 ml. of water, and an oil and a flocculent white solid separated. The addition of a little dilute nitric acid put the solid back into solution, and the oil was extracted into three 100-ml. portions of ether. The aqueous layer was treated with aqueous silver nitrate, and the silver bromide which precipitated was recovered on a filter and dried. It amounted to 31.9 g. (85%). After drying, the ether was evaporated from the extract under reduced pressure, and the 9.6 g. of oil remaining was distilled through a 1.5 x 12 cm. packed column. There was obtained 2.5 g. (22%) of ethyl cyclopropanecarboxylate, b.p. 50–51° (40 mm.), n_D^{20} 1.4196, d_4^{20} 0.958 [lit. (5) b.p. 132.4–132.6° (760 mm.), n_D^{20} 1.4190, d_4^{20} 0.961.] The infrared spectrum of this material showed no hydroxyl band and no olefin band, and an intense carbonyl band at 1725 cm.$^{-1}$.

Ethyl α-(bromomethyl)acrylate. To a solution of 22.8 g. (0.368 mole) of dry, distilled ethylene glycol in 75 ml. of dry tetrahydrofuran was added cautiously 5.3 g. (0.221 mole) of sodium hydride. After the first vigorous reaction had subsided, the mixture was heated under reflux for 24 hours. The syrupy suspension of sodium ethylene glycolate resulting was cooled to room temperature, and then added slowly to a solution of 50.5 g. (0.184 mole) of ethyl β,β'-dibromoisobutyrate in 75 ml. of tetrahydrofuran. The temperature was kept below 45° by controlling the rate of addition. When addition was complete, the mixture was stirred for 90 minutes and then poured into 800 ml. of water. The organic layer which separated was extracted into three 150-ml. portions of methylene chloride. The aqueous layer was acidified with 5 *N* nitric acid and treated with aqueous silver nitrate. After drying, the silver bromide precipitate weighed 30.0 g. (87%). The methylene chloride was evaporated under reduced pressure, and the residue was fractionated through a 1.5 x 12 cm. packed column. There was obtained 16.3 g. (61%, based on starting material not recovered) of ethyl α-(bromomethyl)acrylate, b.p. 44–45° (1.7 mm.), n_D^{20} 1.4787; 1.4 g. of an intermediate cut; and 12.3 g. of recovered ethyl β,β'-dibromoisobutyrate, b.p. 57–60° (0.3 mm.), n_D^{20} 1.4930. The infrared spectrum of ethyl α-(bromomethyl)acrylate showed no hydroxyl band, a carbonyl band at 1720 cm.$^{-1}$, and an olefin band at 1632 cm.$^{-1}$.

Anal. Calc'd for $C_6H_9BrO_2$: C, 37.33; H, 4.70; Br, 41.40.
Found: C, 37.28; H, 4.66; Br, 41.05.

Ethyl α-(hydroxymethyl)acrylate. To a solution of 26.5 g. (0.12 mole) of silver trifluoroacetate in 100 ml. of anhydrous ether was added over 15 minutes 19.3 g. (0.10 mole) of ethyl α-(bromomethyl)acrylate. Silver bromide began to precipitate almost immediately. After the mixture had stood for 16 hours the silver bromide was filtered out, dried, and weighed. It amounted to 17.8 g. (95%). Then 5.7 g. (0.04 mole) of methyl iodide was added, and the mixture was allowed to stand for 3 hours. The silver iodide precipitate was filtered out, and the solvent was evaporated under reduced pressure. There was recovered 20.4 g. (90%) of crude ethyl α-(trifluoroacetoxymethyl)acrylate. The infrared spectrum of this material showed no hydroxyl band, a trifluoroacetoxy carbonyl band at 1789 cm.$^{-1}$, a normal carbonyl band at 1720 cm.$^{-1}$, and an olefin band at 1639 cm.$^{-1}$. The crude product was added slowly to a suspension of 12.6 g. (0.15 mole) of sodium bicarbonate in 100 ml. of water. The reaction flask was attached to a wet test meter to permit measurement of the amount of gas evolved. At the end of 5 hours gas evolution had ceased, and a total of 1480 ml. (STP) (66%) had been evolved. The aqueous mixture was extracted with four 50-ml. portions of ether. After drying, the solvent was evaporated under reduced pressure, and the residue was fractionated through a 1.5 x 12 cm. packed column. There was obtained 1.3 g. of slightly impure ethyl α-(ethoxymethyl)acrylate, b.p. 29–30° (0.8 mm.), n_D^{20} 1.4290; 0.4 g. of an intermediate cut; and 2.7 g. (21%) of ethyl α-(hydroxymethyl)acrylate, b.p. 46.5–47.5° (0.8 mm.), n_D^{20} 1.4482. Analysis of the ethyl α-(ethoxymethyl)acrylate indicated that it was not quite pure, but its infrared spectrum was identical to that of the pure ethyl α-(ethoxymethyl)acrylate described below. The infrared spectrum of ethyl α-(hydroxymethyl)acrylate showed a hydroxyl band at 3360 cm.$^{-1}$, a carbonyl band at 1708 cm.$^{-1}$, and an olefin band at 1636 cm.$^{-1}$.

Anal. Calc'd for $C_6H_{10}O_3$: C, 55.37; H, 7.75; Sap. equiv., 130.1.

Found: C, 55.12; H, 7.56; Sap. equiv., 131.7.

Ethyl α-(ethoxymethyl)acrylate. In 75 ml. of anhydrous ethanol was dissolved cautiously 2.8 g. (0.12 mole) of sodium hydride. This solution was added over 2 hours to a solution of 19.3 g. (0.10 mole) of ethyl α-(bromomethyl)acrylate in 25 ml. of anhydrous ethanol. There was little or no temperature rise, but a white precipitate gradually appeared. The mixture was allowed to stand for 2 hours, at the end of which time it was neutral to test paper. It was poured into 400 ml. of water, and the organic layer was extracted into three 150-ml. portions of methylene chloride. The aqueous layer was acidified with 5 *N* nitric acid and treated with aqueous silver nitrate. The silver bromide recovered amounted to 17.9 g. (95%). After drying, the solvent was evaporated from the extract under reduced pressure, and the residue was distilled through a 1.5 x 12 cm. packed column. There was obtained 11.8 g. (75%) of slightly impure ethyl α-(ethoxymethyl)acrylate, b.p. 41.5–42° (1.7 mm.), n_D^{20} 1.4295. A 9.0-g. sample of this material was redistilled to give 6.2 g. of pure ethyl α-(ethoxymethyl)acrylate, b.p. 59–59.5° (3.0 mm.), n_D^{20} 1.4289. The infrared spectrum of this material showed no hydroxyl band, a carbonyl band at 1716 cm.$^{-1}$, and an olefin band at 1636 cm.$^{-1}$.

Anal. Calc'd for $C_8H_{14}O_3$: C, 60.74; H, 8.92; Sap. equiv., 158.2.

Found: C, 60.31; H, 9.11; Sap. equiv., 157.7.

Action of concentrated hydrobromic acid on diethyl bis(hydroxymethyl)malonate (7.5:1 ratio). A mixture of 220 g. (1.0 mole) of diethyl bis(hydroxymethyl)malonate and 827 ml. (7.4 moles) of 48% hydrobromic acid was heated until liquid began to distill from it, and then was distilled vigorously for 2 hours. From the aqueous distillate there was recovered 107.2 g. (49%) of ethyl bromide. The reaction mixture was chilled in ice for an hour, and the crystals which precipitated were recovered on a filter and dried. The crystalline material amounted to 72.2 g. The filtrate was neutralized with sodium carbonate, made just strongly acid with 48% hydrobromic acid, and extracted continuously with 1500 ml. of ether for 16 hours. After drying, the ether was evaporated under reduced pressure to leave 63.6 g. of viscous liquid.

The two portions of crude acid were esterified separately. The solid acid was heated under reflux for 16 hours with a mixture of 92.2 g. (2.0 moles) of ethanol, 500 ml. of benzene, and 2 ml. of concentrated sulfuric acid. The condensate was passed through 60 g. of anhydrous magnesium sulfate. The reaction mixture was worked up as described for previous esterifications, and the mixture of esters produced was fractionated through the 1.5 x 12 cm. packed column. There was obtained 20.3 g. (11%) of ethyl α-(bromomethyl)acrylate, b.p. 60–62° (4.5 mm.), n_D^{20} 1.4701; 4.8 g. of an intermediate cut; and 23.7 g. (9%) of ethyl β,β′-dibromoisobutyrate, b.p. 68–70° (0.8 mm.), n_D^{20} 1.4954. The liquid acid was esterified in the same way with a mixture of 138.3 g. (3.0 moles) of ethanol, 500 ml. of benzene, and 2 ml. of concentrated sulfuric acid. Fractionation of the product gave 14.9 g. of a mixture of ethyl α-(bromomethyl)acrylate and α-(hydroxymethyl)acrylate, b.p. 49–60° (1.6 mm.), n_D^{20} 1.4590; 6.9 g. (5%) of ethyl α-(hydroxymethyl)acrylate, b.p. 60–62° (1.7 mm.), n_D^{20} 1.4450; 12.1 g. of higher-boiling material, b.p. 63–85° (0.5 mm.); and 14.3 g. of polymeric residue.

Action of 50% sulfuric acid on diethyl bis(hydroxymethyl)malonate. To a solution of 408 g. (4.0 moles) of concentrated sulfuric acid in 376 g. of water was added 220 g. (1.0 mole) of diethyl bis(hydroxymethyl)malonate. The mixture was heated to vigorous boiling and was boiled for 45 minutes until the organic layer had disappeared. The solution was cooled to room temperature and extracted continuously with 1500 ml. of ether containing 1.0 g. of hydroquinone for 24 hours. After drying the ether was removed under reduced pressure to leave 105.6 g. (theoretical 102.0 g.) of viscous syrup. The infrared spectrum of this material showed a broad hydroxyl absorption band, as well as bands ascribed to the carbonyl (1711 cm.$^{-1}$) and olefin (1630 cm.$^{-1}$) functions.

In 1000 ml. of methanol were dissolved 1.0 g. of hydroquinone, 3 ml. of concentrated sulfuric acid, and 80.1 g. (0.786 mole) of the crude α-(hydroxymethyl)acrylic acid described above. The mixture was heated under reflux for 16 hours, then cooled and neutralized with a solution of sodium methoxide in methanol. Removal of the methanol under reduced pressure and filtration to remove sodium sulfate left 66.1 g. (72%) of crude oil. Distillation under reduced pressure gave 18.4 g. (20%) of liquid boiling at 45–49° (0.4 mm.). A large amount of polymeric residue was left. Products from this and a smaller scale preparation were combined and fractionated through a 1.5 x 12 cm. packed column. From 23.2 g. of once-distilled material there was obtained 15.8 g. (14%) of methyl α-(hydroxymethyl)acrylate, b.p. 63–65° (2.3 mm.), n_D^{20} 1.4518, n_D^{16} 1.4532, [lit. (4) b.p. 81° (9 mm.), n_D^{16} 1.4548]. The infrared spectrum of methyl α-(hydroxymethyl)acrylate showed a hydroxyl band at 3360 cm.$^{-1}$, a carbonyl band at 1711 cm.$^{-1}$, and an olefin band at 1632 cm.$^{-1}$.

Action of concentrated hydrochloric acid on diethyl bis(hydroxymethyl)malonate. To 856 ml. (10.0 moles) of concentrated hydrochloric acid was added 440 g. (2.0 moles) of diethyl bis(hydroxymethyl)malonate. The mixture was heated under reflux for 2 hours and then cooled to room temperature. It was neutralized with solid sodium carbonate decahydrate, and then enough concentrated hydrochloric acid was added to make it just strongly acid. The resulting solution was extracted continuously with 3000 ml. of ether for 17 hours. After drying, the ether was removed under reduced pressure to leave 185.8 g. of viscous syrup. The infrared spectrum of this material showed a hydroxyl band at 3250 cm.$^{-1}$, a carbonyl band at 1717 cm.$^{-1}$, and an olefin band at 1633 cm.$^{-1}$.

The crude acid described above was mixed with 420 g. (9.1 moles) of ethanol, 1000 ml. of benzene, and 3 ml. of concentrated sulfuric acid. The resulting solution was heated under reflux for 5 hours, the condensate being passed through 120 g. of anhydrous magnesium sulfate before being returned to the reaction flask. Then 900 ml. of a mixture of benzene and ethanol was removed by distillation, 500 ml. of benzene was added, and another 600 ml. of distillate was removed. The residue was poured into 500 ml. of water, and the resulting mixture was neutralized with solid sodium bicarbonate. The mixture was extracted with four 150-ml. portions of ether. The solvent was evaporated under reduced pressure, and the residue was fractionated under reduced pressure through a 1.5 x 12 cm. packed column. There was obtained 7.5 g. (2%) of impure ethyl α-(chloromethyl)acrylate, b.p. 56–61° (7.0 mm.), n_D^{20} 1.4451; 5.0 g. of an intermediate cut; and 28.3 g. (11%) of impure ethyl α-(hydroxymethyl)acrylate, b.p. 65–70° (1.7 mm.), n_D^{20} 1.4450. Redistillation of the ethyl α-(hydroxymethyl)acrylate gave 11.1 g. of purer material, b.p. 66–68° (2.7 mm.), n_D^{20} 1.4451. Analysis indicated that this material was still slightly impure, but its infrared spectrum was identical to that of the pure ethyl α-(hydroxymethyl)acrylate described above.

Two more distillations of the ethyl α-(chloromethyl)acrylate gave 1.4 g. of fairly pure material, b.p. 45° (3.4 mm.), n_D^{20} 1.4480. Its infrared spectrum showed no hydroxyl band, a carbonyl band at 1720 cm.$^{-1}$, and an olefin band at 1634 cm.$^{-1}$.

Anal. Calc'd for $C_6H_9ClO_2$: C, 48.50; H, 6.10; Cl, 23.86.
Found: C, 48.77; H, 6.15; Cl, 22.98.

Diethyl bis(chloromethyl)malonate. To a solution of 44.0 g. (0.20 mole) of diethyl bis(hydroxymethyl)malonate in 32.4 g. (0.41 mole) of pyridine was added slowly 95.2 g. (0.80 mole) of thionyl chloride. The temperature was kept below 55° by controlling the rate of addition. When all the thionyl chloride had been added, the solution was heated under reflux for an hour, and then the excess thionyl chloride was removed by distillation. The residue was poured into 500 ml. of water, and the organic layer was extracted into three 100-ml. portions of ether. The ether solution was washed with two 50-ml. portions of 2.5 N hydrochloric acid, two 50-ml. portions of 5% aqueous sodium carbonate, and 50 ml. of water. After drying, the ether was evaporated under reduced pressure to leave 35.6 g. of oil. This was distilled under reduced pressure to give 19.6 g. (38%) of diethyl bis(chloromethyl)malonate, b.p. 74–76° (0.1 mm.), n_D^{20} 1.4477, d_4^{20} 1.203. The infrared spectrum of this material showed no hydroxyl band and a strong carbonyl band at 1743 cm.$^{-1}$.

Anal. Calc'd for $C_9H_{14}Cl_2O_4$: C, 42.04; H, 5.48; Cl, 27.57.
Found: C, 42.52; H, 5.11; Cl, 27.34.

SUMMARY

Experiments are reported which indicate that the action of mineral acid on diethyl bis(hydroxymethyl)malonate yields α-(hydroxymethyl)acrylic acid as the first isolable product. If the acid is a halogen acid, displacement of the allylic hydroxyl by halide ion may occur, and this may be followed by addition of the halogen acid to the double bond. When a large excess of hydrobromic acid was used, both these reactions took place to give β,β′-dibromoisobutyric acid in good yield. Elimination of hydrogen bromide from the ethyl ester of this acid constituted a useful synthesis of ethyl α-(bromomethyl)acrylate.

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