

of the lower funnel and pushed down through the cork almost to the bottom of the lower globe. If the lower globe is covered with black paper, or painted with black paint, there will be no deposition of carbenes on the sides of the lower globe, and the vapors will drain the sides clean.

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THE ACTION OF ALCOHOLS, ACIDS AND AMINES ON METHYL OXOMALONATE.

BY RICHARD SYDNEY CURTISS AND F. GRACE C. SPENCER.

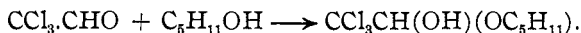
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Anschütz and Parlato¹ produced ethyl oxomalonate, $O:C(CO_2C_2H_5)_2$, by the dissociation of ethyl acetylbromtartronate, when distilled under reduced pressure. They were not able to separate the two liquids and obtain the pure keto ester. They also prepared it by the distillation of ethyl dihydroxymalonate under reduced pressure, passing the vapors through a tube containing phosphorus pentoxide. This did not give a pure product inasmuch as the water formed in the process of distillation reassociates with the ethyl oxomalonate to form ethyl dihydroxymalonate.

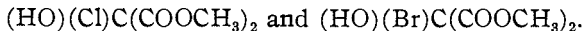
Owing to the great reactivity of the carbonyl group of the ester, a strong dehydrating agent is required to remove the water as soon as it is dissociated. We tried at first, mixing the methyl dihydroxymalonate with zinc chloride, and with barium oxide, and distilling the mixtures, but with unsatisfactory results. We succeeded only when phosphorus pentoxide was chosen. This gave a yield of 92 per cent. of pure anhydrous methyl oxomalonate.

We have studied the reactions of ethyl, methyl and propyl alcohols on methyl oxomalonate. Ethyl alcohol gives a crystalline body, methyl ethoxytartronate, $(C_2H_5O)(HO)C(CO_2CH_3)_2$. The reaction products of methyl and propyl alcohols with methyl oxomalonate were thick glycerol-like oils, changed by moist air into alcohols and methyl dihydroxymalonate.

In a somewhat similar manner, Kuntz² has succeeded in adding several members of the alcohol series on the carbonyl group of chloral,



We have succeeded in adding hydrochloric and hydrobromic acids to methyl oxomalonate forming compounds of the structure



This class of compounds has few representatives. Vorländer³ has

¹ *Ber.*, 25, 3616.

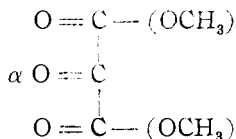
² *Chem. Centr.*, 1, 79, 1560 (1908).

³ *Ann.*, 341, 1 (1905).

recently obtained in the crystalline form, the monohydrobromide of benzaldehyde as well as the monohydrochlorides and monohydrobromides of anisaldehyde, piperonal, chloral and bromal.

The best proof of the structure assigned to these addition products, that they are not oxonium compounds, is based on analogy with all other like reactions of methyl oxomalonate where tartronic ester derivatives result, and upon the fact that in their formation, the green color of the ketone ester is entirely discharged, forming colorless products. This is true of all the addition products of the ketone ester thus far studied.

According to the theory of Baly, Stewart and Desch¹ recently proposed to explain the cause of color in all organic compounds, this phenomenon depends upon the rapid oscillatory vibrations of adjacent supplementary valencies and is of such a character as to produce ether vibrations of the order of those which give us the spectrum colors. In this ketone ester this phenomenon depends upon the three adjacent carbonyl groups which together act as a chromophore:



This is shown by the fact that when the central carbonyl group has its valencies saturated, as it does in all these addition reactions, the color at once vanishes, and returns again as soon as the added particles are dissociated, by heating or otherwise, regenerating a double bond on the carbon.

For this reason the discharge of color on the addition of hydrochloric or hydrobromic acids on the ketone ester shows that the reaction has eliminated this chromophore group and that the compound is therefore an additive one on the carbon-oxygen double bond. That the acid adds on a carbonyl of the carboxyl group, is not at all likely for reasons given above.

The action of aniline was also tested on this keto ester and an addition product of the structure $(\text{C}_6\text{H}_5\text{NH})(\text{HO})\text{C}(\text{COOCH}_3)_2$ was formed.

Experimental.

Preparation of Pure Anhydrous Methyl Oxomalonate.—Twenty-five grams (one mol.) of pure methyl dihydroxymalonate were thoroughly mixed in a distilling bulb with 22 grams of phosphorus pentoxide (3 mol.) and allowed to stand air-tight for two hours. At the end of that time it was a faint yellow, porous mass, from which a quantity of yellow liquid had separated out. The best yield is obtained when the mixture stands twenty-four hours. The methyl oxomalonate was then obtained by fractional distillation under reduced pressure. Pure methyl oxomalonate distils at a constant temperature of 106° (uncorr.) and 40 mm. pressure.

¹ *J. Chem. Soc.*, 85, 1029; 87, 766. *Proc. Chem. Soc.*, 22, 33.

Methyl oxomalonate, $O:C(COOCH_3)_2$, is a yellow-green oil having a specific gravity of 1.2464 at 27°. It possesses a remarkable reactivity on the carbonyl group, which accounts for its rapid change back into the hydrated form when exposed to the air. We have found that it reacts with great vigor with ammonia and its derivatives, haloid acids, acid amides and various other reagents which contain an easily dissociated hydrogen atom.

Action of Alcohol on Methyl Oxomalonate.

Ethyl Alcohol on Methyl Oxomalonate.—1.4 cc. of absolute alcohol were added from a pipette to 4.2 cc. (mol. quantities) of the ketone ester. The temperature rose 70°. It was then chilled and the green color of the ketone ester slowly disappeared, leaving a thick, faintly tinted sirup, which became colorless with the addition of four or five drops of alcohol. In all these reactions the gradual loss of color serves as a means of following the rapidity of addition on the double bond of the central carbonyl group of the keto ester.

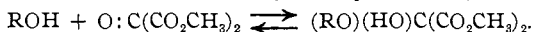
When the alcohol addition product is cooled it crystallizes in balls of colorless, radiating needles. These were purified by recrystallization from absolute alcohol, filtered on a pump, washed with cold alcohol, and dried in the air.

Calculated for $(C_2H_5O)(HO)C(CO_2CH_3)_2$: C, 43.75; H, 6.25.

Found: C, 43.65, 43.52; H, 6.35, 6.23.

Methyl ethoxytartronate melts at 58°, at which temperature it partially dissociates into alcohol and ester, forming a green oil. It is easily soluble in benzene, ether, acetone, chloroform, absolute alcohol, amyl alcohol, methyl alcohol, and water; fairly soluble in carbon tetrachloride; and but slightly soluble in cold ligroin.

Methyl Alcohol on Methyl Oxomalonate.—1.6 grams (1 mol.) of methyl alcohol were added to 4.8 cc. (1 mol.) of methyl oxomalonate. The temperature rose 65°. When the mixture cooled it was a thick, slightly green oil, which became colorless on the addition of 10 per cent. excess of alcohol. The rise in temperature, the loss of color, and the viscosity of the liquid indicated an additive reaction. There was no indication of crystallization. When the substance was allowed to stand in the air a crystalline compound having a melting point of 78°, and found to be methyl dihydroxymalonate, was formed. This shows the addition compound to be unstable and that it is readily hydrolyzed by the moisture of the air. When the substance is boiled a green sirup results, showing that dissociation occurs regenerating the keto ester and alcohol; and on cooling the color partially discharges, indicating a reassociation of these bodies. The same phenomenon is observed with methyl ethoxytartronate,



Propyl Alcohol on Methyl Oxomalonate.—1.4 grams (1 mol.) of propyl alcohol were added to 2.2 cc. (1 mol.) of methyl oxomalonate. The temperature rose rapidly and the color entirely disappeared. No crystalline product was separated and, like the product with methyl alcohol, the substance was hydrolyzed into alcohol and methyl dihydroxymalonate when exposed to moist air.

The methyl and propyl alcohol addition products are both colorless, glycerol-like sirups and inasmuch as they dissociate on heating and, hence, cannot be purified by distillation and cannot be crystallized, we have not obtained them in the pure form for analysis.

Action of Haloid Acids on Methyl Oxomalonate.

Action of Hydrochloric Acid Gas on Methyl Oxomalonate.—A weighed flask containing 1.208 grams of ketone ester was chilled to -15° for a few minutes. Hydrochloric acid gas, dried by running through concentrated sulphuric acid, was passed into the flask containing the pure ketone. The flask was provided with a small exit

tube closed with a calcium chloride bulb. The reaction was marked, heat was evolved and in about five minutes the thin, green oil became a nearly colorless glycerol-like sirup. The substance was then placed in a freezing mixture and it began to crystallize in dry, colorless, radiating balls. The reaction was perfectly quantitative, exactly one molecule of hydrochloric acid was added, as shown by the increased weight of the flask and by the analysis. After all corrections for gaseous hydrochloric acid in the flask the analytical data obtained were as follows:

By addition of hydrochloric acid gas: Calculated for $(\text{HO})(\text{Cl})\text{C}(\text{CO}_2\text{CH}_3)_2$: Cl, 19.43. Found: Cl, 19.25. A silver chloride determination gave Cl, 19.58.

Methyl chlortartronate has a melting point of about 42° , is extremely unstable, and very reactive. It passes over quickly to the crystalline methyl dihydroxymalonate in moist air. It has, however, been kept well sealed for a year with little apparent

change. It dissociates $\left(\begin{array}{c} \text{H} \text{ O} \\ | \quad | \\ \text{C} \end{array} \right) \text{C}(\text{CO}_2\text{CH}_3)_2$, in certain dry organic solvents, as ligroin

and ether, as is shown by the green color of the solution due to the presence of the keto ester, while in other solvents it is not dissociated. It is easily soluble in benzene and acetic ester, and fairly soluble in ligroin.

Action of Ethyl Alcohol on Methyl Chlortartronate.—In order to prove the structure of methyl chlortartronate 0.42 cc. of ethyl alcohol was added to 1.5046 grams (mol. quantities) of the pure product in a closed flask. Heat was generated and hydrochloric acid gas was formed under pressure. The product is a liquid from which a new substance quickly crystallizes out in bunches of flat, crystal plates. After the hydrochloric acid gas has been driven from the bottle by dry carbon dioxide, the product was pulverized and washed in sodium-dry ether. After being dried in a sulphuric acid desiccator over night, it had a melting point of 58° . It was recrystallized from absolute alcohol, dried, and analyzed.

Calculated for $(\text{C}_2\text{H}_5\text{O})(\text{HO})\text{C}(\text{CO}_2\text{CH}_3)_2$: C, 43.75; H, 6.25. Found: C, 44.04; H, 6.50.

This product is identical in properties with the methyl ethoxytartronate mentioned above. Water converts methyl chlortartronate instantly into methyl dihydroxymalonate.

Action of Hydrobromic Acid Gas on Methyl Oxomalonate.—Hydrobromic acid gas, made by the action of bromine on phosphorus in water and dried first by passing it over red phosphorus, then through a tube containing anthracene and phosphorus pentoxide, was run into a small quantity of the pure keto ester. The color gradually disappeared as the substance thickened. It was then cooled in a freezing mixture and little balls of colorless prisms formed slowly. At about 30° the crystals melted and the brown color suggested the liberation of bromine. The crystals liberated hydrobromic acid when exposed to the air, were easily soluble in dry ether, and fairly soluble in benzene. When heated to 40° hydrobromic acid is dissociated and the keto ester is formed. The methyl bromtartronate has not been analyzed, but the method of formation, its reaction and general behavior, leave little doubt but that it has an analogous structure, $(\text{HO})(\text{Br})\text{C}(\text{CO}_2\text{CH}_3)_2$, to that of the methylchlortartronate.

Action of Hydriodic Acid Gas on Methyl Oxomalonate.—Hydriodic acid gas, which was dried by running through a flask containing red phosphorus and a tube containing phosphorus pentoxide, was run into methyl oxomalonate at -15° . The keto ester became lighter colored, and thinner, and a few crystals formed in indistinct granular bunches which melted slightly above the room temperature. When exposed to the light the substance decomposes and gives off iodine. The product is very unstable and was not analyzed.

This class of compounds will be further studied, in connection with the action of haloid acids as catalytic agents.

Various other reactions were tested with derivatives of ammonia and it was found that the intensity of reaction varied directly with the positive character of the substituted radicle in the ammonia molecule. Ammonia gas and urethane both form crystalline addition products but the addition product of aniline was the only one which has yet been thoroughly studied.

Action of Aniline on Methyl Oxomalonate.—A molecular quantity of aniline dissolved in an equal volume of sodium-dry ether was added drop by drop to one molecule of keto ester. The reaction was intense, with considerable heat liberated. After the substance stood in a freezing mixture for a few minutes it began to crystallize in little balls of needles. It formed a solid, yellow tinted mass. It was then filtered and washed carefully with dry ether. After crystallizing from the same solvent it was filtered on a pump, washed, and then dried in a vacuum desiccator over sulphuric acid. The yield was quantitative.

Calculated for $(C_6H_5NH)(HO)C(CO_2CH_3)_2$: C, 55.23; H, 5.44; N, 5.85

Found: C, 55.25; H, 5.54; N, 6.22

Methyl anilinetartrate melts at 102° and is a pure white, crystalline substance. It is easily soluble in hot methyl alcohol, acetone, and hot ethyl alcohol, is fairly soluble in cold ethyl and methyl alcohols and benzene, slightly soluble in carbon tetrachloride, ligroin and carbon bisulphide, and very slightly soluble in water. Hydrochloric acid forms a colorless solution. Nitric acid forms a deep colored liquid, which when diluted with water turns a light green after discharging the blue color. Hot water dissociates it and gives methyl dihydroxymalonate and when the product cools aniline separates out as an emulsion of characteristic appearance and odor.

Several very interesting reactions have been studied with methyl anilinetartrate, the most important being the action of phosphorus pentoxide upon it, forming methyl phenyliminomalonate, $C_6H_5N=C(CO_2CH_3)_2$. This substance appears to be an analogue of phenyl isocyanate, and is extremely reactive at the point of double union of the carbon and nitrogen atoms. These reactions are being studied further. The senior author and his coworkers have been engaged for some time in a comprehensive study of oxomalonate esters with various acid amides, primary and secondary amines, and other classes of compounds having easily dissociated hydrogen atoms. The further results of these investigations will appear soon in THIS JOURNAL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

6-NITRO-3-METHYL-4-SULPHOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

BY W. J. KARSLAKE AND R. C. HUSTON.

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In a previous paper by Karslake and Bond¹ upon an investigation of the oxidation products of 6-nitro-1-3-dimethylbenzene-4-sulphonic acid, a dilute alkaline solution of potassium permanganate being used as the oxidant, it was shown that three different acids were obtained which were regarded as 4-nitro-5-methyl-2-sulphobenzoic acid (I), 6-nitro-3-methyl-4-sulphobenzoic acid (II), and 6-nitro-4-sulphoisophthalic acid

¹ THIS JOURNAL, 31, 405.