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DIMETHYL TARTRONATE.

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In the course of an investigation which was undertaken in this laboratory, it was found necessary to know the properties of the dimethyl ester of tartronic acid. Although many of the combinations of this hydroxy acid with homologues of methyl alcohol are known, a search through the literature failed to show any record of the preparation of the first member of the series. This work is presented not only that the list of esters of tartronic acid may be made more complete, but also because its preparation by some of the usual methods does not seem feasible.

Tartronic acid (hydroxy malonic acid) is most easily prepared according to Osten¹ by treating tartaric acid with fuming nitric acid and phosphorus pentoxide. It was found, however, that, when the mixture was allowed to stand for 21 days instead of the 14 days recommended, the yield was almost tripled. The acid was purified by recrystallization from water.

An attempt was made to prepare the ester by dissolving the anhydrous acid in methyl alcohol and treating the solution with dry hydrogen chloride in the usual manner. No product was obtained.

The ester was successfully prepared by the action of methyl iodide on the silver salt of the acid. This can be done as follows. A concentrated solution of tartronic acid in water is neutralized with ammonium hydroxide and boiled to remove any excess of ammonia. The calculated amount of silver nitrate dissolved in a little water is added while the mixture is stirred constantly. The mixture should be allowed to cool in the dark. The silver tartronate which precipitates is separated with the aid of suction, thoroughly washed with cold water and dried in the oven at 60°. Yield, about 86%.

Slightly more than 2 moles of methyl iodide is placed in a dry flask with some absolute methyl alcohol as a solvent. Benzene, or still better, more methyl iodide, may be employed instead of the alcohol. A long-bulbed reflux condenser is attached by means of an addition tube and one mole of dry, powdered silver tartronate is added in small quantities at a time. The mixture is then refluxed on the water-bath for several hours. The silver iodide is filtered off and washed with a small amount of the solvent. The filtrate is distilled, and when almost all the solvent has passed over, the residue is poured into a beaker and cooled. The crystals of practically pure dimethyl tartronate are filtered off with the aid of suction and washed with a small amount of methyl alcohol. The substance can be recrystallized from this solvent. It is soluble in water and in all the common organic solvents.

¹ Osten, *Ann.*, **343**, 154 (1905).

After 3 recrystallizations, the product melted at 53.3–53.5° corr.

Subs., 0.2028: CO₂, 0.3026; H₂O, 0.0965.

Calc. for C₈H₈O₃: C, 40.52; H, 5.45. Found: C, 40.69; H, 5.33.

The sample for the combustion had been weighed out in a boat inside a boat tube ("piggy") while the operation of running a blank determination and bringing the absorption train to constant weight was in progress. Just before commencing the combustion it was noticed that a small amount of the ester had sublimed to the top of the "piggy," and a new sample had to be taken. This circumstance indicates the extreme volatility of this compound in the solid state.¹

It is obvious that the reason for the lack of success in the attempt to prepare the substance by the dry hydrogen chloride method was the fact that the stream of gas removed the ester almost as fast as it was formed. The comparatively low and varying yields (about 50%) obtained by the method adopted may also be traced to the volatility of the dimethyl tartronate, since the distillate (*i. e.*, the solvent) always contained some ester of which only a small amount could be recovered.

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THE IDENTIFICATION OF ACIDS. VI. SEPARATION OF ACIDS BY MEANS OF PHENACYL ESTERS.

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In several recent papers³ various crystalline derivatives of a number of organic acids have been described with the object of laying a foundation for the positive identification of such acids when found alone or in mixtures. Having thus become acquainted with the derivatives prepared from individual acids, the first step towards unknown mixtures is a study of the separation of acids from unknown mixtures. A number of such separations have been studied, special attention being given to mixtures likely to be met with in natural products. This paper is a direct continuation of our work on phenacyl esters.⁴ The separations are given in detail so that one dealing with such mixtures may know just what to expect.

¹ Furthermore, it points out a possible source of error in conducting combustions of volatile solids—to eliminate which the sample should be weighed out immediately prior to the actual combustion.

² The experimental work described in this paper except that on phenacyl acetate was carried out in the laboratory of the Department of Agricultural Chemistry of the Arkansas Agricultural Experiment Station.

³ THIS JOURNAL, 39, 124, 304, 701, 1727 (1917); 41, 75 (1919); 42, 1043 (1920).

⁴ *Ibid.*, 41, 75 (1919).