

formula which has just been proposed by investigators working on the same problem in another laboratory, and it has led to the conclusion that the facts are best represented by the structure shown in formula XIX.

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NOTE

A Method for the Preparation of Diethyl Oxalate.—In the preparation of ethyloxalacetic ester which was used in the synthesis of thymine to be reported later, considerable amounts of diethyl oxalate were needed. The present paper reports a somewhat simpler method than the most satisfactory ones now employed which gives correspondingly high yields. The removal of any water already present and of that formed during esterification, which is essential for the completion of the coupling between oxalic acid and ethyl alcohol, is brought about by a preliminary distillation of alcohol from the mixture whereby the water is carried over in the distillate with the alcohol. Clarke¹ employs a ternary mixture of alcohol, water and carbon tetrachloride to bring this about, while Kenyon² resorts to a continuous drying of the water laden alcohol with anhydrous potassium carbonate and the return of the dried alcohol vapor to the flask containing the reactants. In our method sufficient of the water has been removed by the preliminary distillation so that after the addition of a second lot of alcohol the esterification is almost quantitatively completed.

Experimental.—One kilogram of c. p. crystalline oxalic acid ((COOH)₂·2H₂O) and 2 liters of absolute alcohol are heated on a water-bath with a reflux condenser until solution is effected (usually about two hours). The mixture is subjected to vacuum distillation (25 mm.) on a water-bath at 80° until the temperature of the vapors reaches about 60°. At this point a considerable quantity of unesterified oxalic acid crystallizes out on the sides of the flask. About 35% of the oxalic acid is in the form of diethyl ester. Two liters of absolute alcohol are mixed with the ethyl oxalate, oxalic acid and the small amount of ethyl alcohol remaining in the flask. This is refluxed for three hours. The excess alcohol containing most of the balance of the water is again removed by distillation under diminished pressure. The remaining ester is dried overnight with anhydrous sodium sulfate, filtered and distilled. The fraction boiling at approximately 97°

¹ Clarke, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1922, Vol. II, p. 22.

² Kenyon, *ibid.*, 1925, Vol. V, p. 59.

at 25 mm. pressure is collected. The yield of distilled ester averages about 85%.

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COMMUNICATIONS TO THE EDITOR

THE BROMINE-SENSITIZED OXIDATION OF UNSATURATED HYDROCARBONS

Sir:

If one absorbs a pure unsaturated hydrocarbon (C_2H_4 , C_3H_6 or C_4H_8) in the presence of pure oxygen by means of bromine water, more gas is absorbed than corresponds to the hydrocarbon present. This extra decrease in volume is not accounted for by the solubility of oxygen in bromine water, for the same results were obtained when the bromine water was presaturated with oxygen.

Thus a bromine-sensitized formation of carbon dioxide and water, both of which would be dissolved in aqueous solution, was suspected. In order to test this assumption in a simple experiment, one side of a 300-cc. sphere was connected to a high vacuum pump through a stopcock and a liquid air trap, the other side communicated, through an ordinary stopcock, a capillary, and a three-way stopcock, with a mercury manometer and a mercury Toepler pump. A tube containing some bromine was also attached to the bulb. The two stopcocks adjacent to the sphere were lubricated with Stephens' stopcock grease [H. N. Stephens, *THIS JOURNAL*, **52**, 635 (1930)]. The system was evacuated, the bromine evaporated and frozen out again with liquid air. The procedure was repeated and the sphere filled with bromine corresponding to its vapor pressure at about 30° (about 100 cc., N. T. P.). The bromine tube and the pumping line were sealed off between sphere and stopcock. The bromine was again frozen out and a mixture of specially purified ethylene (56.7 cc., N. T. P.) and oxygen (55.2 cc.) was filled in on top of the frozen bromine. The manometer was then opened and read. The two stopcocks were closed, leaving some oxygen in the manometer, and the capillary between the stopcocks was cut in two. The sphere was exposed to direct sunlight, then the liquid air removed and the sphere gently rotated¹ to distribute the bromine. The bromination took place immediately. After two hours of exposure the sphere was immersed to exactly the same point in liquid air and again sealed on the system. The

¹ This seemed to be of great importance.