

added and the mixture agitated with hydrogen chloride gas until it becomes homogeneous. From this solution thorium chloride octahydrate precipitates as pure white crystals, which are filtered off, washed with ether and dried. A sample of the salt when dissolved in water gives a negative thiocyanate test for iron.

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The Action of Monoethanolamine on Ethyl Bromomalonate

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In the course of work being carried out in these Laboratories dealing with the synthesis of diureides, the condensation of monoethanolamine with ethyl bromomalonate was attempted. As ordinarily carried out, we find condensation does not result; rather the bromine atom in the ester is replaced by hydrogen. This reaction is analogous to the action of alkaline reagents and halogen acids on similar compounds containing active halogen atoms.

The ethyl bromomalonate was prepared by the action of bromine on ethyl malonate dissolved in carbon tetrachloride. The product was carefully purified by several distillations through a column under reduced pressure. The fraction boiling at 126–127° under 18 mm. pressure was used.

Forty-six grams of monoethanolamine (0.752 mole) and 90 g. of the ethyl bromomalonate (0.376 mole) were refluxed together for six hours. On cooling, the mixture separated into two layers, the lower one eventually solidifying. The solid material was identified as monoethanolamine hydrobromide. The liquid upper layer was extracted with diethyl ether, thus effecting separation from any excess monoethanolamine, and the ether extract dried over anhydrous magnesium sulfate. The ether was distilled off and the resulting liquid fractionated. A low-boiling fraction, b. p. 58–60° (2 mm.), was shown to be ethyl malonate by its refractive index (n_D^{20} 1.4144) and density (d_4^{20} 1.055). The yield was 11 g. A higher boiling fraction (36 g.), b. p. 92–93° (2 mm.), was identified by its boiling point and density (d_4^{20} 1.426) as unchanged ethyl bromomalonate.

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The Mutarotation of α -D-Glucose in Dioxane-Water Mixtures at 25°

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The mutarotation of α -D-glucose has been an object of study for many years by numerous investigators. Though the majority of the experiments concerned this phenomenon in aqueous solution both with and without catalysts, a few have been studied in mixed aqueous solvents. Worley and Andrews² studied the mutarotation in methanol-water mixtures; Richards, Faulkner and Lowry³ in both methanol-water mixtures and ethanol-water mixtures; Lowry and Faulkner⁴ in pyridine-water mixtures; and more recently Rowley⁵ in ethanol-water mixtures at 25°. The mutarotation of glucose in solution is believed by many to be catalyzed by acids and bases and since water is a complete catalyst, having both acidic and basic properties, the reaction is fairly rapid in pure water. Absolute methanol is amphiprotic and apparently a complete catalyst but much inferior to pure water⁶ as is absolute ethanol.⁵ On the other hand, pyridine is not amphiprotic but is a fairly strong base so mixtures of this solvent and water should be a fair catalyst for the mutarotation.

In continuing the studies of the mutarotation of α -D-glucose in mixed aqueous solvents, it was decided to use an inert organic solvent which probably does not itself catalyze the reaction. Unlike the alcohols, which have been used in previous studies, dioxane has no apparent acid group and its basic properties are probably relatively weak. Thus it might be assumed that its catalytic effect on the mutarotation will be exceedingly small. This appears to be justified by subsequent experimental work. Since α -D-glucose is fairly soluble in mixtures up to ninety weight per cent. of dioxane, the mutarotation of this sugar was studied in dioxane-water mixtures at 25°.

Discussion of Results

The solutions were made by dissolving a weighed amount of pure anhydrous α -D-glucose in dioxane-water mixtures of known composition. The concentration ranged from 4.0 g. of sugar/

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(2) Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 1880 (1927).

(3) Richards, Faulkner and Lowry, *J. Chem. Soc.*, 1733 (1927).

(4) Lowry and Faulkner, *ibid.*, **127**, 2883 (1925).

(5) Rowley, *THIS JOURNAL*, **62**, 2563 (1940).

(6) Rowley and Bailey, *ibid.*, **62**, 2562 (1940).