

refractivity values of other authors¹³ are used. The refractivity increment per methylene group appears to be less than the estimated value of 4.65 generally given.¹³

The Eykman constant was computed over the range 20–26° and appears constant within the estimated limits of experimental error.

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(13) (a) W. Hückel, *Theoretische Grundlagen der Organischen Chemie*, 4th Ed., Vol. II, p. 142, Akademische Verlag., Leipzig, Germany, 1943. (b) A. I. Vogel, *A Textbook of Practical Chemistry*, 3rd Ed., p. 1035, Longmans, Green and Co., Inc., New York, N. Y., 1956. (c) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 2nd Ed., p. 107, John Wiley and Sons, Inc., New York, N. Y., 1940.

High Temperature Chlorination of Dioxane to Give Trichloroacetyl Chloride

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Received February 7, 1957

Several workers¹⁻⁴ have reported the chlorination of *p*-dioxane at temperatures of 130–160° to give a number of chlorinated dioxanes. Boeseken, *et al.*² noted that the ring was broken and that "acid chlorides were probably present" when dioxane was subjected to prolonged chlorination at 130–150°.

When trichloroacetyl chloride was isolated from the products of a dioxane chlorination experiment, the work described below was carried out to determine the extent to which trichloroacetyl chloride was formed. Although the experiment was stopped before the ultimate yield of trichloroacetyl chloride was obtained, sufficient information was obtained to show that trichloroacetyl chloride is a major product of the prolonged high temperature chlorination of dioxane. The factors which account for the different results of the previous and present work are the temperature, which was kept near or above 160° when trichloroacetyl chloride was formed, and the large excess of chlorine which was used in this work.

(1) C. L. Butler and L. H. Cretcher, *J. Am. Soc.*, **54**, 2987 (1932).

(2) J. Boeseken, F. Tellegen, and P. C. Henriquez, *J. Am. Chem. Soc.*, **55**, 1284 (1933).

(3) J. J. Kucera and D. C. Carpenter, *J. Am. Chem. Soc.*, **57**, 2346 (1935).

(4) R. K. Summerbell, R. R. Umboeff, and G. R. Lapin, *J. Am. Chem. Soc.*, **69**, 1352 (1947).

EXPERIMENTAL

Two hundred and sixty g. (2.95 moles) of *p*-dioxane was heated to 90° in a flask equipped with a condenser, an inlet tube, and a thermometer. Chlorine was added at a rate of 20 to 30 g. per hr. At the end of 60 hr. the pot temperature had risen to 115° and the net weight increase was 530 g. Infrared analysis indicated less than 2% carbonyl chloride present. Chlorination was continued at 155–160° for 11 hr. Distillation of the crude products at 75 mm. gave 144 g. of trichloroacetyl chloride, b.p. 47–48, n_D^{24} 1.4662, confirmed by the infrared spectrum. The residue was then chlorinated for 15 hr. at 165–180° after which reduced pressure distillation yielded 88 g. of trichloroacetyl chloride. Again the distillation residue was chlorinated at 175–190° for 10 hr.; no condenser was used and the vent gases were passed directly into a cold trap. During this period 160 g. was collected. Distillation of the condensate gave 84 g. of trichloroacetyl chloride. The pot residue solidified on cooling. Infrared and chlorine analysis showed the solid to be hexachloroethane. The total yield of trichloroacetyl chloride was 316 g. (1.74 moles).

An attempt was made to distill the reaction residue (462 g.) at 2 mm. The column and condenser immediately plugged with hexachloroethane. According to the infrared spectrum, the residue contained above 20% hexachloroethane.

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Preparation of Malonaldehyde bis-Bisulfite, Sodium Salt

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Received February 12, 1957

Malonaldehyde (I) reacts with 2-thiobarbituric acid to give a characteristic pink coloration. This reaction is useful for the estimation of 2-deoxysugars and nucleosides containing 2-deoxysugars. For this purpose, it is considered important to have a stable derivative of I, since I has been reported¹ as an unstable crystalline monomer. This report is concerned with the preparation of a stable crystalline bisulfite addition compound suitable for investigations of reactions of I.²

EXPERIMENTAL³

A suspension of 10 ml. of malonaldehyde bis(dimethyl acetal)⁴ in 5.5 ml. of 3.7% aqueous hydrochloric acid was shaken for 1 min. in a water bath at 60° to effect dissolution. The resulting yellow solution was kept at room temperature for 40 hr. and then cooled to 4°. A freshly prepared saturated solution of sodium *meta*-bisulfite was chilled in an ice bath

(1) R. Hüttel, *Ber.*, **74**, 1825 (1941).

(2) U. S. Patent No. 2,671,800 has been granted for a related process for preparing bisulfite addition products of malonaldehyde [*Chem. Abstr.*, **49**, 4014 (1955)]. However, no proof of identity of the proposed compounds is recorded, and apparently no physical or chemical studies were undertaken to characterize the compounds.

(3) Microanalyses for C, H, S, and Na were performed by Dr. W. C. Alford and his associates.

(4) Obtained from Kay-Fries Chemicals, Inc., 180 Madison Ave., New York 16, N. Y.