NOTES

A New Synthesis of Iodoacetaldehyde Diethyl Acetal

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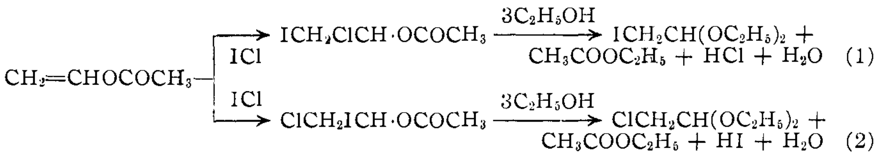
Received June 4, 1952

Iodoacetaldehyde diethyl acetal can be synthesized by the iodination of acetal with iodine and hydroiodic acid,[1,2] or by heating the mixture of bromoacetal and sodium iodide with dry acetone[3] or ethyl alcohol[4] in a sealed tube. The former is time consuming and the yield is very poor, the latter is rather troublesome. On the other hand, Filachione[5] has reported the synthesis of bromoacetals by the bromination of vinyl acetate followed by acetalization with alcohols. Recently Bedoukian[6] has improved this method by brominating vinyl acetate in carbon tetrachloride solution.

Bedoukian's method suggested to us the application of his method to the synthesis of iodoacetal by using iodine instead of bromine, but our attempt was not successful because the addition of iodine to the vinyl double bond was very poor. But if iodine monochloride was employed as the iodinating agent in carbon tetrachloride solution, the addition took place, yielding iodoacetal as well as chloroacetal as the by-product. The result indicated that the reactions seemed to proceed in two directions



$$CH_2{=}CHOCOCH_3 \begin{cases} \xrightarrow{ICl} ICH_2ClCH{\cdot}OCOCH_3 \xrightarrow{3C_2H_5OH} ICH_2CH(OC_2H_5)_2 + CH_3COOC_2H_5 + HCl + H_2O & (1) \\ \xrightarrow{ICl} ClCH_2ICH{\cdot}OCOCH_3 \xrightarrow{3C_2H_5OH} ClCH_2CH(OC_2H_5)_2 + CH_3COOC_2H_5 + HI + H_2O & (2) \end{cases}$$

and the yield of iodoacetal, even under optimum conditions, was below 50% from vinyl acetate.

Then, an attempt was made to use the mixture of iodine monochloride and concentrated hydrochloric acid as the iodinating agent. In this case, the addition is very rapid, yielding α-chloro-β-iodoethyl acetate in almost theoretical quantities. As any chloroacetal was not obtained in this case, the reaction appeared to proceed as in (1). This method is applicable to small or large scale preparations and the yield is 82–85%. Iodoacetal has a pungent odor and a slight decomposition takes place on standing for a long time.

Experimental

Twenty grams of vinyl acetate (b.p. 72–72.5°) was added to 80 ml. of carbon tetrachloride and cooled in an ice–salt-bath. To this solution, a mixture of 30 ml. of hydrochloric acid (39%) and 40 g. of iodine monochloride was added with gentle stirring. The temperature should be kept below 5°, and the stirring should be regulated not to mix the two layers too vigorously because the main reaction is believed to occur on the intersurface of organic and inorganic phase. After about 20 minutes, when iodine monochloride was no longer decolorized, the iodination was complete. At this point, the lower organic layer was separated rapidly, and was added to the mixture of 150 ml. of ethyl alcohol (99.5–100%) and 15 g. of calcium chloride. The whole was allowed to stand for three days at 10–15°. The temperature of acetalization so seriously influenced the yield, that the yield was halved if it was kept at 25°. Then the light red mixture was poured into 300 ml. of water, and the lower organic layer was separated, and was washed successively with dilute sodium thiosulfate solution, then with water. After drying over calcium chloride, the product was distilled under reduced pressure. Iodoacetaldehyde diethyl acetal (47 g. or 84%) distilled at 53.5–54° (2 mm.), $n^{22}\text{D}$ 1.4734, d^{22}_{22} 1.492.

Anal. Calcd. for $C_6H_{13}O_2I$: C, 29.51; H, 5.37. Found: C, 29.42; H, 5.36.

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[1] J. Hesse, *Ber.*, **30**, 1442 (1897).

[2] M. S. Losanitsch, *ibid.*, **42**, 4046 (1909).

[3] F. Beyerstedt and S. M. McElvain, This Journal, **58**, 529 (1936).

[4] F. Beyerstedt and S. M. McElvain, *ibid.*, **59**, 2268 (1937).

[5] E. M. Filachione, *ibid.*, **61**, 1705 (1939).

[6] P. Z. Bedoukian, *ibid.*, **66**, 651 (1944).

The High Field Conductance of Mercuric Chloride at 25 and 45°[1]

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Received June 9, 1952

Onsager[2] has suggested that the high field conductance of mercuric chloride should be interesting from two points of view: since it is a weak salt yielding ions other than the very mobile hydrogen ion it should exhibit greater hydrodynamic effects than weak acids, and, in addition, it might be liable to greater chemical relaxation time lags than acids. Such acids as have been investigated[2,3] show no particular deviation from the theory of Onsager for weak electrolytes and no unusual relaxation time effects, while insufficient data are available on bases to allow any distinctions between the behavior of acids and bases to be drawn. We present herewith some high field conductance measurements on mercuric chloride, approximately 9.3×10^{-3} molar, at 25 and 45°, using potassium chloride as reference electrolyte. The experimental results are not sufficiently unambiguous as to permit a clear assessment of Onsager's predictions, but they constitute yet another addition to the list of peculiarities of this unusual salt.[4]

Experimental

Mercuric chloride was purified by recrystallization from conductivity water; the solid was separated from the mother liquor, dried between absorbent paper, and further dried in a desiccator at room temperature over calcium sulfate.

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[1] Contribution No. 1105 from the Department of Chemistry, Yale University.

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[3] F. E. Bailey and A. Patterson, This Journal, **74**, 4756 (1952).

[4] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, New York, N. Y., 1950, p. 324.