THE REDUCTION OF SOME HALOGENATED COMPOUNDS BY CHROMOUS CHLORIDE

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Reduction of annotinine chlorohydrin by chromous chloride gave two compounds (1, 2), (*a*) "hydroxylactone" and (*b*) "unsaturated lactone A", neither of which was the "normal" reduction product which would be formed by replacement of chlorine by hydrogen. Anet and Marion (2) suggested that these two compounds were formed by 1,2-elimination, analogous to the reduction of *vic*-dibromides to alkenes (3), and involving a chlorine atom and a β-nitrogen atom in the case of the "hydroxylactone", and a chlorine atom and a β-hydroxyl group in the case of the "unsaturated lactone A".

In order to obtain analogies for the reduction of annotinine chlorohydrin, whose structure is now firmly established (4, 5), we have studied the chromous chloride reduction of some simple β-halogenated alcohols and amines. 2-Chloroethanol was not reduced under the conditions used. 2-Bromoethanol was reduced slowly and gave 20% ethylene, isolated as the dibromide, but a considerable amount of starting product was hydrolyzed. 2-Bromoethylamine was reduced to a mixture of ethylamine, ammonia, and ethylene. In this case the "normal" reduction product, formed by simple replacement of halogen by hydrogen, was a reaction product, whereas the "normal" reduction product of annotinine chlorohydrin has not been observed. Nevertheless, the same type of reduction was found in the simple model compounds as occurred in annotinine chlorohydrin.

EXPERIMENTAL

Preparation of Aqueous Chromous Chloride Solution

Chromic chloride hexahydrate (100 g.) was dissolved in 15% hydrochloric acid (600 ml.) and reduced with amalgamated mossy zinc (100 g.) under an atmosphere of nitrogen. An apparatus of the type suggested by Lingane and Pecsok (6) was used for the reduction and storage of the reagent.

Reduction of 2-Chloroethanol

2-Chloroethanol (0.1 mole) was treated with chromous chloride solution (0.2 mole) under an atmosphere of nitrogen. The reaction mixture was heated under reflux for 3 hours and all escaping vapors were passed through an all-glass system to a series of bromine traps. During this time there was no evidence of any evolution of gas and no visible loss of blue color in the chromous solution. The bromine in the traps on being worked up yielded no trace of ethylene bromide, and distillation of the reaction mixture yielded no ethanol.

Reduction of 2-Bromoethanol

2-Bromoethanol (0.05 mole) was reduced with chromous chloride solution (*ca.* 0.1 mole). The mixture was heated under reflux in an atmosphere of nitrogen for 3 hours during the last half-hour of which a slow stream of nitrogen was allowed to pass through the system to entrain any ethylene produced and carry it to the bromide absorption traps. A trap containing water was placed before the bromide traps to scrub out any ethanol entrained.

Can. J. Chem. Vol. 36 (1958)

The dibromide collected was washed with water and sodium carbonate solution until colorless. The dibromide layer was separated, the washings extracted with ether, and the combined extract, after being dried over calcium chloride, yielded on distillation 2.1 g. of pure ethylene dibromide (22% yield).

A Schotten–Baumann reaction modified (7) to detect small quantities of ethanol in aqueous solution failed to produce any ethanol derivative either from the water trap or from the initial distillate of the reaction mixture.

Control on Hydrolysis of 2-Bromoethanol

2-Bromoethanol (5 g.) was heated under reflux with 15% hydrochloric acid (30 ml.) for 3 hours. The mixture was salted out with sodium chloride and extracted five times with small quantities of ether. The ether extracts were combined, dried over magnesium sulphate, and evaporated, leaving slightly less than 1 g. of residual oil.

Reduction of 2-Bromoethylamine Hydrobromide

2-Bromoethylamine hydrobromide (0.05 mole) was reduced under nitrogen with chromous chloride solution (0.1 mole) by heating under reflux for 3 hours. The ethylene evolved was converted to the dibromide as described above, yield 4.6 g. (49%).

The residue was rendered alkaline with sodium hydroxide and steam-distilled into a dilute hydrochloric acid solution. The acidic solution was evaporated to dryness, yielding 3.49 g. of white solid. By fractional crystallization from ethanol the ammonium chloride was separated from ethylamine hydrochloride, m.p. 96°–98°, which did not depress the melting point of a known sample of ethylamine hydrochloride, and formed a benzoyl derivative, m.p. 70° (lit. m.p. 71° (8)). The ammonium chloride was estimated to comprise approximately 60% of the mixture, the ethylamine hydrochloride 40%.

ACKNOWLEDGMENT

The authors are indebted to the National Research Council for a grant in support of this work.

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RECEIVED OCTOBER 29, 1957.
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GAS-LIQUID PARTITION CHROMATOGRAPHY OF ORGANIC SULPHUR COMPOUNDS[1]

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To assist in the identification of organic sulphur compounds in cracked distillates derived from Canadian crudes the relative elution times of a number of such compounds

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[1] *Issued as N.R.C. No. 4615.*