CCXXXIX.—*A New Synthesis of Oxazines.*

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SYNTHESES of oxazines are usually brought about by the preliminary formation of a nitrogen linking, followed by the completion of an oxazine ring, according to the following scheme :

This has the disadvantage, however, of affording no simple method of preparation of amino-derivatives, the reduction of nitro-oxazines being by no means easy; and it otherwise very greatly limits the type of substance obtainable.

Research now in progress (compare the previous paper, this vol., p. 1036) has resulted in a different formation of oxazines, which is the converse of the usual process, that is, it consists in the closing of a simple ether chain by the elimination of water from an amino- and a hydroxyl-group :

The oxazines being of very considerable interest, both technically (compare Justin-Mueller, *Rev. Gen. Col.*, 1920, **24**, 130; also, in connexion with amino-derivatives, Kehrman, *Ber.*, 1905, **36**, 481, 483) and, more especially, scientifically (compare Knorr, *Ber.*, 1899, **22**, 1209; Kehrman, *loc. cit.*, p. 479), this alternative and rather unexpected possibility of their synthesis appears sufficiently useful to be put on record, the only previous example of a preparation in any way similar which has come to the notice of the authors being a condensation of amino- and carboxyl-groups (Bischoff, *Ber.*, 1900, **33**, 1593), the carbonyl of the latter remaining in the ring produced, and not readily allowing of reduction to the parent oxazine.

EXPERIMENTAL.

2 : 4-Dinitrophenyl β -Hydroxyethyl Ether, and its Reduction.

This substance was prepared by a method similar to that employed in the case of the corresponding ether of glycerol (*loc. cit.*), a small quantity of aqueous sodium hydroxide solution proving successful, however, as condensing agent instead of the sodium derivative of ethylene glycol. To a solution of 8.1 grams of 1-chloro-2 : 4-dinitrobenzene in 18 c.c. of ethylene glycol was added an ethylene-glycollic solution of sodium hydroxide (1 mol.) obtained by dissolving 1.6 grams of the solid alkali in 1 c.c. of water and adding 18 c.c. of the glycol. The mixture was heated on a water-bath for half an hour, during which time crystals of sodium chloride separated. While still hot, the liquid was stirred into 50 c.c. of water, from which, on cooling, were deposited 8.5 grams of acicular crystals. These were recrystallised from 20 per cent. acetic acid and from water, and were then colourless and melted at 109° (Found : C = 42.15; H = 3.75; N = 12.47. Calc., C = 42.11; H = 3.51; N = 12.29 per cent.).

The mother-liquor from the acetic acid crystallisation contained a small quantity of another substance, m. p. 192—195°, which was not sufficient to admit of complete analysis, but an estimation of the nitrogen indicated that the compound was ethylene glycol bisdinitrophenyl ether, $C_2H_4(O\cdot C_6H_3[NO_2]_2)_2$. In other experiments, the ethylene-glycollic sodium hydroxide was prepared by pouring the strong aqueous alkali into the glycol, instead of pouring the glycol into the aqueous alkali, and in the subsequent condensations with chlorodinitrobenzene no trace of the bisdinitrophenyl ether could then be found. It would consequently appear that the presence of excess of the glycol during the whole period of the preparation of the glycollic alkali prevented the formation of the

disodium derivative of glycol, and consequently of the bisdinitrophenyl ether also.

Reduction of 2 : 4-Dinitrophenyl β -Hydroxyethyl Ether.—One part by weight of the monophenyl ether was gradually added to twenty-two parts of water containing two parts of iron and a small quantity of hydrochloric acid, the addition being extended over a quarter of an hour, and being carried out at 74—76°. The whole was maintained at this temperature for a further equal period of time, the product was then filtered and the residue extracted with boiling water. As the resulting diamine was found to be insoluble in ether, and exceedingly difficult to purify in any form, the water was evaporated and the dried material was submitted to dehydration in the crude state, as described below. No specimen of this free diamine has been isolated, but, by boiling the crude product with excess of acetyl chloride and then decanting and diluting the solution obtained, long, colourless needles of the triacetyl derivative were isolated, m. p. 128—130° (Found : $\text{CH}_3\cdot\text{CO} = 43\cdot1$. Calc., $\text{CH}_3\cdot\text{CO} = 43\cdot8$ per cent.).

6-Amino-2 : 3-dihydro-1 : 4-benzisooxazine (6-Aminobenzo-

The crude diamine mentioned above was dissolved in 10 parts by weight of concentrated sulphuric acid, and heated slowly to 150°, at which temperature it was maintained for several minutes. The product was cooled, poured into water, and extracted with ether after neutralisation with sodium hydroxide. The ethereal extract was dried over solid sodium hydroxide, and the ether was removed by evaporation, when a mass of colourless, acicular crystals was obtained, which, after recrystallisation from water, melted at 80° (Found : N = 18·9. Calc., N = 18·6 per cent.).

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