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The Reduction of Unsymmetrical Dichloracetone by Yeast.

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The reduction of chlorinated ketones does not appear to have been studied hitherto, although the reduction of aldehydes and ketones in general by yeast has been the subject of thorough investigation by Neuberg[1] and his co-workers. Their work conclusively proves the value of yeast as a reducing agent, which must play an important part in ordinary fermentation as also in natural syntheses. The first important example of bio-chemical reduction of this nature was furnished by Linter,[2] Liebig, and Lüers who reduced chloral hydrate and made the preparation of trichlorethyl alcohol accessible in the laboratory. The importance of reducing monochloracetone, or indeed, of any of the unsymmetrical chloracetones by means of yeast, lies firstly in the fact that these acetones after reduction give rise to alcohols containing an asymmetric carbon atom as is evident from the following :

$$CHCl_2 \cdot CO \cdot CH_3 \xrightarrow{H_2} CHCl_2 \cdot \underset{*}{C}HOH \cdot CH_3$$

Secondly, these chlorinated secondary alcohols would form the basis of urethane derivatives, valuable as soporifics. In ordinary chemical reduction it is the

[1] C. Neuburg and J. Kerb. Ber. *46*, 2225 (1913).

[2] C. J. Linter and H. J. V. Liebig H. 72, 449 (1911); Linter and Lüers. H. *88*, 122 (1913).

racemic form that is invariably obtained, as the chance of formation of the dextro-form is equal to the chance of formation of the laevo-form. In the case of biochemical reduction, the chance of obtaining optically active components is usually great due to the selective action of enzymes, and if in any way the preponderance of one isomer over the other can be secured, the resulting compound should exhibit optical activity (compare Neuberg and Kerb; Neuberg and Nord). An early example of the selective action of ferments or bacteria is to be found in Le Bel's work on the fermentation of inactive propylene glycol by *bacterium termo*. A further example of interest is to be found in the work of Peré,[1] who studied the biochemical oxidation of propylene glycol in contact with *tyrothrix tenuis*. It is significant that this investigator obtained a dextro-rotating propyl glycol, as distinct from the laevo rotatory propyl glycol obtained by Le Bel. The explanation must evidently lie in the use of different bacteria, which would seem to indicate with a degree of certainty that the action of the two bacteria upon racemic propyl glycol is selective.

The particular reaction described in these pages is a case of reduction by yeast in a fermenting solution of sugar. Here also the yeast exerts a selective action and from unsymmetrical dichloracetone gives rise to an optically active dichlorisopropyl alcohol. The rate of this reduction, however, in the case of dichloracetone is relatively rapid as the reduction is probably completed in 24 hours if not in 12 hours. The operation of adding a 20 per cent. alcoholic solution of 10 grams dichloracetone to a fermenting solution of sugar requires 3-4 hours, after which the mixture is allowed to stand

[1] Annales de Institut Pasteur, 1896, II, 600-8.

overnight in an incubator at 35°C. Next morning the odour of dichloracetone is scarcely to be noticed in the reaction mixture, and the sugar is also found to have disappeared to the extent of 96-97 per cent. The further addition of yeast, or of yeast and sugar, is only to secure certainty of reduction of any dichloracetone that might have remained unacted upon. Dichloracetone does not seem to be appreciably poisonous to beer-yeast and the yield of dichlorisopropyl alcohol is not affected by the rate of addition of the dichloracetone to the fermenting sugar solution. In one experiment in which accidentally the stopper of the dropping funnel was dislodged, about half of the alcoholic solution of dichloracetone fell at once into the fermenting sugar solution without markedly affecting the rate of fermentation of the solution. This non-poisonous character of dichloracetone is convenient and also interesting in view of the fact that Willstätter has recently found bromal very poisonous to yeast and Neuberg (*loc. cit.*) found it necessary to add the aldehydes with which he experimented, very cautiously to the fermenting solution in order to get a good yield of reduction product. Also in some experiments with monocbloracetone the rate of addition was found to be very important. The first experiment was conducted with monochloracetone supplied by Messrs. Kahlbaum of Berlin, an alcoholic solution of which had to be very cautiously added in order to maintain the fermentation of the sugar solution. In fact even with the utmost care, it was difficult to maintain a brisk fermentation throughout the addition, and towards the end the addition of monochloracetone had actually to be suspended, in view of the considerably decreased rate of fermentation. It is to be observed here that in course of further investigation, it was found that the monochloracetone supplied by Messrs.