

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ELI LILLY & COMPANY.]

THE PREPARATION OF 1,2-DICHLORO-ETHER.

BY E. A. WILDMAN AND HAROLD GRAY.

Received April 28, 1919.

An investigation which was recently carried on involved the use of 1,2-dichloro-ether, a substance which is not available on the market. An examination of the literature showed that the best method of preparation was probably, by direct chlorination of ether, a method used by Fritsche and Schumacker,¹ although they did not give sufficient details to enable one to carry out the operation successfully.

The ease with which chlorine and ether react is shown by the fact that a mixture of the two in gaseous form may ignite spontaneously. If a flask is filled with chlorine at room temperature and one or two cc. of ether poured in, there will usually follow within a moment a slight explosion with ignition of the ether and the deposition of a quantity of soot. If during the chlorination of ether, particularly at the first, the temperature is not kept low by cooling with an ice-water bath, and the chlorine run in slowly, there is likely to be an accumulation of chlorine above the liquid which will result in the sudden ignition of the whole mass. As the reaction progresses, the ether becomes saturated with hydrogen chloride which decreases its inflammability and cooling is no longer necessary. The rate of passing in chlorine may also be much increased for the reaction takes place more rapidly than at first.

There is another difficulty which enters when the ether becomes saturated with hydrogen chloride. The latter seems to dissolve to the extent that it forms a supersaturated solution when it suddenly escapes with almost explosive violence, carrying the ether along with it. In one case when 6 liters of ether were being chlorinated in a large wide-mouthed bottle the entire contents with the exception of about 500 cc. was ejected as if from a geyser. Occasional agitation of the material was not sufficient to prevent this. It was found necessary to agitate continuously by means of a rapidly revolving mechanical stirring device.

The operation was carried out as follows:

A two-liter flask was provided with a return condenser, an inlet tube for chlorine and an efficient stirring device connected by means of an oil seal in order that the escaping hydrogen chloride would be forced to go through the condenser. 800 g. of dry ether was placed in the flask and kept cold by a surrounding bath of ice and water. The ether was stirred from the beginning. After passing in a slow stream of chlorine for 35 hours the specific gravity was 0.785 at 25° and hydrogen chloride began to be evolved freely. The temperature was then allowed to rise gradually to that of the room. At the end of 65 hours the specific gravity

¹ *Ann.*, 279, 301 (1894).

was 0.89, and after 82 hours, 0.96. Chlorination was stopped at this point.

The unchanged ether was distilled off under reduced pressure and the remaining material fractionated. There was obtained 375 g. of dichloro-ether, boiling from 66 to 69° at 45 mm., representing a yield of 24.2% of the theoretical amount. The material in the distilling flask remained colorless till near the end, when it became black and there was left a small residue of 65 g.

It had previously been determined that chlorination should be stopped at about the point where the specific gravity was 0.96. In one trial during which it was carried on to the specific gravity 1.11 it was impossible to separate a pure fraction of dichloro-ether from the product.

INDIANAPOLIS, INDIANA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY,
No. 322.]

ACTION OF ENZYMES UPON STARCHES OF DIFFERENT ORIGIN.

BY H. C. SHERMAN, FLORENCE WALKER AND MARY L. CALDWELL.

Received May 5, 1919.

O'Sullivan,¹ working with malt extract and precipitated malt diastase, reported that potato starch was less readily digested to maltose than were the starches of the cereal grains when all were gelatinized by heating in water at 97° and tested under like conditions.

Stone,² also working with malt extract, judging the action by the disappearance of the blue coloration with iodine, found potato starch more digestible than wheat starch, and maize starch less so than either. With saliva, Stone found potato starch more digestible than the cereal starches, and among the latter maize and rice starches appeared more digestible than that of wheat. Stone also reported potato starch more readily digestible than cereal starches by pancreatin and by taka-dia-stase.

Ford³ found the purified starches of rice, barley, maize, wheat, potato and arrow root when similarly prepared to be equally digested by malt extracts and attributed the differences found by other observers to the probable impurities in their starches.

In view of the conflicting results thus shown by the earlier work and the fact that previous observers have in general worked with but few forms of amylase and these usually with no attempt at isolation, a more comprehensive study which should include observations upon purified enzyme preparations, as well as secretions and extracts, seemed desirable.

¹ O'Sullivan, *J. Chem. Soc.*, **85**, 616 (1904).

² Stone, U. S. Dept. Agr., Office of Expt. Sta., *Bull.* **34**.

³ Ford, *J. Soc. Chem. Ind.*, **23**, 414 (1904).