XCI.—*A Simple Method for the Preparation of Maleic Anhydride.*

By Frederick Alfred Mason.

Maleic acid can now be obtained cheaply and conveniently on a commercial scale by the catalytic oxidation of benzene, but the preparation of maleic anhydride by existing methods involves the use of an expensive dehydrating agent such as acetyl chloride or phosphoric oxide (compare Anschütz, *Ber.*, 1879, **12**, 2281; 1881, **14**, 2789; 1882, **15**, 641; Perkin, *Ber.*, 1881, **14**, 2547; 1882, **15**, 1073; Fittig, *Annalen*, 1877, **188**, 87; Volhardt, *ibid.*, 1892, **268**, 255; Tanatar, *ibid.*, 1893, **273**, 32; Van der Riet, *ibid.*, 1894, **280**, 216). The anhydride cannot be prepared by heating maleic acid just above its melting point (Pelouze, *Ann. Chim.*, 1834, **11**, 266), at 130° in a sealed tube (Skraup, *Monatsh.*, 1893, **14**, 500), at 190° (Tanatar, *loc. cit.*), or with water in a sealed tube (Skraup, *Monatsh.*, 1891, **12**, 107), the chief or sole product being fumaric acid in all cases; neither can it be prepared by distilling maleic acid rapidly in small quantities, since, according to Pelouze, the anhydride and the water in the distillate at once regenerate maleic acid.

It has now been found that the anhydride may be obtained from the acid in excellent yield by distilling the latter with a neutral high-boiling solvent such as xylene or, better, tetrachloroethane. The water formed distils at once with the solvent and as soon as all the water is removed the residue is fractionated under reduced pressure; the anhydride then distils in a pure form, only about 10% of the acid remaining behind as fumaric acid.

EXPERIMENTAL.

A mixture of 100 c.c. of tetrachloroethane and 100 g. of commercial maleic acid was heated, preferably in an oil bath, until 90 c.c. of distillate had been collected, consisting approximately of 75 c.c. of tetrachloroethane and 15 c.c. of water (theory requires 15·5 c.c.), the temperature rising from 120° to 150° as indicated by a thermometer placed in the neck of the flask. The residue was then distilled until the thermometer indicated 190° (b. p. of anhydride 197—199°), the receiver changed, and the residual anhydride distilled under reduced pressure, boiling at 82—84°/15 mm. (reduced pressure is desirable but not essential): 70 g. of anhydride were collected, and the middle fraction on refractionation gave a further 5·5 g., the total yield being 75·5 g. or 89·5% of the theoretical. The residue (8·5 g.) of fumaric acid in the flask was removed with alcohol and still contained a small amount of anhydride.

Similar results were obtained when xylene was used as the solvent, but the water came over much more slowly; for instance, the distillate from a mixture of 50 g. of maleic acid and 100 c.c. of xylene contained 2 c.c., 3 c.c., and 5·5 c.c. of water in 50 c.c., 70 c.c., and 80 c.c. respectively.

The anhydride so obtained has a boiling point of 197—199° (uncorr.) and a setting point of 52° (Fittig gives 196° and 60°). It is easily soluble in most organic solvents and crystallises well on cooling. On exposure to the air it absorbs moisture, re-forming maleic acid.

Attention must be directed to the fact that the vapour of the anhydride, although having no perceptible odour at the ordinary temperature, attacks the mucous membrane of the nose and after some time causes inflammation and a heavy catarrh of the nasal passages, the symptoms resembling those of a severe "common cold."

The experiments were carried out in the Organic Chemical Laboratories at Oxford and thanks are due to Imperial Chemical Industries Ltd. for permission to publish the results.

COLLEGE OF TECHNOLOGY,
MANCHESTER.

[*Received, February* 11*th*, 1930].