

modification of von Weimarn's procedure. These sols are contaminated with considerable amounts of sodium chloride or other "diluent" used in the grinding. Subsequent work showed a need for a substantially electrolyte-free charcoal hydrosol. One of us (T. J. S.) suggested that freezing the water in the capillaries of wet charcoal should cause enough expansion to give the required subdivision. This was found to be the case. Several other substances, such as Patrick's silica gel, which are easily wet by water were found to produce hydrosols when an aqueous paste was rapidly frozen and treated with water. This Laboratory not being equipped for precise colloidal work, it has been decided to forego any attempt to study the nature of the systems so obtained. A description of the general methods used by us is given here.

The charcoal or other solid is covered with water and wet by boiling or evacuation or both. Excess water is then decanted, and the resulting paste frozen in a beaker or flask immersed in a freezing mixture. The usual dry-ice-acetone mixture is very satisfactory for this purpose. The mass is thawed and frozen several times and then mixed with a large volume of distilled water. Alternately, after each freezing, about 200 cc. of water per g. of charcoal may be added to the frozen mass and the resulting sol decanted.

Many varieties of commercial carbons and sugar charcoals were found to give fairly stable sols of low concentration. Often better results were obtained if the water was made slightly acid or basic. The usual protective colloids seem to have very little effect.

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### Preparation of 3,4-Dimethylaniline

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In the synthesis of riboflavin, the preparation of 3,4-dimethylaniline is an important step. This xylidine is usually obtained by the method of Karrer, *et al.*,<sup>1</sup> comprising nitration of *o*-xylene, isolation by repeated fractionation of the 4-nitro-*o*-xylene and subsequent catalytic hydrogenation

(1) Karrer, Becker, Benz, Frei, Salomon and Schöpp, *Helv. Chim. Acta*, **18**, 1435 (1935).

of the latter compound. In our hands, Karrer's procedure proved to be tedious and gave relatively low yields; in fact, we confirmed Karrer's 15% yield of xylidine. James, *et al.*,<sup>2</sup> likewise made use of a nitration and reduction method; they obtained a 27% yield of 4-nitro-*o*-xylene by conducting the nitration at a higher temperature. These workers adopted Karrer's laborious fractionation procedure for their subsequent steps of the process.

We have found that 4-bromo-*o*-xylene, obtained from *o*-xylene by bromination and subsequent vacuum distillation in 85% yield, according to Ghigi,<sup>3</sup> may be transformed to 3,4-dimethylaniline, when subjected to high pressure ammonolysis by the procedure of Groggins and Stirton<sup>4</sup> for the conversion of aromatic halides to the corresponding amines. Using pure *o*-xylene as the basic material, 4-bromo-*o*-xylene is obtained free from isomers. Hence, the finally resulting 1,2-dimethyl-4-aminobenzene will likewise be practically free of isomers.

In a bomb of a high-pressure hydrogenator, 200 g. of 4-bromo-*o*-xylene, 14 g. of copper wire and 600 ml. of 28-29% ammonia containing 12 g. of cuprous chloride were placed and treated at 195° and 900-1000 lb. pressure for fourteen hours under agitation by tilting back and forth. The bomb was emptied after cooling, the two layers were separated and 40 ml. of 40% alkali was added to the organic layer. The product was steam distilled and the crude xylidine, which crystallized on cooling, was further purified by dissolving it in 500 ml. of 8% hydrochloric acid and extracting the acid solution twice with 100-ml. portions of ether. The acid solution was made alkaline with 160 ml. of 40% alkali and steam distilled. The distillate was cooled and filtered and the dry product thus obtained was further purified by vacuum distillation at 116-118° and 22-25 mm.

The yield was 103 g. of 3,4-dimethylaniline (79%). A mechanically stirred autoclave may be more suitable than the apparatus employed, since more uniform mixing appears to result in a better yield. It is not known whether a large excess of ammonia is necessary for the reaction.

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(2) James, Snell and Weissberger, *This Journal*, **60**, 2084 (1938).

(3) Ghigi, *Ber.*, **71**, 634 (1938).

(4) Groggins and Stirton, *Ind. Eng. Chem.*, **28**, 1051 (1936).