

CCCXXIX.—*Preparation of α -Trioxymethylene and a New Polymeride of Formaldehyde.*

By DALZIEL LLEWELLYN HAMMICK and ALFORD REGINALD BOEREE.

PRATESI (*Gazzetta*, 1885, **14**, 139) prepared α -trioxymethylene, $(\text{CH}_2\text{O})_3$, a colourless, crystalline substance melting at 61° . He obtained it by heating the amorphous, polymerised form of formaldehyde known as paraform with "a trace" of sulphuric acid in a sealed tube at 115° .

Pratesi's work could not be repeated by Kraut (*Annalen*, 1890, **258**, 95), by Auerbach and Barschall (*Arb. Kais. Gesundheit. Amt.*, 1905—6, **27**, 220), or by Dunlop (T., 1914, **105**, 1155). Auerbach and Barschall (*loc. cit.*), however, prepared the substance by subliming paraform (or a mixture of β - and γ -polyoxymethylenes) in a slow current of nitrogen into a small quantity of ice-water. They give 63 — 64° as the melting point of the pure substance, purified by recrystallisation from ether or by sublimation.

Attempts to repeat Pratesi's method of preparation using "dry" paraform (containing about 1 per cent. of moisture) met with no success. Moreover, many experiments were carried out before the precise conditions were found under which the substance could be prepared in reasonable yields by Auerbach and Barschall's method. As described below, it has, however, been found possible to prepare α -trioxymethylene in about 10 per cent. yield by a modification of Pratesi's method, in which considerable quantities of sulphuric acid and water are used instead of "a trace" of acid. Directions are also given for preparing the substance in a yield of about 20 per cent. by Auerbach and Barschall's method.

ϵ -Polyoxymethylene : a New Polymeride of Formaldehyde.

α -Trioxymethylene, purified by repeated sublimation at 46° in a bent, closed and exhausted tube, was found to melt at 64° . After eight sublimations, a trace of moisture apparently still remained (as indicated by mistiness forming on the cool parts of the tube before the deposition of the slender needles of α -trioxymethylene occurred). The last traces of water were removed by recrystallisation from sodium-dried ether, which was evaporated by a current of dry air. The crystals thus obtained melted at 64° , as before; but on resubliming at 46° in an exhausted tube the dry substance was found to behave differently from the slightly moist preparation. The sublimate appeared in the form of large, stout prisms instead of the usual long needles. Many of the prisms were not entirely

transparent but contained white, opaque regions. On inverting the tubes and resubliming, α -trioxymethylene passed to the cold end of the tube, leaving behind a white, silky, paper-like substance. By repeated sublimation, the whole of the α -trioxymethylene was converted into this substance (Found : C = 39.9; H = 6.6. $[\text{CH}_2\text{O}]_n$ requires C = 40.0; H = 6.7 per cent.).

The compound is thus a polymeride of formaldehyde (ϵ -polyoxymethylene). It is doubly refracting, although it possesses no distinct crystalline form. It melts with decomposition and depolymerisation at 195—200° (uncorr.). On heating in an open tube, the smell of formaldehyde is noticed and a white sublimate is obtained which melts at 163°. This substance is probably one (or several) of the polyoxymethylenes described by Auerbach and Barschall (*loc. cit.*), all of which melt below 170°.

ϵ -Polyoxymethylene is insoluble in water, sodium sulphite solution, and the usual organic solvents. Like the other polyoxymethylenes, it dissolves in boiling nitrobenzene and separates as an amorphous powder on cooling. No measurable depression of the freezing point of nitrobenzene was found. On boiling with ammoniacal silver nitrate, the surface of the substance blackens, but no silver mirror is obtained and the liquid remains clear; in this respect, the new polymeride is clearly differentiated from the previously known polymerides. It could not be acetylated by the method of Barnett (*J. Soc. Chem. Ind.*, 1921, **40**, 8T) and therefore probably contains no hydroxyl groups.

Preparation of α -Trioxymethylene : Modification of Pratesi's Method.

Paraformaldehyde (10 parts) and a mixture of equal volumes of sulphuric acid and water (1 part) were placed at the bottom of glass tubes (18" \times 1") closed at one end. The open ends were drawn out and sealed after exhaustion of the tubes by the water-pump. The ends of the tubes containing the formaldehyde-acid mixture were immersed in an oil-bath at 115°. Long, slender needles began almost immediately to form in the cool parts of the tubes. After about fifteen minutes, the tubes were removed, the portions containing the crystalline α -trioxymethylene cut off, and the crystals scraped out.

Owing to the fact that methyl formate and other volatile liquids are produced in the tubes (Dunlop, *loc. cit.*) the heating in the oil-bath must be stopped as soon as liquids begin to condense on the cool parts of the tubes. If this precaution is not taken, the α -trioxymethylene is washed out of the upper portions of the tubes and cannot be regained.

The yields obtained by this method, after purification by resub-

limation, were about 10 per cent. calculated on the formaldehyde used.

Preparation of α -Trioxymethylene : Auerbach and Barschall's Method.

The success of Auerbach and Barschall's method was found to depend on the volume of the "small quantity of water" into which the above workers sublimed paraformaldehyde. They do not specify the actual amount of water used; it was found, however, that 40 grams of ice-water per 100 grams of paraformaldehyde (or β - and γ -polyoxymethylenes) gave the most satisfactory results.

As found by Auerbach and Barschall, the mixture of β - and γ -polyoxymethylenes obtained by slowly adding 4 volumes of concentrated sulphuric acid to 10 volumes of 40 per cent. "formalin" and keeping for two days in the ice-chest, gave better yields of α -trioxymethylene than crude paraform. The mixture of polyoxymethylenes was placed in a round flask fitted with a cork carrying a tube for leading in a current of carbon dioxide and a short, wide, bent tube leading below the surface of ice-water in a test-tube immersed in ice and water. The flask was heated rapidly to 200° in an oil-bath, a slow current of carbon dioxide being maintained through the apparatus until the contents of the flask had passed into the ice-water.

The ice-water solution was distilled with the aid of a short fractionating column. If too little water had been used to absorb the products of the sublimation of the polyoxymethylenes in carbon dioxide, the condensate was jelly-like and on distillation choked the column and condenser with solid products. Too much water led to poor yields. With the quantities given above (100 of β - and γ -polyoxymethylene to 40 of water in the receiver) the product distilled easily and gave a substance which on the addition of sodium chloride and extraction with ether yielded α -trioxymethylene to the extent of about 20 per cent. calculated on the original polymerised formaldehyde.

Summary.

i. α -Trioxymethylene can be prepared by heating paraformaldehyde in sealed tubes with water and sulphuric acid.

ii. The conditions necessary for the successful use of Auerbach and Barschall's method for the preparation of α -trioxymethylene are recorded.

iii. A new polymeride of formaldehyde, ϵ -polyoxymethylene, is obtained by the repeated sublimation of dry α -trioxymethylene.

THE DYSON PERRINS LABORATORY,
OXFORD.

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