

Anal. Subs., 20.90 mg.: CO₂, 63.482 mg.; H₂O, 11.11 mg. Calcd. for C₁₃H₁₂O: C, 84.74; H, 6.57. Found: C, 84.08; H, 6.04.

Determination of Phenol Coefficient.—This was carried out on *B. typhosus*, using the method of the Hygienic Laboratory. The material under investigation was added as an emulsion in water which was prepared by mixing a solution in very little alcohol with water.

My thanks are due to Dr. Ross who carried out the determination of the phenol coefficient.

Summary

Two methods are given for the preparation of 2,4-dihydroxydiphenylmethane and a method for the preparation of 2,4-dihydroxydiphenylethane. Both compounds which may be regarded as aryl-substituted resorcinol derivatives show a high germicidal action, the phenol coefficients being 22 and 40, respectively. The corresponding 4-hydroxydiphenylmethane is, however, only 4.6 times stronger than phenol from which it is derived. Thus the benzylation of resorcinol leads to a more active compound than that of phenol.

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[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, No. 503]

THE DIMORPHISM OF FURFURYL FUROATE

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In a previous paper one of us¹ described the preparation and some of the properties of furfuryl furoate, pointing out the fact that two forms existed, melting at 19.5° and 27.5°. It seemed desirable to investigate further this interesting compound, especially in regard to its crystallography and the densities of its two crystalline forms.

For the sake of brevity we shall designate the two crystal forms as alpha and beta forms. The alpha form is the unstable form melting at 19.5° and the beta the stable form melting at 27.5°.

Crystallography.—The growing of crystals for the purpose of angular measurements was a very simple matter in so far as the beta form was concerned. Large crystals could easily be "nursed" from the liquid phase of the ester until they attained from 10 to 20 mm. in diameter. In growing these large crystals it was found advantageous to use instead of the pure ester, a sample to which 0.5% of furfuryl alcohol had been added. From such solutions the crystallization was much slower and single crystals grew gradually without interference from the mass of small crystals which rapidly appeared from the pure ester.

¹ THIS JOURNAL, 47, 1452 (1925).

These crystals were transparent and colorless but on standing became slightly yellowish and the faces became dull.

The growing of crystals of the alpha form was a much more difficult proposition and only small crystals of at most 3 mm. in diameter could be obtained. This was due to the fact that they pass with extreme ease to the beta form and in no case could they be "nursed" by transfer from one dish of liquid to another. The pressure exerted in removing them or the mechanical disturbance caused by scratching their surface unintentionally caused them to pass to the beta form. The best specimens were obtained by cooling the liquid phase from the surface. This was conveniently done by exposing a dish of the liquid floating on water, to the outdoor temperature when the thermometer was in the neighborhood of 10°. The crystals began to form on the surface and when heavy enough sank, thus giving an opportunity for all faces to grow. As soon as a large number of crystals began to appear the larger crystals were removed with a blunt glass spatula and kept in the cold.

The measurements of the angles of the alpha form show that these crystals belong to the monoclinic system, prismatic class. The following are the measurements obtained.

α -Furfuryl Furoate.—
 Rhombic prisms (h0l) (hkl);
 pinacoids, (100) (001).
 Crystal Angles: Angle
 (100) : (h0l) = 63°30' (by
 subtraction); angle (h0l) :
 (\bar{h} 0l) = 33°, measured; angle (00 $\bar{1}$) : (\bar{h} 0 $\bar{1}$) = 78°30', measured; angle
 (hkl) : (\bar{h} k \bar{l}) = 68°, measured.

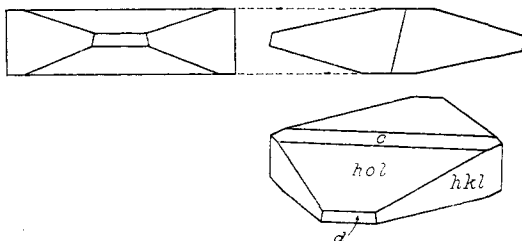


Fig. 1.— α -Furfuryl furoate—monoclinic prismatic.

The crystal is shown in Fig. 1 in both clinographic and orthographic projection, front and side elevations being chosen for the orthographic projection.

The stubby, prismatic crystals of the β -furfuryl furoate belong to the triclinic system, pinacoidal class. The following are the measurements obtained.

β -Furfuryl Furoate.—Pinacoids (100) (010) (hkl) (0hl) (0 \bar{h} l) (\bar{h} k \bar{l}) (\bar{h} k \bar{l}). Angle (100) : (010) = 101°, measured; angle (010) : (0k1) = 53°, measured; angle (0 $\bar{1}$ 0) : (0 \bar{k} 1) = 57°, measured; angle (hkl) : (100) = 52°, measured; angle (\bar{h} k \bar{l}) : (100) = 52°30', measured.

A crystal of this form is shown in Fig. 2 in clinographic projection, together with a front elevation and plan of the orthographic projection. The projection may be oriented by comparison with the clinographic view which is drawn with the crystallographic *c*-axis vertical.

No attempt was made to assign axial ratios or Miller indices instead of symbols because the angular measurements were not sufficiently complete. The crystal faces of the specimens examined were not smooth enough to allow precise reflection measurements and the low melting point of the crystals which made it necessary to carry out some of the measurements out of doors in cold weather limited the angles obtained to a few simple zones. Consideration of the observed symmetry of both crystals combined with careful plotting of the angles that could be measured was sufficient, however, to establish the crystal system and class of each variety.

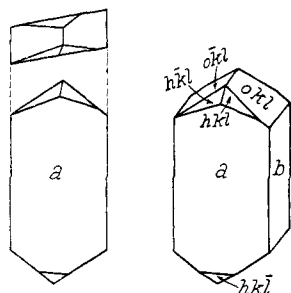


Fig. 2.— β -Furfuryl furoate—triclinic system. Pinacoidal class.

Densities.—The determination of the density of the beta form was a simple matter as the crystals could be easily obtained and readily weighed. They showed an average density of d_4 1.395. The alpha crystals again presented a more difficult problem. Individual crystals were too small and too unstable to go through all the necessary manipulations of a specific gravity determination. The density was determined by freezing portions of a freshly distilled ester in small test-tubes and loosening the rods thus formed, by slight warming. With a sample of the pure ester the resulting rods were very compact, smooth and showed depressions or holes usually only at the top. Those that showed imperfections on the sides were not used, as the ester is not wetted by water and air inclusions were certain to result. In all other cases the upper portion was broken off and the rods which were about 32 mm. long and weighed from 3 to 4 g. were rapidly weighed in air and in water at 4° . The room temperature was maintained at about 10° during the determination. After the weighing was done the melting point was determined, to make certain there had been no formation of the beta form.

The average of four determinations gave $d_4 = 1.330$.

Pseudomorphism of the Beta Form.—When crystals of the alpha form are allowed to stand for a few days in the cold they will pass into the beta form but will maintain the crystalline form of the alpha. The melting point of these crystals which soon after their formation was 19.5° becomes 27.5° and if placed in a supercooled liquid phase of the ester they will grow into crystals of the beta form. The rearrangement into the beta form evidently takes place gradually and without passage through the liquid phase. This was probably due to their being kept at a temperature of 0° , when the heat of transformation was so rapidly radiated that no melting took place. This is not the case where the crystals of the alpha form are brought in contact with the beta at ordinary temperature

just below 19° for then the alpha crystals can be seen to melt and the liquid to recrystallize into the beta form.

Discussion.—We are dealing here without doubt with a case of dimorphism. The very marked difference in melting point of the two forms, a difference which cannot be accounted for on the basis of chemical composition, would be sufficient evidence. In addition, however, we have shown the difference in the crystalline structure, the stable form belonging, as usual, to a less symmetric system than the unstable. Again, the difference in densities is quite marked, being higher by nearly 6% in the case of the stable beta form.

Furthermore, the fact brought out in a previous paper that the passage from the alpha to the beta form takes place with evolution of heat settles the question as to which is the stable and which the unstable form under atmospheric conditions.

Summary

1. The two forms of furfuryl furoate have been shown to crystallize in different systems. The unstable form crystallizes in the monoclinic system, prismatic class and the stable beta form in the triclinic system, pinacoidal class.

2. The alpha form shows d_4 1.330 and the beta form d_4 1.395.

3. Attention is called to the pseudomorphism of the beta form.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

ORIENTATION IN THE BENZENE RING. THE BROMINATION OF PYROGALLOL-2,6-DIMETHYL ETHER

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In an investigation on the oxidation of certain halogenated derivatives of pyrogalloldimethyl ether, it was desired to make the *p*-bromo derivative. On account of the strong orienting influence of the methoxyl groups, it did not seem certain that the bromine would enter the *para* position to the hydroxyl. For instance, Brand and Collischonn¹ showed that the action of acetic anhydride introduces an acetyl group *meta* to the hydroxyl. On the other hand Hofmann,² and Graebe and Martz³ showed that by the Reimer-Tiemann's reaction, syringic aldehyde is formed.

It has been found that the first bromine atom substitutes in the *meta* position, giving the 3-bromo derivative as the sole product that can be

¹ Brand and Collischonn, *J. prakt. Chem.*, 103, 329 (1922).

² Hofmann, *Ber.*, 11, 1455 (1878).

³ Graebe and Martz, *Ber.*, 36, 1031 (1903).