[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BIRMINGHAM-SOUTHERN COLLEGE]

The Structure of X-Chlororesorcinol

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In a recent investigation, the author obtained a considerable quantity of a material which corresponded in all its characteristics with the compound listed in Beilstein as "x-chlororesorcinol." This material was first prepared by Reinhard,[1] who obtained it by treating resorcinol with sulfuryl chloride. In an attempt to determine the structure of this compound, Reinhard endeavored to replace the chlorine atom with a hydroxyl group by fusion of the compound with sodium hydroxide and also potassium hydroxide, but he obtained no trihydroxybenzene, even when he heated the materials as high as 250°. Heating above 250° caused charring to take place.

The author attempted to convert chlororesorcinol into the corresponding trichlorobenzene by prolonged heating with phosphorus pentachloride. A sample of chlororesorcinol, even when heated for eight hours at 250° with phosphorus pentachloride, gave only a rubber-like residue from which no material resembling any of the trichlorobenzenes could be extracted. When a temperature lower than 250° was used, no reaction took place.

It seemed likely that the chlorine atom was in the ortho position with respect to one hydroxyl group and para with respect to the other; accordingly, a synthetic method for making this compound was devised. The physical constants of the material obtained, as well as those of several of its derivatives, were then found and compared with those obtained by Reinhard with his "x-chlororesorcinol."

Chlorobenzene was chosen as the starting point, and from it 2,4-dinitrochlorobenzene was prepared. The nitro compound was then reduced to the corresponding amine, 2,4-diaminochlorobenzene. The physical constants for these materials compared closely with those recorded in the literature. The amino compound was diazotized and the diazonium groups then replaced by hydroxyl groups.

Experimental

2,4-Dinitrochlorobenzene.—The method of Einhorn and Fry[2] was used in the preparation of this compound, m. p. 49.5° (corr.) from alcohol.

2,4-Diaminochlorobenzene.—For the reduction of the nitro compound, the method of Beilstein and Kurbatow was used, m. p. 90–91° (corr.) from alcohol.[3]

Chlororesorcinol.—20.0 grams (0.140 mole) of 2,4-diaminochlorobenzene was dissolved in 500 cc. of 10% hydrochloric acid, to which had been added 200 g. of cracked

[1] Reinhard, *J. prakt. Chem.*, [II] **17**, 322 (1878).

[2] Einhorn and Fry, *Ber.*, **27**, 2457 (1894).

[3] Beilstein and Kurbatow, *J. Russ. Phys.-Chem. Soc.*, **11**, 370 (1879).

ice; 19.5 g. (0.280 mole) of c. p. sodium nitrite, dissolved in 200 cc. of water, was slowly added and the solution stirred constantly. The solution was then allowed to come slowly to room temperature. After standing overnight, the solution was distilled with steam. Nitrogen was evolved and a cream-colored crystalline material appeared in the distillate. When no more crystals came over, the distillate was filtered and the crystals carefully dried on a porous plate; yield 15.2 g. (96%). The crude material melted at 87–87.5°, and after two recrystallizations from alcohol it melted at 88.5–89.0° (corr.). Reinhard obtained a melting point of 89° for "x-chlororesorcinol." A mixed melting point determination, made on a portion of the material mixed with a sample of chlororesorcinol made by Reinhard's method, gave a value of 88.5–89.0°.

The bromine derivative, prepared according to Reinhard's method, melted at 103.5–104.0°, after one recrystallization from alcohol. Reinhard obtained a melting point of 105° for this compound.

The dibenzoyl derivative melted at 97° as compared with the value of 98° reported by Reinhard.

Analysis of the purified chlororesorcinol, as obtained by the above method, gave the following results: calcd., Cl, 24.53; found, Cl, 24.63. The method of Lemp and Broderson[4] was used in this analysis.

Conclusion

As a result of a synthetic method, in which chlororesorcinol was prepared from compounds of known structure, it has been shown that "x-chlororesorcinol" has the structure 1-chloro-2,4-dihydroxybenzene.

[4] Lemp and Broderson, THIS JOURNAL, **39**, 2069 (1917).

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Lipases of Wheat. I

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No studies of any of the lipases of wheat or its products have been reported in the literature. Furthermore, no references have been made concerning the importance of lipase in relation to the quality and storage of wheat products. Therefore considerable preliminary work is necessary in establishing the following fundamental facts (a) the most reliable method for the measurement of the lipase activity of wheat; (b) the best methods of extraction to increase the concentration of the enzyme from any given wheat product; (c) the distribution of the enzyme in the different milling separations of wheat; (d) the optimum conditions of time, temperature and P_H for wheat lipase activity as well as the specificity of different buffer mixtures, the effect of various activators and inhibitors and the action of the enzyme on various substrates. These preliminary experiments described here are intended to establish some of the variables influencing the activity of the lipases of wheat and its products.