solution was treated with 2.54 g. of iodine and shaken for half an hour. Mercuric iodide precipitated. The mixture was allowed to stand overnight and then refluxed for 15 minutes, treated with 0.5 g. of iodine in excess and refluxed for 15 minutes longer. The suspension was filtered from the mercuric iodide and excess of iodine. The filtrate was boiled to remove the color due to the dissolved iodine, concentrated to 30 cc. and cooled. On cooling, a pinkish crystalline precipitate formed; this was separated and dried at 100°. It became white. On concentrating the filtrate further a second precipitate of white crystals formed. The filtrate from these was evaporated to dryness. The residue weighed 2.5 g. and was ground with phosphorus pentachloride to form the acid chloride. The amide was prepared from the chloride and ammonium carbonate. The melting points of the amide and chloride were 185° and 68.9°, respectively.

Samples of the known compounds were prepared from 2-aminotoluene-4-sulfonic acid by diazotizing, replacing with iodine and preparing the acid chloride and amide in the usual way. The melting points of the amide and chloride prepared in this way were 68.2° and 184.5°, respectively.

Mixed melting points of the amide obtained from the mercury compound and the amide of the known 2-iodotoluene-4-sulfonic acid were obtained as follows: 184.5–185° for a ratio of known to unknown of 1:2, and 184–184.5° for a ratio of 2:1.

Summary

1. The mercuration of aromatic sulfonic acids takes place with extreme ease and rapidity.

2. The mercuration of sodium aromatic sulfonates is a much slower process.

3. *p*-Toluenesulfonic acid is mercurated in the position *meta* to the sulfonic acid group to form 2-hydroxymercuri-toluene-4-sulfonic acid.

Evanston, Illinois

[Contribution from the Plaut Research Laboratory of Lehn and Fink, Incorporated]

THE PREPARATION OF 2,4-DIHYDROXYDIPHENYLMETHANE AND OF 2,4-DIHYDROXYDIPHENYLETHANE

By Emil Klarmann

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Alkyl derivatives of resorcinol achieved a prominent interest recently, because it was shown that it is possible to increase the germicidal properties of resorcinol considerably by the introduction of certain alkyl groups into its nucleus. In the course of our investigations on the influence of the nature of the substituent on the germicidal action we studied the introduction of aromatic groups into phenols.

The method of introduction of substituents which was applied by us differs from that used by Johnson[1] and co-workers and by V. Leonard.[2] These authors first allowed a fatty acid to act on resorcinol in the presence of zinc chloride and reduced the keto compound thus obtained. We

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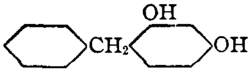
[1] Johnson and Lane, This Journal, **43**, 348 (1921).

[2] Leonard, *J. Am. Med. Assoc.*, **83**, 2005(1924).

obtained a direct substitution with an aryl group in the case of 2,4-dihydroxydiphenylmethane I by the action of benzyl chloride on resorcinol in the presence of aluminum chloride in nitrobenzene solution.

On the other hand, we obtained the same product by first preparing the 2,4-dihydroxybenzophenone from the corresponding keto-imido hydrochloride, using Hoesch's method[3] of condensation of benzonitrile with resorcinol and reduction of the ketone. We further prepared the 2,4-dihydroxydiphenylethane II by the reduction of the corresponding *m*-dihydroxydesoxybenzoin. The latter was prepared by condensation of benzyl cyanide with resorcinol which led first to a keto-imido hydrochloride, and transformation of the latter into the keto compound. This ketone has already been studied by Finzi[4] and E. Chapman and H. Stephen.[5]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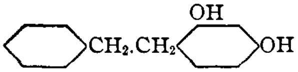
II

The phenol coefficient of the 2,4-dihydroxydiphenylmethane is about 22 and that of 2,4-dihydroxydiphenylethane about 40. Their toxicities are very low, since a preliminary test shows that 0.5 g. of either does not produce any harmful action on guinea pigs. The marked increase of the antiseptic properties of resorcinol by the introduction of the benzyl group suggested the study of the question, whether the introduction of this group in other compounds, such as phenol, would produce a similar action. We therefore prepared the corresponding 4-hydroxydiphenylmethane which was first obtained by Liebmann,[6] the phenol coefficient of which, however, had apparently never been determined. We found the phenol coefficient to be only 4.6; and 0.5 g. is non-toxic to guinea pigs.

Experimental Part

Preparation of 2,4-Dihydroxydiphenylmethane. METHOD 1.—

To a cooled solution of 20 g. of resorcinol in 100 cc. of freshly distilled nitrobenzene were added 12 g. of benzyl chloride and 12 g. of dry aluminum chloride. The flask was then connected with an air condenser fitted with a calcium chloride tube and heated on a water-bath. The evolution of hydrogen chloride fumes started at about 50°. The mixture was heated for two hours, the temperature being gradually increased to 70°. The dark solution was mixed with crushed ice, and after separation from water and the addition of a like amount of ether, was shaken repeatedly with a 10% sodium hydroxide solution until no further coloration of the latter took place.

The collected alkaline extracts were shaken with ether in order to remove the adhering nitrobenzene and then acidified with hydrochloric acid. A heavy, dark oil separated. The entire mixture was boiled for a half hour. After cooling, the mixture was extracted with ether. The oil obtained after the evaporation of ether was then subjected to a vacuum distillation. The main portion distilled at 210° to 215° (12 mm.)

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[3] Hoesch, *Ber.*, **48**, 1122 (1915).

[4] Finzi, *Monatsh.*, **26**, 1128 (1915).

[5] Chapman and Stephen, *J. Chem. Soc.*, **123**, 404 (1923).

[6] Liebmann, *Ber.*, **14**, 1844 (1881).

as a heavy, light yellow oil, which began to solidify after several days. This process of solidification could be accelerated by rubbing under petroleum benzine; m. p., 76–77° when recrystallized from benzene; yield, 50%.

Anal. Subs., 24.983 mg.: CO_2, 71.80 mg.; H_2O, 13.4 mg. Calcd. for $C_{13}H_{12}O_2$: C, 78.00; H, 6.04. Found: C, 78.34; H, 6.01.

METHOD 2.—For the preparation of 2,4-dihydroxybenzophenone, the method of Hoesch[3] was rather closely followed.

Five g. of resorcinol and 5 g. of benzonitrile were dissolved in 40 cc. of dry ether, 2 g. of zinc chloride was added and a dried stream of hydrogen chloride was allowed to pass through the mixture in the course of three hours. The resulting sirupy mass was allowed to stand overnight in the ice box. Then 30 cc. of 1:1 hydrochloric acid was added and the mixture shaken and cooled until it was filled with a yellow crystalline mass of the keto-imido hydrochloride. This was filtered off, washed first with water, then with ether, dried, dissolved in 500 cc. of water and boiled for 25 minutes. The *m*-dihydroxybenzophenone precipitated in the cold as fine needles; they showed the properties demanded by Komarowsky and v. Kostanecki.[7]

This product was reduced. Five g. was heated with 25 g. of amalgamated zinc and 1:3 hydrochloric acid for eight hours. The reaction product was shaken out with ether, the latter evaporated, and the oil distilled in a vacuum. We obtained a compound showing the same properties as those described above; yield, 30% of the resorcinol.

Preparation of 2,4-Dihydroxyoxydiphenylethane.—The condensation of benzyl cyanide and resorcinol, leading first to *m*-dihydroxydesoxybenzoin, was carried out in the same way as described for the dihydroxybenzophenone; yield, about 75%.

After recrystallization from water and drying in a vacuum the product melted at 121°. This differs from the melting point obtained by Finzi[4] (m. p., 104°), and by Chapman and Stephen[5] (m. p., 115°). It gave a dark red coloration with ferric chloride. Finzi reported a black-violet color with this reagent.

Anal. Subs., 10.443 mg.: CO_2, 28.160 mg.; H_2O, 5.040 mg. Calcd. for $C_{14}H_{12}O_3$: C, 73.66; H, 5.30. Found: C, 73.56; H, 5.40.

This compound was subjected to reduction by heating with amalgamated zinc and 1:3 hydrochloric acid for 16 hours and occasional addition of fresh acid. After recrystallization from water the product melts at 131°; yield, 70% of the keto compound used. It gives no coloration with ferric chloride.

Anal. Subs., 10.513 mg.: CO_2, 30.090 mg.; H_2O, 6.780 mg. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.06; H, 7.21.

Preparation of 4-Hydroxydiphenylmethane.—The interaction between benzyl chloride and phenol (equimolecular parts) was effected in the presence of zinc chloride according to the method of Liebmann. The reaction product was isolated by means of sodium hydroxide as described in the case of the dihydroxydiphenylmethane Method 1.

After the distillation in a vacuum, several fractions were isolated. The fraction boiling at 160–165° (10 mm.) was redistilled. A colorless oil was obtained which solidified instantly when the walls of the vessel were rubbed with a glass rod. The crystalline mass was spread on a porous porcelain plate. The crystals after drying melted at 82° to 83°.

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[7] Komarowsky and v. Kostanecki, *Ber.*, **27**, 1998 (1894).

Anal. Subs., 20.90 mg.: CO_2, 63.482 mg.; H_2O, 11.11 mg. Calcd. for $C_{13}H_{12}O$: 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.

BLOOMFIELD, NEW JERSEY

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

THE DIMORPHISM OF FURFURYL FUROATE

BY J. E. ZANETTI AND P. F. KERR

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In a previous paper one of us[1] 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).