Diphenyl-di-(2-dimethylaminoethoxy)-methane.—A solution of 18 g. (0.2 mole) of 2-dimethylaminoethanol, 27 g. (0.1 mole) of diphenyldichloromethane[5] in 100 ml. of xylene was refluxed for one hour then 18 g. of powdered anhydrous potassium carbonate added. This mixture was refluxed with vigorous stirring for five days. Potassium carbonate was added at twenty-four hour intervals until a total of 72 g. of carbonate had been introduced. The product was separated by distillation *in vacuo*. Redistillation gave 15 g. (44%) of the desired ketal, b. p. 190–195° (5 mm.)

Anal. Calcd. for $C_{21}H_{30}O_2N_2$: N, 8.19. Found: N, 7.87.

Diphenyl-di-(2-dimethylaminoethoxy)-methane Disuccinate.—A solution of 3.42 g. (0.01 mole) of the preceding ketal in 20 ml. of acetone and 2.36 g. (0.02 mole) of succinic acid in 50 ml. of absolute ethanol gave a crystalline product. Two recrystallizations of this product from acetone yielded 3.9 g. (68%) of very hygroscopic crystals, m. p. 97–100°.

Anal. Calcd. for $C_{29}H_{42}O_{10}N_2$: N, 4.85. Found: N, 4.85.

Diphenyl-di-(2-diethylaminoethoxy)-methane.—This compound was prepared in 51% yield from 2-diethylaminoethanol and diphenyldichloromethane in the manner previously described, b. p. 217–223° (5 mm.).

Anal. Calcd. for $C_{25}H_{38}O_2N_2$: N, 7.03. Found: N, 6.75.

Diphenyl-di-(2-dimethylaminoethoxy)-methane Dimethiodide.—A solution of diphenyl-di-(2-dimethylaminoethoxy)-methane in benzene was added to an excess of methyl iodide. The white precipitate was filtered to give 88% of the dimethiodide, m. p. 232–233° (dec.).

Anal. Calcd. for $C_{23}H_{36}O_2N_2I_2$: N, 4.47. Found: N, 4.31.

Diphenyl-di-(2-piperidinoethoxy)-methane.—This substance was prepared by the above method. The yield was 23% of the theoretical, b. p. 215–230° (1 mm.).

Anal. Calcd. for $C_{27}H_{38}O_2N_2$: N, 6.64. Found: N, 5.96.

Diphenyl-di-(2-piperidinoethoxy)-methane Disuccinate.—This salt was prepared from the above ketal as in the previous experiments, m. p. 76–78°.

Anal. Calcd. for $C_{35}H_{50}O_{10}N_2$: N, 4.25. Found: N, 4.36.

---

[5] Gattermann and Schultze, *Ber.*, **29** 2944 (1896).

DENTON, TEXAS RECEIVED NOVEMBER 25, 1949

Preparation of Gentisic Acid

BY FRANK J. VILLANI AND JOSEPH LANG[1]

The recent publication of Morris[2] on the synthesis of 2,5-dihydroxybenzoic acid, gentisic acid, (I) prompted us to report some of the work carried out in our laboratory on the synthesis of this compound. Two methods were studied for the preparation of this compound. Hydroquinone monomethyl ether on treatment with carbon tetrachloride and concentrated sodium hydroxide in the presence of catalytic quantities of copper powder under the conditions of the Reimer–Tiemann reaction gave 70–75% of 2-hydroxy-5-methoxybenzoic acid (II), Method A.[3] The demethylation of II with hydrobromic acid yielded gentisic acid in yields of 60–65%.

The second procedure, Method B, involves the sodium hypochlorite oxidation of 2,5-dimethoxyacetophenone (III) to 2,5-dimethoxybenzoic acid (IV) and subsequent demethylation of IV to gentisic acid. The over-all yield in this method was 65–70%. Compound III was obtained by the Friedel–Crafts acylation of hydroquinone dimethyl ether.[4]

The melting point of gentisic acid has been reported by several authors[5] to be between 196–200°. Our preparation of gentisic acid, which was purified by sublimation under reduced pressure and final recrystallization from an ether–petroleum ether mixture, melted at 204.5–205°. This melting point is in agreement with that reported by Morris.[2]

Experimental

Method A. 2-Hydroxy-5-methoxybenzoic Acid.—A mixture of 62 g. (0.5 mole) of hydroquinone monomethyl ether, 100 g. of carbon tetrachloride, 300 cc. of 50% aqueous sodium hydroxide and 2 g. of copper powder was heated with stirring under reflux for eight hours. The mixture was cooled, poured into water, acidified with concentrated hydrochloric acid and filtered. The precipitate was dissolved in dilute sodium bicarbonate, treated with charcoal, filtered and the filtrate acidified with hydrochloric acid. The product was filtered and recrystallized from water, yield 66 g. (74%), m. p. 142–144°, m. p. lit.[6] 143.5°.

Gentisic Acid.—Twenty-five grams of 2-hydroxy-5-methoxybenzoic acid was heated under reflux for four hours with a mixture of 30 cc. of 48% hydrobromic acid and 30 cc. of glacial acetic acid. The glacial acetic acid was removed by vacuum concentration and the residue was extracted with ether until the aqueous solution produced no coloration with a ferric chloride solution. After removing the ether, the residue was triturated with petroleum ether and filtered. The yellowish-white crystalline product was dissolved in the minimum quantity of ethyl acetate, treated with charcoal and precipitated with petroleum ether; yield 14 g. (65%), m. p. 189–191°, m. p. lit.[5] 196–200°.

Method B. 2,5-Dimethoxyacetophenone.—This procedure is a modification of that reported in ref. 4a by which the yield of the product has been increased from 46 to 71%.

To a well-stirred ice-cold solution of 27.6 g. (0.2 mole) of hydroquinone dimethyl ether, 18.7 g. of acetyl chloride and 50 cc. of carbon disulfide, 60 g. (0.45 mole) of anhydrous aluminum chloride was added portionwise under anhydrous conditions. After all the aluminum chloride had been added (three-quarters to one hour), the flask was removed from the ice-bath, and allowed to warm to room temperature and finally heated on the steam-bath for three hours. The thick, viscous mixture was poured onto ice and the carbon disulfide removed by warming on the steam-bath. After cooling, the residue was extracted with ether, the ether extracts dried and distilled. There was obtained 25.5 g. (71%) of a yellow oil boiling at 156–160° (15 mm.), b. p. lit.[4] 155–158° (14 mm.).

2,5-Dimethoxybenzoic Acid.—Chlorine gas was bubbled into a solution of 60 g. (1.5 moles) of sodium hydroxide in 85 cc. of water and 350 g. of ice until 44.7 g. (1.26 atoms) was absorbed. This mixture was warmed to 50° and 25 g. (0.14 mole) of 2,5-dimethoxyacetophenone was added

---

[1] Present address: Florida State University, Tallahassee, Florida.

[2] Morris, THIS JOURNAL, **71**, 2056 (1949).

[3] The carboxylation of hydroquinone to gentisic acid is described in German Patent 258,887 (1912). We were unable to duplicate this procedure employing hydroquinone, but excellent results were obtained with hydroquinone monomethyl ether.

[4] (a) Klages, *Ber.*, **37**, 3996 (1904); (b) Kauffmann and Beisswenger, *ibid.*, **38**, 789 (1905).

[5] Senhofer and Sarlay, *Monatsh.*, **2**, 448 (1881); Miller, *Ann.*, **220**, 113 (1883); Tiemann and Müller, *Ber.*, **14**, 1988 (1881); Raistrick and Simonart, *Biochem. J.*, **27**, 628 (1933); Mauthner, *J. prakt. Chem.*, **156**, 150 (1940).

[6] Graebe and Martz, *Ann.*, **340**, 215 (1905).

dropwise with stirring, maintaining the temperature at 60–70°. After one hour, the excess sodium hypochlorite was removed by the addition of 14 g. of sodium bisulfite in 60 cc. of water, the mixture cooled and acidified with hydrochloric acid. The precipitated acid was recrystallized from water after charcoal clarification; yield 18 g. (72%), m. p. 78–79.5°, m. p. lit.[7] 76°.

Gentisic Acid.—Fifteen grams of 2,5-dimethoxybenzoic acid was demethylated by refluxing with 25 cc. of 48% hydrobromic acid and 25 cc. of glacial acetic acid for eighteen hours. The gentisic acid was isolated as in Method A; yield 7.5 g. (60%).

Purification of Gentisic Acid.—The gentisic acid, obtained from several demethylation experiments, was combined and sublimed at 1 mm. pressure at a bath temperature of 120–140°. The sublimed product was recrystallized from ether–petroleum ether giving white crystalline gentisic acid melting at 204.5–205°.

---

[7] Tiemann and Muller, *Ber.*, **14**, 1993 (1881).

CHEMICAL RESEARCH DIVISION
SCHERING CORPORATION
BLOOMFIELD, NEW JERSEY

RECEIVED OCTOBER 13, 1949

An Initial Increase in Capillary Rise Shown by Aging Aqueous Solutions of 4-*n*-Hexylresorcinol

BY E. ROGER WASHBURN AND H. N. DUNNING

During an investigation of the changes in surface tension which accompany the aging of these solutions, an unexpected increase in capillary rise was sometimes observed at the start of the study. Since no published explanation was found which seemed to account for the phenomenon, a careful study of it was undertaken.

The 4-*n*-hexylresorcinol, m. p. 68.3°, was supplied by the Sharpe and Dohme Company. The redistilled water used in preparing the solutions contained no surface active impurities.

The capillarimeter and cathetometer and the general procedure for locating the large meniscus have been described by Transue.[1] The measurements were made at 25.00°.

Solutions of 0.00025 and 0.00250 molarity were investigated many times with carefully observed and controlled procedures. The results may be summarized as follows. Whenever a certain procedure, which we refer to as the ordinary procedure, was used, the capillary rise was observed to decrease continuously from the start, rapidly at first and then more slowly, until an equilibrium value was reached. For example a 0.0025 *m* solution showed an initial rise of 4.11 cm., after 27 min. 3.98 cm., and after 227 min. 3.67 cm. After 20 hours the capillary rise was 3.17 cm.

In this ordinary procedure the liquid was forced nearly to the top of the capillary, and allowed to drain down, several times before the initial characteristic position was located.

When the procedure was modified either by taking care never to wet the capillary tube more than a very small distance above the characteristic position or by making certain that it was not wet for more than a very short time before taking the first reading, a different behavior was noted on aging. In place of the continuous fall from the start, an initial rise to a maximum was observed. The usual fall then took place. Typical results observed with a 0.00250 molar solution are presented in Table I.

TABLE I

Age, min.	Cap. rise, cm.	Age, min.	Cap. rise, cm.	Age, min.	Cap. rise, cm.
1	4.20	13	4.76	40	4.41
2	4.25	15	4.78	50	4.30
3	4.30	17	4.78	60	4.23
5	4.36	19	4.78	70	4.16
7	4.41	21	4.73	90	4.07
9	4.55	25	4.64	110	3.99
11	4.68	30	4.55	1408	3.11

It seems improbable that ionization of the solute, which has been suggested for what may be a similar case,[2] offers an explanation for this case.

Because of the low volatility of the solute it seems improbable that differences in the rates of its evaporation and diffusion[3] are responsible for the increase in this case.

An important difference in the two procedures of determining the initial characteristic position of the meniscus is that in the ordinary procedure opportunity is given for the glass surface in the vicinity of the characteristic position to become covered or saturated with the surface-active solute before the position is located. In the modified procedure no such opportunity is provided. Adsorption at the liquid–glass interface in the vicinity of the meniscus may remove solute from the liquid–air surface layer more rapidly than it can be replaced by diffusion to and absorption within this layer.

The solution making up this layer of the meniscus thus becomes more dilute and therefore rises in the capillary tube above its initial characteristic position.

However, the adsorption of the solute at the liquid–air interface is continually going on and its effect is to lower the surface tension of this interface. Eventually, this effect plus the action of gravity equals and then predominates over the tendency to increase the surface tension of the liquid–air interface due to adsorption of the solute at the liquid–glass interface. The slowing down of the rate of adsorption at the liquid–glass due to increased distance for diffusion and to a decrease in proportion of active spots available for adsorption makes it possible for the adsorption at the liquid–air interface to equal and then surpass that for the liquid–solid interface. The capillary rise then decreases as the solution ages.

AVERY LABORATORY
UNIVERSITY OF NEBRASKA
LINCOLN 8, NEBRASKA

RECEIVED OCTOBER 4, 1949

---

[1] L. F. Transue, E. R. Washburn and F. H. Kahler, THIS JOURNAL, **64**, 272 (1942).

[2] J. M. Andreas, E. A. Hauser and W. B. Tucker, *J. Phys. Chem.*, **42**, 1001 (1938).

[3] E. R. Washburn and C. H. Shildneck, THIS JOURNAL, **55**, 2354 (1933).