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3-PHENYLCATECHOL AND RELATED SUBSTANCES

C. F. H. ALLEN AND J. A. VANALLAN

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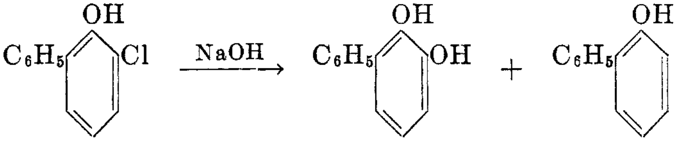
All the homonuclear dihydroxybiphenyls except the 2,3-dihydroxy derivative, 3-phenylcatechol, have been described in the literature.[1] Since this substance appeared to be of interest in connection with other work, its preparation was undertaken.

The reaction employed was alkaline fusion of 2-chloro-6-phenylphenol, essentially by the patented procedure (5), using a mixture of aqueous sodium and barium hydroxides. Upon vacuum-distillation of the reaction product, after acidification, two fractions in about equal amount were collected. The lower-boiling fraction proved to be *o*-phenylphenol, while the higher-boiling one was the expected 3-phenylcatechol. The reaction, thus, proceeds according to the outline.



The replacement of halogen by hydrogen in alkaline fusions is not uncommon; it is called reduction (9).

In view of the unexpected formation of so much *o*-phenylphenol, a similar fusion of 3-bromo-4-hydroxybiphenyl was carried out. The crude material likewise consisted of two fractions, but in very unequal portions; the lower-boiling fraction (approximately one-eighth of the material) was 4-hydroxybiphenyl, while the higher-boiling one was 4-phenylcatechol. It was not possible to separate completely the 4-phenylcatechol from the 4-hydroxybiphenyl by recrystallization. Although the melting points of the catechol and its diacetate were close to that recorded in most of the literature, a single recrystallization of the diacetate raised its melting point fifteen degrees. Furthermore, regeneration of the dihydroxy compound by hydrolysis gave a 4-phenylcatechol with a good melting point, lower than that recorded in the literature. The various melting points of the catechol and its diacetate are collected in Table I.

After this work had been completed, an abstract of a paper by Abe (1) appeared;[2] on consulting the original article, it was found that he, too, recorded the higher melting point for the diacetate and the lower for the catechol, and that his values were in complete agreement with ours. By Abe's method of preparation there was no possibility of contamination with 4-phenylphenol; hence these values must be regarded as correct.

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[1] The isomers are 3,4-(4-phenylcatechol) (1, 5, 8); 2,4- (9); 2,5- (3); 2,6- (7); and 3,5- (9).

[2] This abstract is entirely erroneous. A correct abstract appears in *Chem. Abstr.*, **43**, 2181 (1949).

The properties of all the monohydroxy- and homonuclear dihydroxybiphenyls, and related substances, are collected in Table II.

TABLE I

MELTING POINTS OF 4-PHENYLCATECHOLS AND THEIR DIACETATES

SOURCE	CATECHOL, °C.	DIACETATE, °C.
Norris, *et al.* (8)	136–136.5	77–77.5
Harvey (5)	144.8–145.2	77.5–78
Our Crude	146–148	75–77
Our Pure	139–140	90.5–91.5
Technical grade	147–149	—
Abe (1)	141	92

TABLE II

PROPERTIES OF HYDROXYBIPHENYLS AND RELATED SUBSTANCES

SUBSTANCE	M.P., °C.	B.P., °C.	M.P., °C. DIACETATE	M.P., °C. DIBENZOATE
2,3-Dihydroxybiphenyl (3-Phenylcatechol)	113–114	325–328/746	78–79	88–89
3,4-Dihydroxybiphenyl (1, 5, 8) (4-Phenylcatechol)	139–140	363–366/755	90.5–91.5	96–97
2,4-Dihydroxybiphenyl (9)	145	—	—	—
2,5-Dihydroxybiphenyl (3)	96	—	73	—
2,6-Dihydroxybiphenyl (7)	138.5	—	—	—
3,5-Dihydroxybiphenyl (9)	157–158	—	—	—
2-Phenylphenol	57–58	260–263/762 142–144/10	63–64	71–72
3-Phenylphenol (6)	78	—	34–34.2 (11)	—
4-Phenylphenol	159–160	310–314/752	88–89	150

EXPERIMENTAL

Starting materials. (a) *2-Chloro-6-phenylphenol.* The available "Practical" grade of this substance, m.p. 67–71°, evolved hydrogen chloride upon distillation (b.p. 275–278°/762 mm.) and left a residue. However, after one redistillation, followed by a crystallization from ligroin (b.p. 90–120°), it formed pure white plates, m.p. 75–76°.

(b) *3-Bromo-4-hydroxybiphenyl.* This was obtained by following the published procedure (2).

3-Phenylcatechol. A mixture of 204.5 g. (1 mole) of 2-chloro-6-phenylphenol, 120 g. (3 moles) of sodium hydroxide, 315 g. (1 mole) of barium hydroxide octahydrate, 5 g. of copper sulfate (4), and 480 ml. of water was placed in a shaking autoclave and heated to 135°. Shaking was then started, and the temperature was raised to 260–270°, at which point it was kept for ten hours. After cooling to room temperature, the semi-solid contents of the bomb were transferred to a 4-liter beaker and rinsed with water. The combined rinsings and product were then acidified (to Congo Red paper) with concentrated hydrochloric acid, boiled one-half hour, chilled, and extracted with two 500-ml. portions of benzene. The solvent was evaporated and the residue distilled *in vacuo* from a flask having a fractionating sidearm. Two fractions were collected; the lower-boiling portion came over at

135–155°/10 mm. (69 g., 41%) and the higher-boiling one at 155–185°/10 mm. (61 g., 33%). On redistillation of the first fraction at atmospheric pressure, 63 g. (37%) was collected at 260–265°/759 mm.; the solid distillate was then recrystallized from ligroin; it melted at 57–58°, and there was no depression on admixture with an authentic specimen of *o-phenylphenol.*

The second fraction was also redistilled at atmospheric pressure, b.p. 325–328°/746 mm. (175–178°/10 mm.); the yield was 57 g. (30.6%), m.p. 111–113°. On further purification by recrystallization from ligroin, the melting point was raised to 113–114°. *3-Phenylcatechol* is very sparingly soluble in water.

Anal. Calc'd for $C_{12}H_{10}O_2$: C, 77.3; H, 5.4.

Found: C, 77.0; H, 5.7.

4-Phenylcatechol. This substance was obtained by the procedure used for the 3-phenyl isomer, but heating for about ten hours at 180–185°. The two fractions were collected at 170–185°/11 mm. (18.3 g., 17%; m.p. 153–156°) and 185–208°/13 mm. (133 g., 72%; m.p. 136–139°). Upon redistillation at atmospheric pressure, the first fraction gave 14 g. (8.2%) of *p-phenylphenol,* m.p.[3] 159–160°; b.p. 310–314°/752 mm. There was no depression of the melting point on admixture with a specimen of authentic *p*-phenylphenol (4-hydroxybiphenyl).

The second fraction was redistilled and the main product was collected at 358–367°/752 mm.; m.p. 138–140°, in a yield of 126 g. (67.7%). There was no decomposition during any of the distillations. After one recrystallization from xylene, the melting point was 139–140°.

Anal. Calc'd for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4; O, 17.2.

Found: as prepared: C, 77.8; H, 5.6; O, 17.0.

Found: regenerated from diacetate: C, 77.2; H, 5.3.

Other boiling points are 363–366°/755 mm.; 203–205°/13 mm. The product of Norris (8) had a boiling point above 360°, and hence it was largely the *4-phenylcatechol.*

4-Phenylcatechol is soluble in xylene and in warm water, sparingly soluble in ligroin (b.p. 90–120°), but very soluble in methanol and benzene. This distilled product appears to contain a trace of 4-hydroxybiphenyl, judging from the high carbon content. The substance regenerated from analytically pure diacetate gives the correct analysis.

Attempts to prepare 4-phenylcatechol by an Elbs persulfate oxidation (10) of 4-phenylphenol were unsuccessful; most of the phenol was recovered unchanged.

Esters. (a) *4-Phenylcatechol diacetate.* To a solution of 90 g. of 4-phenylcatechol and 450 ml. of acetic anhydride there was added a few drops of concentrated sulfuric acid. The solution became warm and darkened in color. After standing for one-half hour, it was poured into 1 liter of ice water, with rapid stirring. After standing one to two hours, the solid was collected on a filter, washed, and air-dried. The yield was 126 g. (96%), m.p. 74.5–77°. A single recrystallization from 150 ml. of benzene (to which 450 ml. of petroleum ether, b.p. 35–55°, was subsequently added) gave 113.5 g. (90% recovery), with the melting point, 90–91.5°. The melting point was unchanged by a second similar recrystallization, but was very slightly raised (m.p. 90.5–91.5°) by the use of 95% ethanol.

Anal. Calc'd for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2.

Found: C, 71.0; H, 5.3.

Hydrolysis to regenerate 4-phenylcatechol was accomplished by refluxing for one hour a mixture of 90 g. of the diacetate, 180 ml. of 20% hydrochloric acid, and 200 cc. of alcohol. On pouring into cold water with vigorous stirring, beautiful white plates formed; they were washed, and dried at 45° (temperature in drying cabinet). The product melted at 137–139°, with a slight sintering at 136°. The yield was 58 g. (93.5%). It was recrystallized from benzene and petroleum ether, as described above, to obtain an analytical sample.

(b) *4-Phenylcatechol dibenzoate.* A mixture of 90 g. of 4-phenylcatechol, 200 ml. of dioxane, 90 ml. of pyridine, and 155 g. (127 ml.) of benzoyl chloride, was warmed on the steam-bath for fifteen minutes and then cooled by adding ice and 1.5 liters of water. An

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[3] After one recrystallization from xylene.

oil separated, which was partially solid the next day; on stirring, it solidified and was collected on a filter. The yield was 197.5 g., m.p. 84–92°. It was dissolved in 250 ml. of absolute ethanol, decolorized by Norit, allowed to crystallize, and collected as before; the recovery was 167 g. (87.5%), m.p. 94.5–96°, with previous shrinking at 93°. The crystallization was repeated, the product melting at 96–97°; a repetition gave an ester, m.p. 96–96.5°, which was unchanged on recrystallization from ligroin (b.p. 65–90°) or isopropyl alcohol.

Anal. Calc'd for $C_{26}H_{18}O_4$: C, 79.2; H, 4.6.
Found: C, 79.2; H, 4.6.

The *dibenzoate* tends to oil out from alcoholic solutions, and it is often advantageous to inoculate the solution with a little of the solid ester.

Hydrolysis of the dibenzoate, to regenerate 4-phenylcatechol, was accomplished by suspending 5 g. of the ester in 20 ml. of methanol, adding a solution of 1.67 g. of 85% potassium hydroxide in 10 ml. of methanol, and swirling, which resulted in complete solution of the ester. The odor of methyl benzoate became noticeable. After ten minutes, the solution was poured into water, and the ester extracted with ether. A little sodium hydrosulfite was added to lighten the color of the aqueous layer, after which it was acidified by addition of concentrated hydrochloric acid. The yellow oil that separated was seeded with a bit of 4-phenylcatechol, but considerable manipulation was required before satisfactory crystallization was achieved. The crude product, isolated in a yield of 74%, melted at 134–137° with previous sintering; however, on recrystallization from benzene, it melted at 137.5–138°, and a mixed melting point was not depressed.

(c) *3-Phenylcatechol diacetate.* This was prepared by the same procedure as that for the 4-isomer. It may be recrystallized from ligroin (b.p. 90–120°) or alcohol. It melts at 79–79.5°; a mixed melting point with the 4-isomer is 62–70°.

Anal. Calc'd for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2.
Found: C, 71.1; H, 5.2.

(d) *3-Phenylcatechol dibenzoate* was likewise prepared by the Einhorn procedure. It has m.p. 89° after recrystallization from ligroin or alcohol; the mixed melting point with the 4-isomer is 75–80°.

Anal. Calc'd for $C_{26}H_{18}O_4$: C, 79.2; H, 4.6.
Found: C, 79.3; H, 4.2.

(e) *o-Phenylphenol acetate* has a melting point of 63–64° after crystallization from ligroin.

Anal. Calc'd for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7.
Found: C, 79.5; H, 5.6.

SUMMARY

The preparation and properties of 2,3-dihydroxybiphenyl are described.
4-Phenylcatechol and its diacetate have been obtained in a pure condition.

ROCHESTER 4, NEW YORK

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