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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

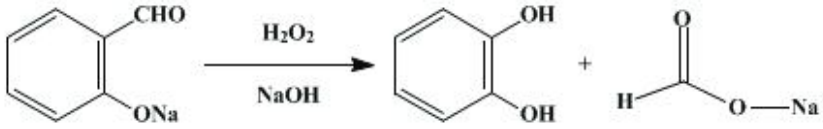
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CATECHOL

[Pyrocatechol]

[(*A*) (*from Salicylaldehyde*)]



Submitted by H. D. Dakin
Checked by H. T. Clarke and E. R. Taylor.

1. Procedure

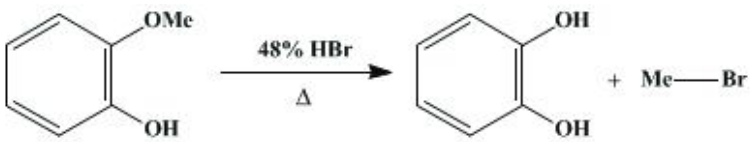
To a solution of 122 g. (1 mole) of pure salicylaldehyde (Note 1) in 1000 cc. of normal sodium hydroxide solution at room temperature, is added 1420 g. (1.2 moles) of 3 per cent hydrogen peroxide. The mixture darkens slightly in color and the temperature rises to 45–50°. The solution is allowed to stand for fifteen to twenty hours, whereupon a few drops of acetic acid are added in order to neutralize any excess alkali, and the solution evaporated to complete dryness on the water bath under reduced pressure.

The solid residue is finely crushed and warmed nearly to boiling with 500 cc. of toluene; the mixture is then poured into the folded filter paper of an extraction apparatus (p. 375) and extracted with boiling toluene for five hours. The toluene is allowed to cool and is decanted from the catechol, which crystallizes out. The insoluble material is again ground up and extracted in the apparatus with the decanted toluene. The combined product, weighing 70–76 g., consists of light brown plates melting at 104°, and is thus pure enough for many purposes. A further 6–12 g. of catechol can be obtained on distilling off the bulk of the toluene from the mother liquor. In order to obtain an entirely pure product, the crude catechol should be distilled under reduced pressure, when it passes over entirely at 119–121° /10 mm. (or 113–115° /8 mm.), and the distillate recrystallized from about five times its weight of toluene. In this way, colorless plates melting at 104–105° are obtained. The yield of the purified product is 76–80 g. (69–73 per cent of the theoretical amount) (Note 2).

2. Notes

1. A considerably lower yield is obtained (50 per cent or less) if technical salicylaldehyde (not purified through the bisulfite compound) is employed.
2. The procedure described is applicable to almost all hydroxyaldehydes in which the hydroxyl and carbonyl groups occupy ortho or para positions relatively to each other;[1] in the latter case derivatives of hydroquinone are produced. When the hydroxyl and carbonyl groups occupy the meta position with respect to each other, no reaction takes place, as is also the case with certain ortho and para compounds containing nitro groups and iodine atoms. *o*-Hydroxyacetophenone and *p*-hydroxyacetophenone are also capable of yielding catechol and hydroquinone, respectively, under the above conditions.
3. Catechol may also be produced from salicylaldehyde by the use of certain derivatives of hydrogen peroxide, such as persulfates or sodium peroxide, but the method is far less convenient.

[(*B*) (*from Guaiacol*)]

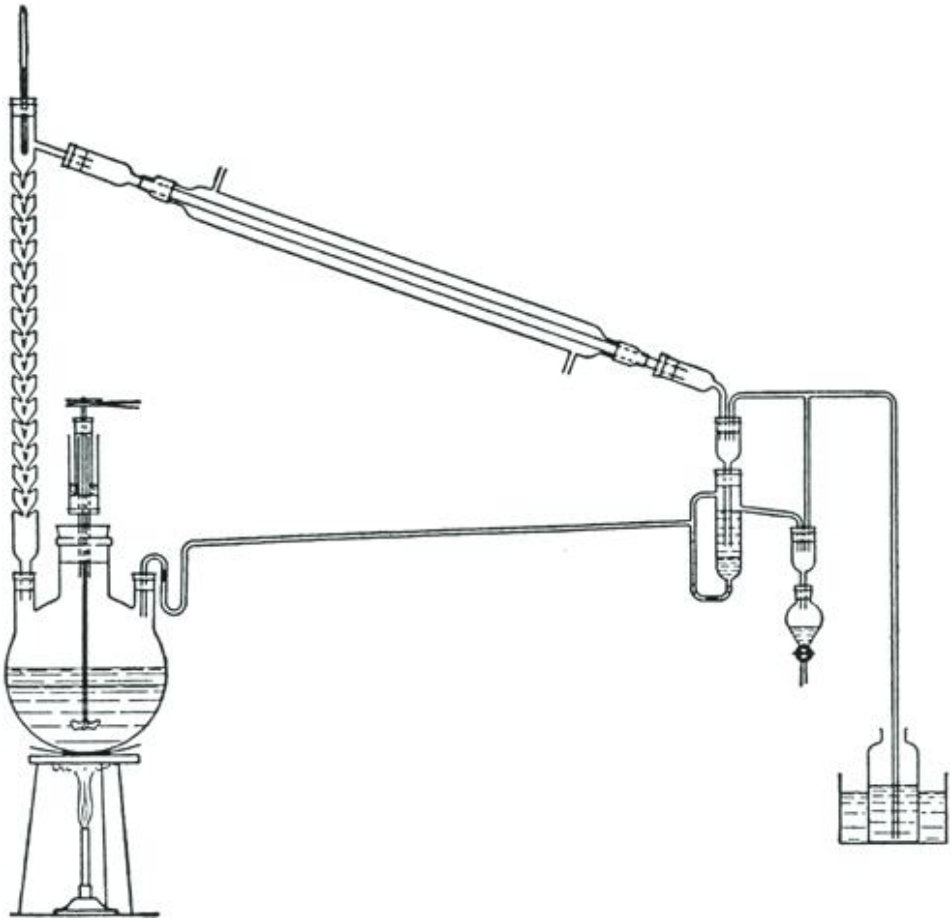


Submitted by H. T. Clarke and E. R. Taylor.
Checked by C. S. Marvel and W. B. King.

1. Procedure

In a 5-l. flask fitted with a stirrer, a thermometer reaching to the bottom, a fractionating column about 40 cm. long (Note 1), and a return inlet tube, are placed 912 g. (7.4 moles) of crystalline guaiacol and 1500 g. (1015 cc., 8.8 moles) of 48 per cent hydrobromic acid (p. 26). This apparatus is connected with a condenser, an automatic separator, and an absorption vessel, as shown in Fig. 10 (Note 2). The mixture is gently heated, with continual stirring, at such a rate that the vapor at the head of the column maintains a temperature of 85–95°. The mixture of water and guaiacol which condenses passes through the automatic separator (Note 3), the guaiacol being returned to the reaction vessel and the water collected in the tap funnel, from which it is removed from time to time. The gaseous methyl bromide is collected in an ice-cooled bottle containing a weighed quantity (about 1600 g.) of methyl alcohol (Note 4).

Fig. 10.



After six to seven hours, the temperature at the head of the column begins to rise above 95° and finally reaches 98°, at which point practically no more guaiacol passes over with the distillate. This requires about one hour more, after which the heating is stopped (Note 5). The increase in weight of the absorption bottle amounts to 400–500 g. (57–72 per cent of the theoretical amount of methyl bromide); the water collected weighs 550–560 g. (Note 6).

The residue in the flask, which has become pink in color, is extracted at 85–95° with three 1500-cc. portions of toluene (Note 7), and the united extracts are distilled under reduced pressure on the steam bath until no more moisture passes over with the vapor. The solution (2–2.5 l.) is then allowed to cool,

whereupon 385–390 g. of catechol separates in colorless plates melting at 104–105°. The mother liquor is further concentrated under reduced pressure and the residue finally distilled, pure catechol passing over at 124–125° / 12 mm. The distillate, on recrystallization from a small quantity of toluene, yields 8–10 g. of pure material.

The aqueous residue from the three extractions with toluene yields, when the bulk of the water has been distilled off on the steam bath under reduced pressure, a further quantity of catechol by extraction with hot toluene, but the crystals so obtained are contaminated with a red impurity. It is therefore preferable to distil the entire residue, again collecting the fraction boiling at 124–125° /12 mm. and recrystallizing it from fresh toluene. In this way 295–305 g. of pure product is obtained. The forerun contains a little aqueous hydrobromic acid, which may be employed in a subsequent batch. The total yield of pure catechol is 690–705 g. (85–87 per cent of the theoretical amount) (Note 8).

2. Notes

1. Any column of standard form is suitable; to work satisfactorily, it is unnecessary for it to be more than 40 cm. in length.
2. In the diagram (Fig. 10) no indication is made of joints in the glass tubing. These are, however, applicable at almost any desired point; but care should be taken to arrange them so that the ends of the glass tube come into contact, since methyl bromide appears to pass readily through the walls of the rubber tubing. It is necessary to make certain that the outlets from the automatic separator descend in an even incline and that the tubing itself is of sufficiently large diameter to prevent any siphoning effects.
3. It is noteworthy that the guaiacol which condenses is saturated with methyl bromide at the condensation temperature, so that it is necessary to prevent it from becoming warmer during its passage through the separator; otherwise the evolution of gas may hinder the ready formation of layers.
4. In order to secure satisfactory absorption of the methyl bromide, the methyl alcohol should be kept below 5° by ice-cooling.
5. Since the formation of the red by-product appears to depend upon the time during which the catechol is heated with hydrobromic acid, it is well to carry out the reaction as rapidly as possible; due care must be taken, however, that the temperature at the head of the column does not rise prematurely above 95°.
6. The water collected during the reaction contains practically no hydrobromic acid but is saturated with guaiacol and methyl bromide. Nevertheless, it scarcely pays to recover the dissolved compounds, for on distillation only 1–2 g. of wet guaiacol can be collected; while the value of the methyl bromide is in any case not very great.
7. It is suggested that carbon tetrachloride rather than toluene be used in the extraction because toluene gives a product which gradually colors, whereas the catechol extracted with carbon tetrachloride remains colorless for a considerably longer time (W. W. Hartman, private communication).
8. The reaction appears to be applicable to many other cases where the constitution of the molecule permits of boiling with strong hydrobromic acid.

3. Discussion

Catechol can be prepared by the oxidation of salicylaldehyde[1] and of phenol;[2] by the demethylation of guaiacol with aluminum chloride[3] and hydriodic acid;[4] by hydrolysis of ortho halogen-substituted phenols or ortho dihalobenzenes under suitable conditions;[5] and by the replacement of sulfonic groups by alkali fusion.[6] A series of reactions involving the oxidation of safrole, opening of the methylenedioxy ring, and decarboxylation also furnishes catechol.[7]

This preparation is referenced from:

Org. Syn. Coll. Vol. 3, 759

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ortho halogen-substituted phenols

ortho dihalobenzenes

acetic acid (64-19-7)

methyl alcohol (67-56-1)

sodium hydroxide (1310-73-2)

hydroquinone (123-31-9)

phenol (108-95-2)

HYDROBROMIC ACID (10035-10-6)

carbon tetrachloride (56-23-5)

aluminum chloride (3495-54-3)

toluene (108-88-3)

Catechol,
Pyrocatechol (120-80-9)

Salicylaldehyde (90-02-8)

hydrogen peroxide (7722-84-1)

sodium peroxide

Guaiacol (90-05-1)

methyl bromide (74-83-9)

hydriodic acid (10034-85-2)

safrole (94-59-7)

o-Hydroxyacetophenone (118-93-4)

p-hydroxyacetophenone (99-93-4)

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