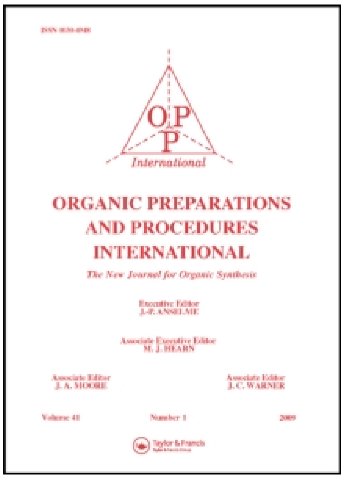

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PREPARATION OF BIS(4-HYDROXYPHENYL) ETHER

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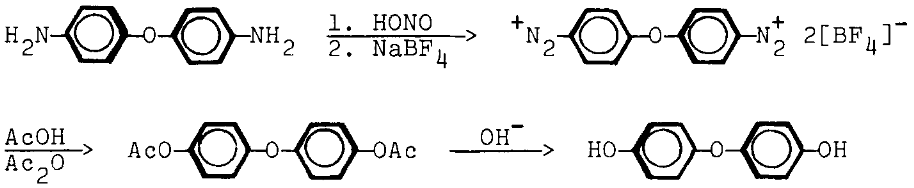
Bis(4-hydroxyphenyl) ether has been prepared by the decomposition of the *bis*-diazonium salt of *bis*(4-aminophenyl) ether with dilute aqueous sulfuric acid; only small amounts of the product could be isolated.[1] When the preparation was repeated in this laboratory, the black tarry mass obtained gave, after a tedious work-up, only 4-5% yield of pure product.

Haller and Schaffer[2] have reported a modified procedure for the preparation of phenols via the acetolysis of diazonium tetrafluoroborates. Although this method has not been used as frequently as the normal hydrolysis of diazonium salts, it seems to be a promising alternative for the preparation of phenols which are not accessible by the normal procedure.[3] This was realized in the following preparation.



Bis(4-aminophenyl) ether was diazotized to _bis_-diazonium chloride which was converted to _bis_-diazonium tetrafluoroborate. A smooth decomposition took place when the dried salt was refluxed in a 1:1 mixture of acetic acid and anhydride. The yield of _bis_(4-acetoxyphenyl) ether was 56% after purification. When either acetic acid or acetic anhydride was used, the yield was decreased to 20-35%. Addition of sodium acetate also had no favorable effect on the yield. The hydrolysis of the acetoxy derivative by methanolic potassium hydroxide gave a 87% yield of pure _bis_(4-hydroxyphenyl) ether.

Experimental

Diphenyl Ether 4,4'-Bis(diazonium tetrafluoroborate). In a 2 ℓ Erlenmeyer flask, 40.0 g (0.2 mole) of _bis_(4-aminophenyl) ether[4] was dissolved in 500 ml of 4N hydrochloric acid with external warming. The clear solution was then cooled with shaking, and fine crystals of the hydrochloride formed. After the hydrochloride suspension was diazotized in the usual manner,[5] a solution of 110 g (1.0 mole) of sodium tetrafluoroborate in 200 ml water was added to the cold diazonium solution with an efficient stirring. The mixture was stirred for an additional two hours with cooling, and the white diazonium fluoroborate was filtered, washed with cold water then with ether, and dried in a vacuum desiccator over calcium chloride. The yield was 78 g (98%). The crude tetrafluoroborate which melted at 93° (dec) was used for the acetolysis without further purification.

Bis(4-acetoxyphenyl) Ether. A mixture of 40.0 g (0.1 mole) of the bis-tetrafluoroborate, 100 ml of freshly distilled acetic anhydride, and 100 ml of glacial acetic acid was heated to gentle reflux in a 500 ml flask. After five hours, the clear reddish brown solution was cooled and poured into 1 ℓ of ice water. The white precipitate was removed by filtration, washed with water, dried, and recrystallized from hexane to give 16 g (56%) white plates, m.p. 110-112°.
IR bands: 1748 cm^{-1}(vs), 1220 cm^{-1}(vs), 1185 cm^{-1}(vs).
Anal. Calc'd. for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 67.24; H, 5.18.

Bis(4-hydroxyphenyl) Ether. A suspension of 14.3 g (0.05 mole) of bis(4-acetoxyphenyl) ether in 250 ml of 4N methanolic potassium hydroxide was refluxed for six hours. The reaction mixture was cooled and poured into ice water. The white precipitate which solidified on standing was collected on a Buchner funnel, washed with cold water, dried, and recrystallized from water to give 9.0 g (87%) of colorless platelets, m.p. 161-163°, lit.[1] 160-161°.
IR bands: 3360 cm^{-1}(vs,br), 1213 cm^{-1}(vs), 845 cm^{-1}(ms), 828 cm^{-1}(ms), 788 cm^{-1}(ms).

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