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4-METHOXYBENZENETHIOL

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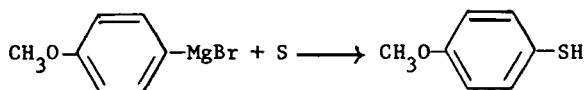
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4-METHOXYBENZENETHIOL

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We would like to bring to your attention a convenient and efficient procedure for the preparation of 4-methoxybenzenethiol by the treatment of p-methoxyphenylmagnesium bromide with sulfur¹, which has been overlooked in the literature in preference to other methods. Thus, 4-methoxybenzenethiol has been prepared by reduction of p-methoxyphenylsulfinic acid with zinc²; by reduction of p-methoxyphenylsulfonyl chloride with zinc³, tin⁴, red phosphorus and iodine⁵, or by electrolytic reduction⁶; and by diazotization of p-anisidine followed by treatment with potassium ethyl xanthate and alkaline hydrolysis.⁷

Experimental

p-Methoxyphenylmagnesium bromide A 5 l., three neck, round bottom flask, equipped with a condenser, thermometer, addition funnel and air-stirrer, was flame dried under nitrogen. Magnesium (38.8; 1.6 mole) was placed in the flask and covered with ether. One crystal of iodine was added, then about 20 ml of a solution containing 300 g. (1.6 mole) of p-bromoanisole in 1600 ml. of ether. Reaction started in a few minutes and the mixture was then stirred and refluxed while the rest of the above solution was

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added during about 1.5 hr. After the addition was completed, the mixture was refluxed for 1 hr.

4-Methoxybenzenethiol The above mixture was cooled to 30°. Solid sulfur (46.4 g; 1.45 mole) was added portionwise over 30 min. with only occasional cooling so that the temperature was 30-35°. The mixture was then stirred for 1 hr. at room temperature, cooled to 0° with a methanol-ice bath and decomposed by slow addition of 1600 ml. of 2.5 N hydrochloric acid keeping the temperature below 5°. The organic layer was separated⁸ and extracted with 2 N sodium hydroxide (5 x 200 ml.). The basic extract was cooled in ice and acidified with 650 ml. of 10% hydrochloric acid (check pH). The product was extracted with ether (4 x 200 ml.). The ether extract was washed with 200 ml. of saturated sodium chloride solution, dried (MgSO₄) and evaporated to give 134 g. of residue. Distillation through a 15 cm. Vigreux at 13 mm gave 110.6 g. (49% yield) of an oil boiling at 100-103° (no forerun, some pot residue present). $\frac{\text{EtOH}}{\lambda_{\text{max}}}$ 239 μ (10,000); 285.5 (1,300), sh 291 (1,250); $\frac{\text{Nujol}}{\nu_{\text{max}}}$ SH: 2560; C=C: 1590, 1570, 1490; C-O: 1285, 1240, 1180, 1175, 1030; aromatic: 820, C-S: 635, 625. Nmr (CDCl₃ solution, 60-Mc, tetramethylsilane): SH singlet at 201 cps, area 1; OCH₃ singlet at 244 cps, area 3; aromatic = typical para substituted pattern centered at 408 and 437 cps.

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8. Dissemination of bad odor can be avoided by working in a good hood without spilling and letting all the used equipment soak in 5% sodium hydroxide solution overnight.

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