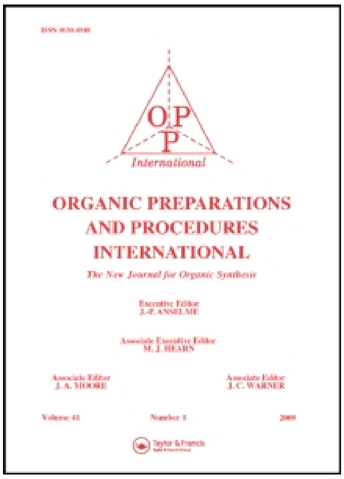

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4-METHOXYBENZENETHIOL

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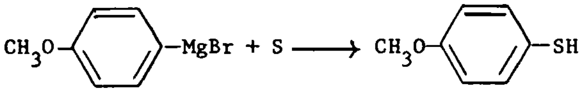

We would like to bring to your attention a convenient and efficient procedure for the preparation of 4-methoxybenzenethiol by the treatment of p-methoxyphenylmagnesium bromide with sulfur[1], which has been overlooked in the literature in preference to other methods. Thus, 4-methoxybenzenethiol has been prepared by reduction of p-methoxyphenylsulfinic acid with zinc[2]; by reduction of p-methoxyphenylsulfonyl chloride with zinc[3], tin[4], red phosphorus and iodine[5], or by electrolytic reduction[6]; 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 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 separated[8] 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 ($MgSO_4$) 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). λ_{max}^{EtOH} 239 mμ (10,000); 285.5 (1,300), sh 291 (1,250); ν_{max}^{Nujol} SH: 2560; C=C: 1590, 1570, 1490; C-O: 1285, 1240, 1180, 1175, 1030; aromatic: 820, C-S: 635, 625. Nmr ($CDCl_3$ solution, 60-Mc, tetramethylsilane): SH singlet at 201 cps, area 1; OCH_3 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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