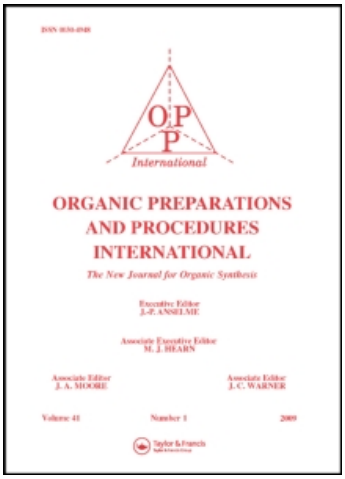

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A SIMPLE SYNTHESIS OF O-ISOPROPOXYPHENOL

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A SIMPLE SYNTHESIS OF O-ISOPROPOXYPHENOL†

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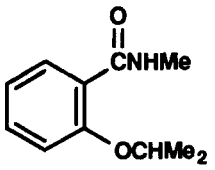
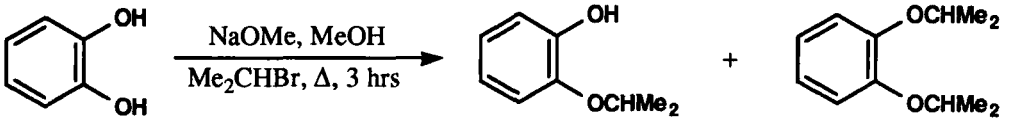
O-Isopropoxyphenol (**3**)[1] is a synthon for the carbamate insecticide propoxur (**1**).[2] Various methods have been reported for the preparation of (**3**) by dehydrogenation[3] of 1,2-cyclohexanedione monoenol ether or by monoalkylation[4] of catechol by isopropyl bromide. All the reported methods involve high temperature, pressure, long reaction time and use of phase-transfer catalysts. As most of the previous literature is covered by patents, details of the preparative methods are not known.



1

We now report a simple method for the preparation of **3** from catechol in 63% yield by refluxing catechol with isopropyl bromide in the presence of sodium methoxide in methanol for a short time. A simple and clean work-up allows the separation of the products.



2 **3** **4**

EXPERIMENTAL SECTION

The petroleum ether refers to fraction of bp. 60-80°. The IR spectra were recorded on a Pye-Unicam SP-3 IR spectrophotometer and the NMR spectra were obtained on a Varian T60 spectrometer using TMS as an internal standard. Yields are based on catechol consumed.

O-isopropoxyphenol (3).- Metallic sodium (1.3 g, 0.055 atom) was added to methanol (30 ml) and a solution of pyrocatechol (5.5 g, 0.05 mol) in methanol (10 ml) was added, followed by addition of isopropyl bromide (9 g, 0.075 mol). The mixture was refluxed for 3 hrs, cooled and diluted with water (80 ml). The solution was acidified with conc. HCl and extracted with petroleum ether (3 x 60 ml), followed by extraction with ethyl acetate (3 x 60 ml). The latter extract was washed with water, brine and dried (Na_2SO_4). Removal of solvent gave 2.3 g, (42%) unchanged pyrocatechol, mp. 105°. The petroleum ether extract was washed with 20% KOH (3 x 5 ml), water, brine, dried (Na_2SO_4). The solvent was removed and the residue was distilled to give 1,2-diisopropoxybenzene (**4**)[5] bp. 140°/4 mm, lit.[5] bp. 215°/630 mm, as a pale yellow oil (0.9 g, 16%). IR (neat): 3000, 1610, 1510, 1400, 1390, 1140, 980, 760 cm^{-1}. ^1H NMR (CCl_4): δ 1.2, 1.3 (d, 12H, J = 6 Hz, 2 x -CH(CH_3)$_2$), 4.43

(sept, 2H, 2 x -CH($C\underline{H}_3$)$_2$), 6.8 (s, 4H, aromatic).

The alkaline layer was acidified with conc. HCl and extracted with petroleum ether (3 x 60 ml). The organic layer was washed with water, brine, dried (Na_2SO_4). Removal of solvent and the distillation of the residue furnished a pale yellow oil (2.89, 63%) of O-isopropoxyphenol (**3**),[1] bp. 130°/4 mm, lit.[1] bp. 100-102°/11 mm. IR (neat) 3560, 3000, 1610, 1510, 1480, 1400, 1390, 1135, 790, 750 cm^{-1}. ^1H NMR (CCl_4): δ 1.23, 1.33 (d, 6H, J = 6 Hz, -CH($C\underline{H}_3$)$_2$), 4.46 (sept., 1H, -CH($C\underline{H}_3$)$_2$), 5.73 (s, 1H, OH), 6.6-6.9 (m, 4H, aromatic).

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SYNTHESIS OF METHOXYTAMOXIFEN

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In continuation of our earlier utilization of the heteroatom-facilitated lithiation of aromatic compounds[1] for the preparation of radiolabelled estrogens[2] and antiestrogens,[3] we needed to prepare methoxytamoxifen (**6**) and its radiolabelled derivatives. The key step in the synthesis of these antiestrogens is a Grignard reaction (Eq. 2). Since compounds having ether, hydroxy, amino and other similar groups are known to form the Grignard reagents in low yields, perhaps because of their