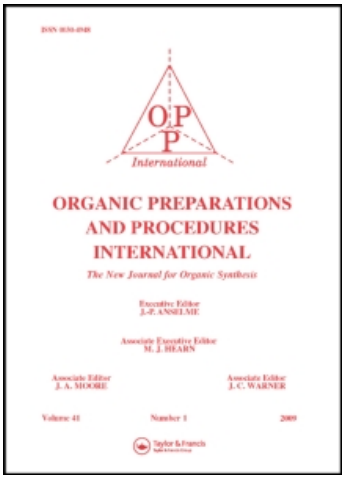

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SELECTIVE PREPARATION. 44. PREPARATION OF 4-HYDROXYPHENYL PHENYL THIOETHER USING *t*-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP

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SELECTIVE PREPARATION. 44.

PREPARATION OF 4-HYDROXYPHENYL PHENYL THIOETHER USING t-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP†

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(1/28/83)

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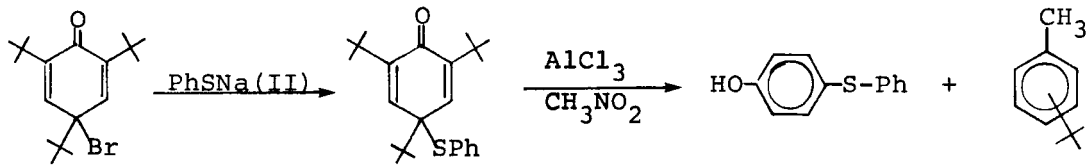
The aluminum chloride-catalyzed transalkylation of 4-aryloxy-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-ones, which were prepared by reaction of 4-bromo-2,4,6-tri-(t-butyl)-2,5-cyclohexadien-1-one (I) with the corresponding sodium phenoxides, afforded the corresponding 4-hydroxyphenyl aryl ethers.[1]

In the present work, the title compound (III) was prepared from I by application of the above reaction.



I III IV V

When I was reacted with sodium thiophenoxide (II) in THF at 70° for 5 min, the expected III was obtained together with IV and V. However, compound III was so labile that its purification could not be carried out by recrystallization or chromatography on silica gel.[2] Therefore, transalkylation of the crude III was carried out in toluene in the presence of $AlCl_3$-CH_3NO_2 catalyst at 60° for 3 hrs. The desired compound IV was obtained in 48% yield calculated from I together with V.

EXPERIMENTAL SECTION

Reaction of I with II.- To a solution of $NaOCH_3$ in methanol, prepared by addition of 0.67 g of Na in 20 ml of methanol, was added 3.2 g (20 mmol) of thiophenol under cooling with ice-water. The mixture was evaporated in vacuo to give sodium salt II. After a mixture of the obtained II and 9.9 g (20 mmol) of I in 60 ml of THF was heated at 70° for 5 min, the precipitated NaBr was filtered. The filtrate was evaporated in vacuo to give 3.8 g of crude III, which was used as a starting compound for preparation of IV without purification.

Transalkylation of III.- After a mixture of 3.8 g of the crude III and $AlCl_3$-CH_3NO_2 catalyst ($AlCl_3$ 4.1 g and CH_3NO_2 6 ml) in 163 ml of toluene was heated at 60° for 3 hrs with stirring, it was poured into a large amount of water and extracted with ether. The ethereal extract was extracted with aq. 10% NaOH. The alkaline solution was acidified with aq. 10% HCl and extracted with ether. The ethereal extract was washed with water, dried over Na_2SO_4 and evaporated in vacuo to leave the residue which was chromatographed on silica gel using benzene as an eluent to give 2.5 g (48% calculated from II used) of IV as a pale brown oil. IR(NaCl): ν_{OH} 3430 cm^{-1}; ^{1}H-NMR($CDCl_3$): δ 6.32 (s, 1H, O<u>H</u>) and 6.78 ∿ 7.48 (m, 9H, aromatic protons). The IR spectrum of IV agreed with that of an authentic sample.[3]

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2. For example, chromatography on silica gel using a mixture of hexane and benzene (1:1) as eluent, gave diphenyldisulfide and 2,4,6-tri-(t-butyl)phenol in 63% and 69% yields respectively.

3. O. Hinsberg, Ber., 36, 107 (1903).

SYNTHESIS OF 3-ACETOXY-1-METHYL AND 1-ETHYLINDOLES

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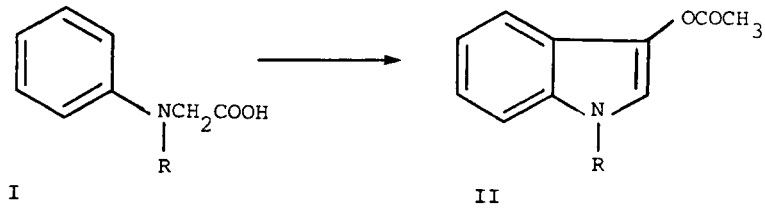
Indol-3(2H)-ones (indoxyls) (II) may be synthesized by the cyclization of the appropriate phenylglycines (I) or the appropriate 2-carboxyphenylglycine. Cyclizing agents for the former include sodium or potassium hydroxide[1] at 260° or sodamide with cyanide moderators;[2] however, the indoxyl once formed has a great tendency to oxidize to indigo unless air is rigorously excluded from the reaction and work-up procedures and yields tend to be low. Although cyclization of 2-carboxyphenylglycines proceeds smoothly using acetic anhydride and sodium acetate at reflux temperatures,[3,4] the corresponding N-substituted 2-carboxyphenylglycines are not readily available and



I II

a) R = CH_3 b) R = CH_3CH_2