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METAL-ASSISTED REACTIONS. PART 9. RAPID REPLACEMENT OF PHENOLIC HYDROXYL GROUPS BY HYDROGEN.

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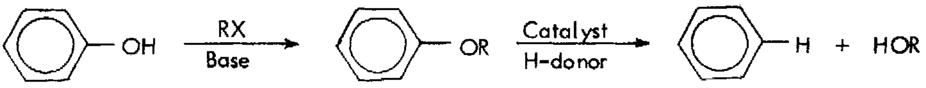
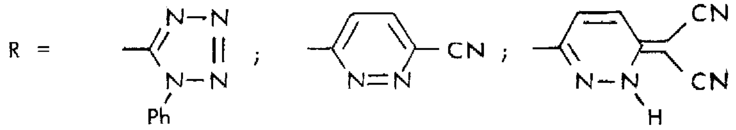
Abstract: Conversion of phenolic ethers to hydrocarbons by catalytic transfer hydrogenation is reported.

The removal of a phenolic hydroxyl group and its replacement by hydrogen is potentially a powerful synthetic reaction.[1-4] We have shown that catalytic transfer reduction using an H-donor can be more selective, rapid, and easier to carry out than catalytic hydrogenation using molecular hydrogen.[5] Our attention was drawn to a recent publication[6] in which the removal of a phenolic hydroxyl is reported for one compound using the conditions of transfer hydrogenation described in our earlier work. This work has prompted us to report our more extensive work carried out over the last two years.

Most of our work has centred on the conversion of the phenol into an electron-withdrawing ether, followed by catalytic transfer reduction of the ether into hydrocarbon (scheme 1). Several different groups, R, were examined but the most consistently successful has been 2-phenyltetrazolyl, as used for the catalytic hydrogenative removal of phenolic hydroxyls.[4] Whilst this, and other groups generally require long reaction times to convert the phenol into the corresponding ether, the conditions described below allow this first stage conversion of the phenol into an ether to be carried out in about 30 min. or less.



(Scheme 1)



Of the various metals investigated as potential catalysts in the reaction, only palladium was found to be fully effective. Metals such as rhodium, rhenium, and platinum were ineffective.

In the work mentioned above,[6] cyclohexene was used as the H-donor in the presence of a large proportion of palladium/charcoal catalyst; the conversion to hydrocarbon was not efficient nor high yielding. We have found cyclohexene to be one of the least effective H-donors in this type of deoxygenation. Of the other H-donors used in our earlier work (hydrazine, formic acid, formates, phosphorous acid, phosphites, phosphinic acid, phosphinates),[5] hydrazine and sodium phosphinate were found to be most effective with palladium/charcoal catalyst in a two-phase solvent system. With this system, reductive removal of the ether (scheme 1) could be carried out in one or two hours under mild conditions.

The following list shows some of the phenols investigated and the percentage yields, in parentheses, of the resulting isolated reduced product: 1-naphthol (naphthalene, 82%), 2-naphthol (naphthalene, 80), 4-methylphenol (toluene, 100), 2-methoxyphenol (anisole, 100), 4-cyanophenol (cyanobenzene, 95), 4-hydroxybenzoic acid (benzoic acid, 80), 4-aminophenol (aniline, 85), 4-hydroxyacetophenone (acetophenone, 85), 4-hydroxybenzaldehyde (benzaldehyde, 10), 4-hydroxybenzaldehyde acetal (benzaldehyde acetal, 61), 7-hydroxycoumarin (coumarin + 3,4-dihydrocoumarin, 91), 1-methylsulphonyl-7-hydroxynaphthalene (1-methylsulphonylnaphthalene, 75). The only observable side-products were caused by a slight amount of hydrolytic cleavage of the ether back to the phenol.

Experimental. In a typical experiment, 1-naphthol (1.5g; 10.4mmole) was dissolved in DMF (25ml) and reacted with 1-chloro-2-phenyltetrazole (1.88g; 10.4mmole) in the presence of potassium t-butoxide (1.23g; 11.0mmole) at 18^0 for approx. 50 min. The resulting 2-phenyltetrazolyl ether of 1-naphthol was recovered by pouring the reaction mixture into iced water. This ether (98.7mg; 0.34mmole) was dissolved in $C_6H_6/EtOH/H_2O$ (7:3:2; 12ml) and stirred with 10% Pd/C (100mg) catalyst (Engelhard). The H-donor, hydrazine (1.5ml; 64% aqueous solution) was added dropwise and stirring continued until t.l.c. showed that no starting material remained. The reaction mixture was filtered from catalyst and poured into alkali to give naphthalene (36.3mg). When sodium phosphinate was used as H-donor, the solution was refluxed gently and proceeded to completion in about the same time.

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