dioxane, benzene, toluene, cyclohexane, carbon tetrachloride, chloroform, dichloromethane, glacial acetic acid, and nitromethane. After removal of nitromethane by boiling to dryness, the recovered brown solid no longer dissolved in cyclohexene. No material could be recovered from cyclohexene solution by dilution with chloroform or with carbon tetrachloride. The spectrum between 2.5 and 15 μ of the brown solid showed absorption maxima at 2.85 (weak), 3.3, 6.2, 6.35 (shoulder), 6.85, 7.2, 7.9, 8.4 (broad), 9.2 (very broad), 9.6 (broad), 11.4 (weak, broad), 11.65, 12.25 (broad), 13.0–13.2 (shoulder), and 14.2–14.5 μ (weak, very broad).

(B).—The same reaction was run with 5.5 g. (0.030 mole) of 2,4,6-trimethylbenzoyl chloride and 1.7 ml. (0.031 mole) of 99.3% sulfuric acid. The residue, after heating, was dissolved in water, and the sulfuric acid removed as after reaction of benzoyl chloride with sulfuric acid. Evaporation of the water left a brown tacky sirup, which did not solidify even after several weeks in a vacuum desiccator over concentrated sulfuric acid.

Selective Etherification of *p*-Hydroxybenzyl Alcohol

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Preparation of the simple *p*-(and *o*-)-alkoxymethylphenols has generally been attended by difficulties on account of their strong tendency to resinify on heating, particularly in the presence of acids or bases.[2] Substituted alkoxymethylphenols are rather more stable in this respect, and it was noted early by Auwers and Baum[3] that these ethers were formed with great ease by merely heating a substituted hydroxybenzyl alcohol with the required etherifying alcohol. This procedure was extended to unsubstituted *o*- and *p*-hydroxybenzyl alcohols by de Jonge and Bibo,[2] who showed that the reaction proceeded without appreciable resinification by heating the mixture in a sealed tube at 150° for several hours.

It has now been found that selective etherification of *p*-hydroxybenzyl alcohol can be carried out by treating its solution in an alcohol with a strong acid cation-exchange resin at room temperature. In this way *p*-methoxymethylphenol and the corresponding ethyl ether have been conveniently prepared in moderate yield on a small scale. When a methanol solution of *p*-hydroxybenzyl alcohol was refluxed with the exchange resin, however, rapid polymerization occurred with formation of a resinous product.

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(2) J. de Jonge and B. H. Bibo, *Rec. trav. chim.*, **74**, 1448 (1955).

(3) K. Auwers and F. Baum, *Ber.*, **29**, 2329 (1896).

Experimental

p-**Methoxymethylphenol.** Zeo-Karb 225 exchange resin in the hydrogen form was thoroughly washed with water, and then methanol. A solution of 1.7 g. of *p*-hydroxybenzyl alcohol[4] in 9 ml. of pure methanol was allowed to stand with 3.4 g. of the resin for 12 hr. at room temperature. The resin was separated, washed with methanol, and the combined filtrate and washings evaporated *in vacuo*. The oily residue soon crystallized, and was washed with cold water and dried. Recrystallization from benzene gave the phenol as compact prisms, yield 1.1 g. (60%), m.p. 81.5–82.5°, (lit.[2] m.p. 82.5–83.5°).

When the methanol solution was refluxed with the exchange resin for 1 hr., and the mixture worked up as before, a white, water-insoluble, resinous material was obtained.

p-**Ethoxymethylphenol.**—Treatment of 1 g. of *p*-hydroxybenzyl alcohol with ethanol and Zeo-Karb 225 in the same way, followed by distillation, gave the phenol as an oil, yield 0.45 g. (37%), b.p. 118–120°/2 mm., which solidified on standing. It was recrystallized from benzene–petroleum ether, m.p. 50–51° (lit. m.p. 50–51°;[5] 56.5–57.5°[2]).

(4) *p*-Hydroxybenzyl alcohol was obtained by the lithium aluminum hydride reduction of ethyl *p*-hydroxybenzoate in the usual way.[6]

(5) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

(6) H. Mitawa, *Bull. Chem. Soc. Japan*, **27**, 53 (1954).

Dehydrogenation of Alcohols by Lithium Metal–Ethylenediamine System

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Previous workers[2,3] have shown that lithium metal in ethylenediamine and in aliphatic monoamines can reduce aromatic compounds to monoolefins. It has been shown[2,3] also that phenol can be reduced to cyclohexanone in the presence of lithium metal in amines. In unpublished work from our laboratories, we have found that lithium metal in ethylenediamine will reduce a variety of phenols to saturated and unsaturated ketones and alcohols.

The proposed mechanism[2b] for this reduction reaction suggests a stepwise 1,4-addition of two moles of hydrogen to the aromatic ring. The addition of a third mole of hydrogen to the isolated double bond is so slow that the monoölefin may be isolated. It is reasonable to predict from this proposed mechanism that the ketones from the reduction of phenols arise from the isomerization of an enol intermediate. The alcohol products

(1) American Chemical Society–Petroleum Research Foundation Undergraduate Fellow, 1961–1962.

(2) (a) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **76**, 631 (1954); (b) R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, *ibid.*, **77**, 6042 (1955).

(3) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).