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

F. H. C. STEWART[1]

Chemical Research Laboratories, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

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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.

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°;[6] 56.5–57.5°[2]).

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[1] Present address: Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, Israel.

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

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

[4] *p*-Hydroxybenzyl alcohol was obtained by the lithium aluminum hydride reduction of ethyl *p*-hydroxybenzoate in the usual way.[5]

[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

SHELBERT SMITH, RICHARD THOMPSON,[1] AND
E. O. WOOLFOLK

*Department of Chemistry, Central State College,
Wilberforce, Ohio*

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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

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[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).

TABLE I

Alcohol	Carbonyl product	% yield	M.p., °C., 2,4-D	
			Obs.	(Lit.)[a]
Cyclohexanol[b]	Cyclohexanone	54	157–158.5	(162)
2-Methylcyclohexanol	2-Methylcyclohexanone	38	134.5–135.5	(137)
n-Pentyl alcohol	*n*-Valeraldehyde	66	103–105	(106)
2-Hexanol	*n*-Butyl methyl ketone	45	103–106	(106)
2-Phenylethanol	Phenylacetaldehyde	25	118–120	(121)
1-Phenylethanol	Acetophenone	24	243–244	(250)
Benzyl alcohol	Benzaldehyde	80	234–236	(237)

[a] R. A. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956. [b] Another run in which 0.01 mole of lithium ethoxide was added to the reaction increased the yield of carbonyl compound to 76%.

could arise from the reduction of the ketones or by the direct reduction of the aromatic ring of the phenol.

This reducing system has been utilized in our studies on the synthesis of terpene compounds. In our studies, we have found that primary and secondary aliphatic and aromatic alcohols can be dehydrogenated to carbonyl compounds in the presence of lithium metal in ethylenediamine. The results of our investigation are shown in Table I.

Verification of the products of the dehydrogenation reactions was by gas chromatography. Confirmatory evidence was obtained by the preparation and determination of the melting points of the 2,4-dinitrophenylhydrazone derivatives of the carbonyl products.

Many references may be found in the literature on the dehydrogenation of alcohols; however, most of these reactions involve the vapor phase dehydrogenation of alcohols over a metal oxide catalyst such as copper oxide. Recently, a similar use of the lithium metal–ethylenediamine system has been reported for the dehydrogenation of certain dienes to yield aromatic hydrocarbons.[4] These authors propose that *N*-lithioethylenediamine is the active dehydrogenation agent. To our knowledge, this is the first reported use of the lithium metal–ethylenediamine system for the dehydrogenation of alcohols.

Experimental

All alcohols used in this work were purchased as C.P. grade chemicals and were used without further purification.

General Procedure.—Lithium Ribbon (0.8 g.-atom) cut in 1-in. strips was added to 77–100 ml. of ethylenediamine in a three-neck flask fitted with a stirrer and reflux condenser. A slow stream of nitrogen was admitted during the addition of lithium metal. The lithium metal–ethylenediamine solution was heated and stirred until all the lithium metal had dissolved, and no more gas evolution was observed. The appropriate alcohol (0.3 mole) was added slowly to the solution. After all the alcohol had been added the solution was refluxed 2–3 hr. The reaction mixture was cooled to room temperature and poured over ice. The solution was neutralized with solid carbon dioxide or hydrochloric acid. The organic material was extracted with ether. The products were then recovered from the ether extract by distillation.

The analysis of the reaction products was by gas chromatography at 150° using a 6 ft. × $^1/_4$-in. column packed with UCON 50 HB 2000 as the partitioning agent. The bands were identified by comparison of retention times with those of authentic samples. Quantitative determinations were made by comparing the area of the band of the carbonyl product and unchanged alcohol from the reaction mixture with the area of the band given by a known amount of an authentic sample of the respective carbonyl compound and alcohol.

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(4) L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958)

Cyclization of *N*-Phenylcarbamates of Ethynylcarbinols

KEIITI SISIDO, KEISUKE HUKUOKA,
MINORU TUDA, AND HITOSI NOZAKI

Department of Industrial Chemistry, Faculty of Engineering, Kyôto University, Kyôto, Japan

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In an attempt to dehydrate ethynylcarbinols (I) to enyne compounds (II), carbinols IB and IC were treated with phenyl isocyanate.[1] Under conditions as specified in the experimental part, however, crystalline products were isolated in both cases. The analyses agreed with the values calculated for the *N*-phenylcarbamates of these carbinols. Although the product similarly obtained from propargyl alcohol (IA) was found actually to be the corresponding *N*-phenylcarbamate (IIIA), those obtained from 1-ethynylcyclohexanol (IB) and ethynylcarbinol of dihydro-β-ionone (IC) did not show the characteristic infrared absorptions of the acetylenic and imide hydrogens.

The constitution IVB was assigned to the reaction product from IB, as the ozonolysis of IVB afforded a crystalline imide which was identical with 3-phenyl-5,5-pentamethylene-2,4-oxazolidinedione (VI) prepared independently from ethyl 1-hydroxycyclohexanecarboxylate (VII) as shown in the accompanying flow sheet. The

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(1) For the dehydration with phenyl isocyanate, see W. J. Bailey and F. Cesare, *Angew. Chem.*, **71**, 470 (1959).