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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Cyclization of *N*-Phenylcarbamates of Ethynylcarbinols

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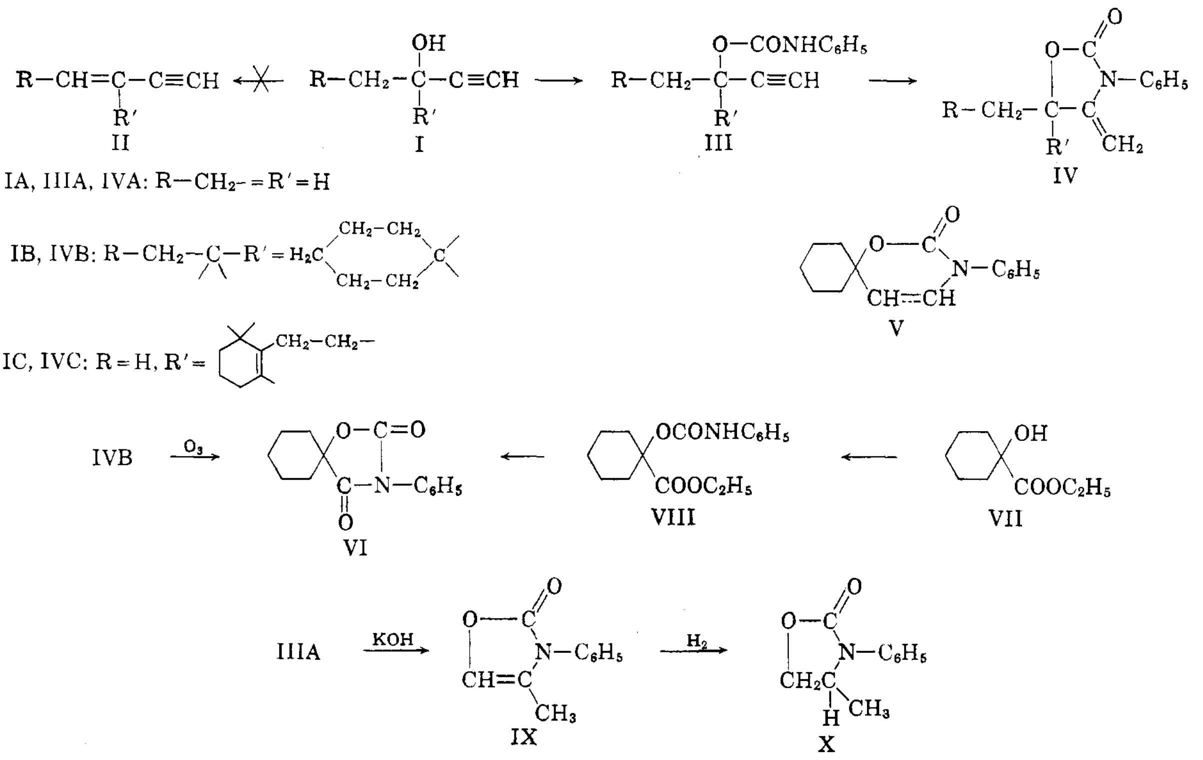
[4] L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958)

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



NMR spectrum[2] of IVB had two apparent singlets at τ 8.4 and 6.0 in an intensity ratio of 5:1. The former absorption is ascribed to the pentamethylene protons and the latter to the olefinic protons. A possibility of the cyclization product being a six-membered product (V) is excluded on the basis of the negligible coupling constant of olefinic protons[3] as well as of behavior on the ozonolysis. We would be safe to assume the constitution IVC for the product from ethynylcarbinol of dihydro-β-ionone in view of the analyses and infrared absorptions which are quite similar to IVB.

When propargyl *N*-phenylcarbamate (IIIA) was treated with potassium hydroxide, isomerization occurred to afford a cyclization product similarly lacking the infrared absorptions due to acetylenic and imide hydrogens. The NMR spectrum of this compound afforded an evidence supporting the constitution IX instead of the expected IVA. A doublet and a quartet were observed at τ 8.1 and 3.4, respectively, in an intensity ratio of 3:1 and with a coupling constant of 2.0 c.p.s. The former absorption is ascribed to methyl protons and the latter to olefinic proton. This product (IX) was subsequently hydrogenated over palladium to 3-phenyl-4-methyl-2-oxazolidinone (X), whose NMR spectrum could again be reasonably interpreted on the basis of the structure given. Methyl absorption appeared as a doublet at τ 8.9 with a coupling constant of 5.0 c.p.s., methine proton as a multiplet at τ 6.3, methylene protons as a polyplet at τ 5.7, and aromatic protons as a multiplet at τ 2.8, all these absorptions being observed in an intensity ratio of 3:1:2:5. Regarding the mechanism of the formation of IX, it would be judicious to assume the cyclization of IIIA to IVA and the following transposition of *exo*-cyclic double bond to an *endo*-cyclic one.[4]

Experimental[5]

NMR Measurements and Presentation.—Spectra were obtained for IVB on a 40-Mc. instrument in chloroform solution, for IX on a 56.4-Mc. instrument in chloroform solution, for X on a 56.4-Mc. instrument in carbon tetrachloride solution with water as an external reference, and for impure IVA containing IX on a 40-Mc. instrument in carbon tetrachloride solution with cyclohexane as an external reference. Chemical shifts actually observed are: for IVB at 5.65 (wt. 5) and 3.30 p.p.m. (wt. 1), higher fields from chloroform peak; for IX at 5.41 (wt. 3) and 0.64 p.p.m. (wt. 1), higher fields from chloroform peak; for X at 3.57 (wt. 3), 0.96 (wt. 1), and 0.36 p.p.m. (wt. 2), higher fields and at 2.55 p.p.m. (wt. 5), lower field from external water reference; and for impure IVA at 0.66 (wt. 0.44), 2.89 (wt. 2), 3.73 (wt. 2), and 5.40 p.p.m. (wt. 0.15), lower fields from external cyclohexane peak. These chemical shifts were converted

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[2] For NMR measurements and chemical shift presentation, see Experimental.

[3] For examples of low coupling constants of vinyl methylene protons, see J. N. Shoolery in the NMR-EPR Staff of Varian Associates, "NMR and EPR Spectroscopy," Pergamon Press, Oxford, 1960, p. 114.

[4] Attempted isolation of IVA afforded in one experiment a crystalline product, m.p. 97–98°, whose NMR spectrum showed two multiplets of equal intensity centering at τ 5.9 and 5.0, respectively, besides absorptions at τ 8.1 and 3.4 indicating the contamination with 13% of IX. The former absorptions should be ascribed to olefinic protons of *exo*-cyclic double bond and allylic protons of IVA. This product, however, could not be obtained in numerous experiments repeatedly carried out thereafter, supposedly due to the facile rearrangement of IVA to IX and to some unknown factors catalyzing the transposition of the double bond.

[5] All temperatures are uncorrected. Elemental analyses were carried out by Miss Kenko Ogawa.

into τ values given above, assuming τ values of 2.73 for internal (solvent) chloroform peak, 5.35 for external water reference, and 8.77 for external cyclohexane reference, for the sake of convenience in comparing shift values.

4-Methylene-5,5-pentamethylene-3-phenyl-2-oxazolidinone (IVB) from 1-Ethynylcyclohexanol (IB).—To a solution of 3.5 g. of IB[6] in 40 ml. of toluene, 3.7 g. of phenyl isocyanate was added and the mixture was heated under reflux for 4 hr. and then the solvent was removed under reduced pressure. The residue was diluted with about 40 ml. of petroleum ether (b.p. 30–60°) and this solution was extracted with 5% methanolic potassium hydroxide solution. The methanol layer was separated, neutralized with dilute hydrochloric acid, and extracted again with petroleum ether (b.p. 30–60°). Concentrating this petroleum ether solution, followed by two recrystallizations of the residue from petroleum ether (b.p. 30–60°), gave 6.4 g. (88%) of the oxazolidinone, m.p. 167–167.5°.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.12; N, 5.76. Found: C, 74.05; H, 7.04; N, 5.83.

Infrared absorptions (Nujol): 1750 (—O—CO—N<), 1643 (>C=C<), 954, 946, 838, 772, 767, 705 cm.$^{-1}$.

5-Methyl-4-methylene-3-phenyl-5-[2-(2,6,6-trimethyl-1-cyclohexenyl)-ethyl]-2-oxazolidinone (IVC).—A mixture of 1.8 g. of the ethynylcarbinol of dihydro-β-ionone,[7] 30 ml. of toluene, and 0.9 g. of phenyl isocyanate was heated under reflux for 4 hr. and the reaction mixture was treated similarly as above. Two recrystallizations of the product from petroleum ether (b.p. 30–60°) afforded the oxazolidinone, m.p. 129–130°.

Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.50; H, 8.72; N, 4.08.

Infrared absorptions (Nujol): 1750 (—O—CO—N<), 1643 (>C=C<), 981, 834, 765, 757, 702 cm.$^{-1}$.

5,5-Pentamethylene-3-phenyl-2,4-oxazolidinedione (VI) from IVB by Ozonolysis.—A solution of 200 mg. of IVB in 40 ml. of methylene chloride was saturated with ozonized oxygen at −75° during 20 min. and the reaction mixture was added dropwise into a suspension of 8 g. of zinc powder in 25 ml. of glacial acetic acid with vigorous stirring. The mixture was stirred for 3 hr. at room temperature, refluxed for 1 hr., and then concentrated. No formaldehyde could be isolated from the lower-boiling products. The concentration residue was diluted with water, filtered, and the filter cake was washed with ether. The filtrate was extracted with ether and all ether washings and extracts were combined, washed with water, dried, and concentrated to afford a crystalline residue, m.p. 133–136°. Recrystallizations from methanol gave colorless needles, m.p. 138–139°.

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16. Found: C, 68.36; H, 6.14.

Infrared absorptions (Nujol): 1810, 1750, and 1730 (—O—CO—N—CO—C), 764, 722, 687 cm.$^{-1}$.

***N*-Phenylcarbamate (VIII) of Ethyl 1-Hydroxycyclohexane Carboxylate (VII).**—To a solution of 2.2 g. of VII[8] in 10 ml. of toluene, 1.5 g. of phenyl isocyanate was added and the mixture was refluxed for 3 hr. and then concentrated. The yellow residue crystallized upon standing overnight. Recrystallization from methanol gave colorless needles, m.p. 109.5–110.5°.

Anal. Calcd. for $C_{16}H_{21}NO_4$: C, 65.95; H, 7.27. Found: C, 65.91; H, 7.41.

Infrared absorptions (Nujol): 3230 (N—H), 1735 (ester carbonyl), 1690, and 1550 (urethane) cm.$^{-1}$.

5,5-Pentamethylene-3-phenyl-2,4-oxazolidinedione (VI) from VIII.—In a small test tube 1 g. of the carbamate (VIII) was heated at 200–210° under 15 mm. for 30 min., then was recrystallized from ethanol to afford colorless needles, m.p. 139.5–140°. Analyses for carbon and hydrogen gave correct values, and the identity with the ozonolysis product of IVB above described was established beyond doubt by a mixed m.p. and by comparison of infrared spectra, which were completely superimposable.

4-Methyl-3-phenyl-4-oxazolin-2-one (IX).—To a solution of 5 g. of propargyl *N*-phenylcarbamate (IIIA)[9] in 200 ml. of ether was added several drops of 10% methanolic potassium hydroxide solution and the mixture was stirred for 10 min. at room temperature. After the reaction mixture was washed and dried, the solvent was removed by distillation and the residue was recrystallized from methanol to afford 2 g. of colorless needles, m.p. 97.5–98°.

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.61; H, 5.18; N, 8.00. Found: C, 68.56; H, 5.18; N, 8.08.

Infrared absorptions (Nujol): 1760 (—O—CO—N<), 1683, 1635 (>C=C<), 773, 740, 712 cm.$^{-1}$.

4-Methyl-3-phenyl-2-oxazilidinone (X).—A mixture of 2 g. of the oxazolinone (IX), 100 ml. of ethanol, and 1.2 g. of 30% palladium-charcoal[10] was shaken in an atmosphere of hydrogen at ordinary pressure and at room temperature. The calculated amount of hydrogen was absorbed during 8 hr. The catalyst was filtered and the solvent was removed. Recrystallization of the residue, which solidified on cooling, from ether afforded colorless needles, m.p. 52–52.5°.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.98; H, 6.39.

Infrared absorptions (Nujol): 1728 (>C=O), 755, 733, 690 cm.$^{-1}$.

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[6] J. H. Saunders, "Organic Synthesis," Coll. Vol. III, John Wiley and Sons, Inc., New York, 1955, 416.

[7] W. Oroshnik and A. D. Mebane, *J. Am. Chem. Soc.*, **71**, 2062 (1949).

[8] (a) J. D. Billimorin and N. F. Maclagan, *J. Chem. Soc.*, 3067 (1951); (b) J. Leon, W. F. Barthel, and S. A. Hall, *J. Org. Chem.*, **19**, 490 (1954).

[9] R. Lespieau, *Bull. soc. chim. France*, [4] **3**, 638 (1908).

[10] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, 1955, 685.

Reaction of Some Organic Compounds with Cupric Bromide

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Cupric bromide in methanol does not react with chalcones or 7-hydroxycoumarins either in the cold or hot. However, when dioxane is used in place of methanol, the reaction does take place to brominate the hydroxycoumarins and the chalcones.

Kochi[1] has reported the use of cupric chloride for the chlorination of acetophenone and diethyl ketone. Fort,[2] considering the usefulness of the applicability of this reaction, brominated isophorone, 3,4,5-trimethylanisole, β-naphthol, and 5,5-dimethylcyclohexane-1,3-dione by using cupric bromide in methanol or methanol–water at room

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[1] J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

[2] A. W. Fort, *J. Org. Chem.*, **26**, 765 (1961).