melting point and analysis identical with those of II but gave depressed mixture melting points with II and exhibited different infrared and p.m.r. spectra. The p.m.r. spectrum of a tetrahydrofuran solution of III showed a doublet centered at δ = 6.75 p.p.m., J_{P-CH} = 12 c.p.s., which integrated at 1:10 relative to the phenyl hydrogens at δ = 7.4 and 7.85 p.p.m.

The p.m.r. spectrum of a deuteriochloroform solution of 1,2-ethylenebis(diphenylphosphine)disulfide prepared from 1,2-ethylenebis(diphenylphosphine)[2] and either thiophosphoryl chloride in tetrahydrofuran or sulfur in benzene (m.p. 224–225° (acetone) (lit.[7] 196–198°). *Anal.* Calcd. for $C_{26}H_{24}P_2S_2$: C, 67.53; H, 5.19; P, 13.42; S, 13.85. Found: C, 67.06; H, 5.38; P, 12.59; S, 13.91) exhibited a doublet centered at δ = 2.8 p.p.m., J_{P-CH} = 2.5 c.p.s., which integrated in the ratio of 1:5 relative to the phenyl protons centered at δ = 7.6 and 7.9 p.p.m.

cis-1,2-Vinylenebis(diphenylphosphine) disulfide and dioxide were converted to *trans*-1,2-vinylenebis(diphenylphosphine) disulfide and dioxide, respectively, by reaction with phosphorus trichloride in refluxing tetrahydrofuran. Initial sulfur exchange followed by isomerization can be assumed.

$$cis\text{-}[(C_6H_5)_2PCH{:}]_2 + 2PSCl_3 \longrightarrow cis\text{-}[(C_6H_5)_2P(S)CH{:}]_2 + PCl_3$$

$$cis\text{-}[(C_6H_5)_2P(S)CH{:}]_2 + PCl_3 \longrightarrow trans\text{-}[(C_6H_5)_2P(S)CH{:}]_2$$

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RECEIVED OCTOBER 14, 1964

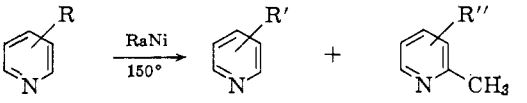
The α-Methylation of Pyridines by Primary Alcohols and Raney Nickel

Sir:

The metal-catalyzed coupling of pyridines and quinolines to their corresponding 2,2′-biaryls has been the object of considerable current research.[1] This communication reports an apparently related reaction in which pyridines are catalytically coupled with a one-carbon fragment to produce the corresponding α-methyl derivatives.

In the course of studies directed at a general synthesis of 1-azabicycloalkanes[2] we observed that reaction of 2-propanolpyridine (**1a**) with W-5 Raney nickel and hydrogen at 210° and 3000 p.s.i. did not produce indolizidine as expected[3] but instead gave a complex mixture whose two major constituents were 2-ethylpyridine (**2a**) and 2-methyl-6-ethylpyridine (**3a**), the products of dehydroxymethylation and dehydroxymethylation plus α-methylation, respectively. At 150° in the absence of an hydrogen atmosphere, 3- and 4-propanolpyridine (**1b** and **1c**) reacted in a similar manner, although under these somewhat milder conditions 2-propanolpyridine (**1a**) was only dehydroxymethylated (see Table I).

TABLE I
REACTION OF PYRIDYL ALCOHOLS WITH RANEY NICKEL



1 **2** **3**

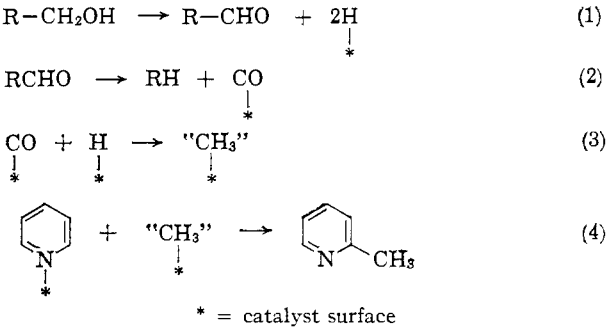
	R	R′ (% convn.[a])	R″ (% convn.[a])
a	2-$(CH_2)_3$-OH	2-C_2H_5 (27)[b]	6-C_2H_5 (24)[b]
a	2-$(CH_2)_3$-OH	2-C_2H_5 (50)	6-C_2H_5 (0)
b	3-$(CH_2)_3$-OH	3-C_2H_5 (28)	5-C_2H_5 (12)
c	4-$(CH_2)_3$-OH	4-C_2H_5 (35)	4-C_2H_5 (15)

[a] After 120 hr. [b] 210°, 3000 p.s.i. hydrogen.

The stoichiometry of these reactions suggests that the origin of the α-methyl group is the carbinol carbon of the starting primary alcohol **1**. This hypothesis was verified by the quantitative conversion of pyridine to α-picoline by means of a primary alcohol and Raney nickel.

In a typical experiment a mixture of 20 g. of *n*-decyl alcohol, 1 g. of pyridine, and 2 g. of W-5 Raney nickel was heated under reflux for 12 hr. at the end of which time the catalyst was removed by filtration and the α-picoline (100% yield) by acid extraction. The nonbasic products of this reaction were nonane (v.p.c., infrared, boiling point) and a small amount of what appeared to be decanal.

A probable mechanism for this reaction involves dehydrogenation of the primary alcohol (eq. 1) followed by decarbonylation of the resulting aldehyde to carbon monoxide and the hydrocarbon containing one less carbon atom (eq. 2).[4] The carbon monoxide, either as such or as some partially reduced species



"CH_3" produced by reaction with the hydrogen on the catalyst surface (eq. 3), then attacks the α-position of a pyridine nucleus which is selectively adsorbed on the catalyst surface by means of the free electron pair on nitrogen (eq. 4).[1]

Two observations consistent with this mechanism for α-methylation are (a) the existence of a pronounced steric effect as demonstrated by the greater difficulty of methylating 2-substituted pyridines (*i.e.*, **1a** → **3a**) and by the exclusive formation of the less hindered α-methyl derivative **3b** from **1b**; (b) the ability of carbon monoxide to act as the source of the new methyl

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(4) (a) V. N. Ipatieff, G. J. Czajkowski, and H. Pines, *J. Am. Chem. Soc.*, **73**, 4098 (1951); (b) J. A. Zderic, W. A. Bonner, and T. W. Greenlee, *J. Am. Chem. Soc.*, **79**, 1696 (1957).

group. Thus, heating a mixture of 3.2 g. of pyridine (0.4 moles), 100 ml. of cyclohexane, 2 g. of Raney nickel, and 0.4 moles of carbon monoxide at 225° and 1.7 atm. for 14 hr. led to a 35–40% conversion to α-picoline. This observation suggests that the α-methylation of pyridines as reported in this communication may be related to the hydroformylation reaction[5] as well as to the catalytic formation of biaryls.[1] Studies which are presently underway to elaborate further the scope and mechanism of this reaction will also investigate this possibility.

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(5) C. W. Bird, *Chem. Rev.*, **62**, 283 (1962).

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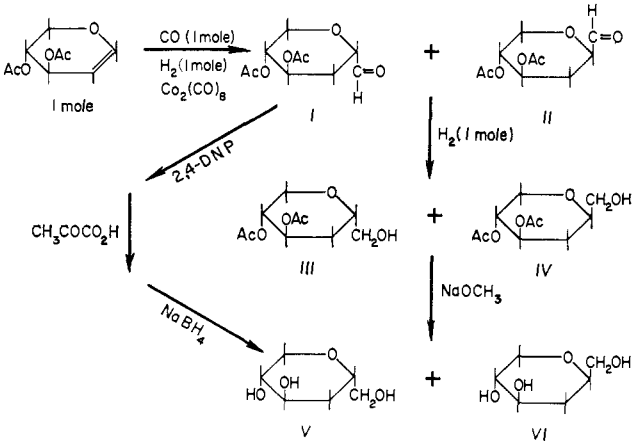
Hydroformylation of Glycals

Sir:

In this communication we wish to report the application of the oxo reaction[1] in the first direct conversion of glycals[2] into anhydrodeoxyaldoses. In earlier work[3,4] it was shown that glycals react with a mixture of carbon monoxide and hydrogen to give primarily a mixture of epimeric anhydrodeoxyalditols. We have now found that careful control of the conditions of this reaction affords mixtures of epimeric anhydroaldoses as well as the corresponding epimeric anhydroalditols. Presumably, under the normal conditions for the oxo reaction,[5] the anhydroaldoses are reduced to anhydroalditols. Under the modified conditions (as described below), 3,4-di-*O*-acetyl-D-xylal, for example, reacts with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl to yield 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*lyxo*-hexose (I) and 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*xylo*-hexose (II), in addition to the epimeric anhydrodeoxyhexitols III and IV.



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(2) B. Helferich, *Advan. Carbohydrate Chem.*, **7**, 209 (1952).

(3) A. Rosenthal and D. Abson, *Can. J. Chem.*, **42**, 1811 (1964).

(4) A. Rosenthal and H. J. Koch, *ibid.*, **42**, 2025 (1964).

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The general procedure used at the present time is as follows. A solution of 3,4-di-*O*-acetyl-D-xylal (12 g.), dicobalt octacarbonyl (3.4 g.), and anhydrous benzene (50 ml.) is allowed to react in a 300 ml. Aminco rocking autoclave with a mixture of 34 atm. of carbon monoxide and about 160 atm. of hydrogen at a temperature of 115°. It is important that the reaction be stopped when 2 moles of gas per mole of substrate is consumed as the aldoses are quite rapidly reduced to the alditols. Work-up of the reaction mixture as described previously[3] afforded 13 g. of sirupy product. The presence of approximately 20% of aldehydoaldoses was demonstrated by the formation of a mixture of 2,4-dinitrophenylhydrazones. A hot ethanolic saturated solution of 2,4-dinitrophenylhydrazine was added portionwise to a boiling solution of the oxo product (1.6 g) in 50 ml. of ethanol containing 4 drops of acetic acid until the color of the solution no longer changed from orange to yellow; addition of water to turbidity then resulted in the precipitation of a bright yellow solid (0.4 g.) which was removed by filtration. This solid was then triturated with warm ethanol and again removed by filtration; recrystallization from chloroform–light petroleum ether gave fine yellow needles, m.p. 225–226° dec., $[\alpha]^{22}D$ −60°. This compound was identified from its n.m.r. spectrum and by conversion to authentic[3] 1,5-anhydro-4-deoxy-D-*arabino*-hexitol (V) as the 2,4-dinitrophenylhydrazone of 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*lyxo*-hexose. The acetylated anhydrodeoxyaldose (I) was regenerated by reaction of the phenylhydrazone derivative with pyruvic acid,[6] and converted by the action of sodium borohydride to a compound which was identical with an authentic sample of 1,5-anhydro-4-deoxy-D-*arabino*-hexitol.[3]

Evaporation of the filtrate obtained from the trituration of the 2,4-dinitrophenylhydrazone mixture gave a residue which was fractionated by thin layer chromatography on silica gel using chloroform as developer to afford the aforementioned 2,4-dinitrophenylhydrazone derivative of I and also the 2,4-dinitrophenylhydrazone of 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*xylo*-hexose (II), m.p. 132°, $[\alpha]^{20}D$ −16°. Compound II was converted into VI following the same procedures as described above to convert I into V.

Similarly, hydroformylation of 3,4,6-tri-*O*-acetyl-D-glucal at 125° afforded a mixture of anhydrodeoxyheptitols (35%) and heptoses (63%). Column adsorption chromatography of this nonde-*O*-acetylated mixture on Florisil[7] using benzene–methanol (97:3 v./v.) as developer yielded four fractions. The fastest moving fraction, which was recrystallized from ether–light petroleum ether, m.p. 110–112°, $[\alpha]^{20}D$ +96°, was proven to be 4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*manno*-heptose (40% yield) by conversion to authentic 2,6-anhydro-3-deoxy-D-*manno*-heptitol. The absolute stereochemistry of the latter substance was established by correlation with authentic 2,6-anhydro-3-deoxy-D-*gluco*-heptitol.[8]

Hydroformylation of 3,4-di-*O*-acetyl-D-arabinal yielded 33% of reducing sugars as determined by the

(6) V. R. Mattox and E. C. Kendall, *ibid.*, **70**, 882 (1948).

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(8) J. Trotter, A. Camerman, A. Rosenthal, and H. J. Koch, *Can. J. Chem.*, **42**, 2630 (1964).