reported[16] for acetolysis of the β-D-ribofuranose tetrabenzoate.

9-(β-L-Ribofuranosyl)adenine (L-adenosine, XII) was prepared from X by coupling of the resultant chloro sugar with chloromercuri-6-benzamidopurine, according to the procedure for D-adenosine[17]; after deblocking of XI and regeneration of XII picrate, the yield of L-adenosine from X was 43%, m.p. 232–235°, $[\alpha]^{25}\text{D}$ +61.4°,[7] $\lambda_{\max}^{\text{pH1}}$ 257 mμ (ϵ 14,600), $\lambda_{\max}^{\text{pH13}}$ 260 mμ (ϵ 15,200). Values for natural D-adenosine, lit.[17] m.p. 233–235°, determined simultaneously were $[\alpha]^{25}\text{D}$ −60.2°,[7] $\lambda_{\max}^{\text{pH1}}$ 257 mμ (ϵ 14,600), $\lambda_{\max}^{\text{pH13}}$ 260 (15,100).

The preparation of other L-nucleosides, for example, those derived from 6-mercaptopurine, guanine, and thioguanine, is in progress.

[16] R. K. Ness and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **76**, 1663 (1954).

[17] J. Davoll and B. A. Lowy, *ibid.*, **73**, 1650 (1951), wherein the chloro sugar was the triacetate.

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Reduction and Isomerization of *cis*- and *trans*-1,2-Vinylenebis(diphenylphosphines) and Disulfides

Sir:

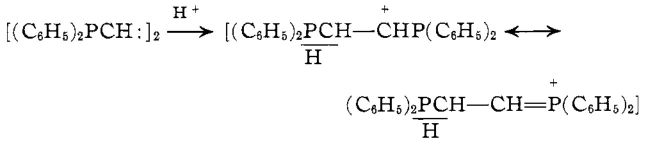
cis-1,2-Vinylenebis(diphenylphosphine) has been reported to be resistive to catalytic hydrogenation.[1] We have found that vinylenebis(diphenylphosphines) react with hydrogen bromide in hot glacial acetic acid, leading to the isolation of 1,2-ethylenebis(diphenylphosphine) monoxide, by aqueous work-up.

$$[(C_6H_5)_2PCH:]_2 + HBr \xrightarrow{HOAC} X \xrightarrow{H_2O} \underset{\text{I}}{(C_6H_5)_2P(O)CH_2CH_2P(C_6H_5)_2}$$

Crystals of I precipitated from the reaction mixture upon standing at room temperature. After air drying, I melted at 190.5–193°. *Anal.* Calcd. for $C_{26}H_{24}OP_2$: C, 75.40; H, 5.80; P, 14.99. Found: C, 74.94; H, 5.77; P, 14.87. The infrared spectrum of I indicates the presence of a phosphoryl group. The p.m.r. spectrum of a deuteriochloroform solution of I shows a phenyl hydrogen complex centered at δ = 7.4 p.p.m. and a doublet centered at δ = 2.37 p.p.m., $J_{\text{P-CH}}$ = 2.0 c.p.s., integrating in the ratio of 5:1, respectively. Whereas the methylenes of 1,2-ethylenebis(diphenylphosphine) showed up as a triplet, those of the corresponding dioxide, di(N-phenylimine), and disulfide appear as doublets in the p.m.r. spectra.[2] The methylenes of 1,2-ethylenebis(triphenylphosphonium) dibromide also give rise to a doublet.[3] The surprising lack of differentiation between the two sets of methylene protons in the monoxide by p.m.r. is not fully understood at present.

Assignment of the ethylenebis(diphenylphosphine) monoxide structure to I is supported by its ready conversion to 1,2-ethylenebis(diphenylphosphine) dioxide and its reaction with benzyl bromide to yield a phosphonium salt. Further support for the structure assignment comes from comparison of the retention times of the two peaks obtained from I on a 3 ft. × 1/8 in. silicone DC-200 column at 310° with those of the last two peaks of the three progressively smaller peaks obtained upon introduction of 1,2-ethylenebis(diphenylphosphine) into the column.[4] The last of these peaks has been shown to be identical in retention time with that of 1,2-ethylenebis(diphenylphosphine) dioxide. The larger, shorter retention-time peak from I is identical with the second, medium-size peak of the diphosphine.

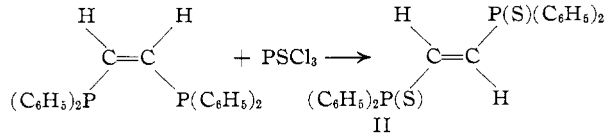
Protonation of the 1,2-vinylenebis(diphenylphosphines) at either the carbon or phosphorus would be expected to lead to a carbonium ion α and β to trivalent phosphorus atoms.



$$[(C_6H_5)_2PCH:]_2 \xrightarrow{H^+} [(C_6H_5)_2\underset{H}{\underline{PCH}}-\overset{+}{C}HP(C_6H_5)_2 \longleftrightarrow (C_6H_5)_2\underset{H}{\underline{PCH}}-CH=\overset{+}{P}(C_6H_5)_2]$$

Similar treatment of α-hydroxy- and alkoxyalkyldiphenylphosphines has been shown by Trippett to lead to alkyldiphenylphosphine oxides, indicating that α-phosphinylcarbonium ions may behave as phosphonium ions.[5] Formation of cyclic polyphosphonium ions followed by hydrolysis cannot be excluded as a possible explanation. β-Phosphinylcarbonium ions would be expected to form cyclic phosphonium salts by either an intermolecular or intramolecular process.

Attempts at pyrolytic or photochemical isomerization of 1,2-vinylenebis(diphenylphosphines) have failed. Phosphorus trichloride is also ineffective. We have found that thiophosphoryl chloride in refluxing tetrahydrofuran converts *cis*- or *trans*-1,2-vinylenebis(diphenylphosphine) to *trans*-1,2-vinylenebis(diphenylphosphine) disulfide (II).



II

Treatment of *trans*-1,2-vinylenebis(diphenylphosphine) with sulfur in benzene also produced II, m.p. 196–197°. *Anal.* Calcd. for $C_{26}H_{22}P_2S_2$: C, 67.82; H, 5.78; P, 13.47; S, 13.91; mol. wt., 460. Found: C, 67.78; H, 4.77; P, 13.48; S, 13.89: mol. wt., 434 (Rast) after recrystallization from ethanol–water. The infrared spectrum of II showed bands at 8.9 (m) and 10.18 (m) μ which are not present in the *cis* isomer or saturated analog, indicative of the *trans* structure. The p.m.r. spectrum of a tetrahydrofuran solution of II showed a triplet centered at δ 8.2 p.p.m., $J_{\text{P-CH}}$ = 24 c.p.s. overlapping with the phenyl protons centered at about δ = 7.6 and 7.92 p.p.m. Integration showed the ratio to be essentially 1:10. Treatment of II with 30% hydrogen peroxide in glacial acetic acid produced *trans*-1,2-vinylenebis(diphenylphosphine) dioxide.[6]

Sulfur treatment of a benzene solution of *cis*-1,2-vinylenebis(diphenylphosphine) led to *cis*-1,2-vinylenebis(diphenylphosphine) disulfide (III), which had a

[1] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

[2] A. M. Aguiar and J. Beisler, *J. Org. Chem.*, **29**, 1660 (1964).

[3] C. E. Griffin, private communication.

[4] A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

[5] S. Trippett, *J. Chem. Soc.*, 2813 (1961).

[6] A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962).

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 $\delta = 6.75$ p.p.m., $J_{\mathrm{P-CH}} = 12$ c.p.s., which integrated at 1:10 relative to the phenyl hydrogens at $\delta = 7.4$ 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 $\delta = 2.8$ p.p.m., $J_{\mathrm{P-CH}} = 2.5$ c.p.s., which integrated in the ratio of 1:5 relative to the phenyl protons centered at $\delta = 7.6$ 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.

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

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

Acknowledgments.—This work was carried out under a grant from the Petroleum Research Fund of the American Chemical Society. All of the proton magnetic resonance work was done by Mr. Gordon Boudreaux of the Spectroscopy Investigation of Cotton Physical Properties Laboratory, U. S. Southern Regional Utilization Research Center, New Orleans, Louisiana.

[7] K. Issleib and D. W. Muller, *Chem. Ber.*, **92**, 3175 (1959).

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

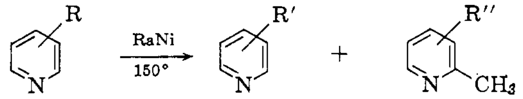
Sir:

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**

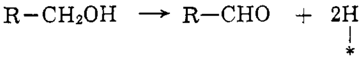
	R	R′ (% convn.[a])	R″ (% convn.[a])
a	2-$(CH_2)_3$-OH	2-C_2H_5 (27)[b]	6-C_2H_5 (24)[b]
a	2-$(CH_2)_3$-OH	2-C_2H_5 (50)	6-C_2H_5 (0)
b	3-$(CH_2)_3$-OH	3-C_2H_5 (28)	5-C_2H_5 (12)
c	4-$(CH_2)_3$-OH	4-C_2H_5 (35)	4-C_2H_5 (15)

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

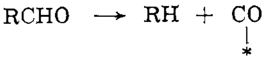
The stoichiometry of these reactions suggests that the origin of the α-methyl group is the carbinol carbon of the starting primary alcohol **1**. This hypothesis was verified by the quantitative conversion of pyridine to α-picoline by means of a primary alcohol and Raney nickel.

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.

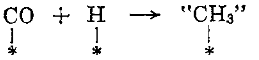
A probable mechanism for this reaction involves dehydrogenation of the primary alcohol (eq. 1) followed by decarbonylation of the resulting aldehyde to carbon monoxide and the hydrocarbon containing one less carbon atom (eq. 2).[4] The carbon monoxide, either as such or as some partially reduced species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



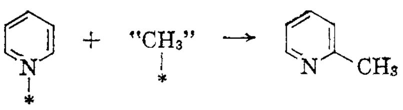
$$\mathrm{R{-}CH_2OH \longrightarrow R{-}CHO + \underset{\overset{|}{*}}{2H}} \qquad (1)$$



$$\mathrm{RCHO \longrightarrow RH + \underset{\overset{|}{*}}{CO}} \qquad (2)$$



$$\mathrm{\underset{\overset{|}{*}}{CO} + \underset{\overset{|}{*}}{H} \longrightarrow \underset{\overset{|}{*}}{\text{"}CH_3\text{"}}} \qquad (3)$$



(4)

* = catalyst surface

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

---

[1] For a recent review see G. M. Badger and W. H. F. Sasse, *Advan. Heterocyclic Chem.*, **2**, 179 (1963).

[2] M. G. Reinecke and L. R. Kray, *J. Org. Chem.*, **29**, 1736 (1964).

[3] V. Boekelheide and S. Rothchild, *J. Am. Chem. Soc.*, **70**, 864 (1948).

[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).