to dryness. The residue was chromatographed on silica gel (Merck, 70—325 mesh), and then recrystallized. Results are shown in Table II.

***p*-Toluenesulfonyl Derivative**——A mixture of an aziridine (2 mmole) and tosyl chloride (3 mmole) in dry pyridine (5 ml) was allowed to stand at room temperature for 24 hr. The mixture was poured into 10% H_2SO_4. The separating oil was extracted with $CHCl_3$, washed with water, dried over $MgSO_4$ and evaporated to dryness. The residue was chromatographed on silica gel (Merck, 70—325 mesh). Results are shown in Table II.

The Beckmann Rearrangement of 2-Benzhydrylcyclohexanone oxime (6)——The Formation of 7-Benzhydrylperhydroazepin-2-one: To an acetone (40 ml) solution of the ketoxime (6) (2.0 g) was added 10% aqueous NaOH (5.0 ml) and then a solution of TsCl (1.5 g) in acetone (5.0 ml) under ice-cooling. After allowing to stand overnight, precipitating NaCl was removed by filtration and the filtrate was concentrated *in vacuo* at 40°. The residue was extracted with $CHCl_3$, washed with water, dried over $MgSO_4$ and evaporated *in vacuo*. The residue was recrystallized from ether and then from benzene–*n*-hexane to give 1.3 g (67%) of needles, mp 131.5—133.5°. *Anal.* Calcd. for $C_{19}H_{21}ON$: C, 81.68; H, 7.57; N, 5.01. Found: C, 81.72; H, 7.60; N, 5.00. IR ν_{max}^{KBr} cm^{-1}: 3197 (NH), 1668 (C=O). NMR (in CCl_4), δ ppm: 2.34 (2H, m, $C\underline{H}_2CONH$).

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Studies on Anticoccidial Agents. VII.[1] An Improved Synthesis of α^4-Norpyridoxol

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The Diels-Alder reaction of 5-ethoxy-4-methyloxazole with unsymmetrical dienophiles was investigated and it was found that steric interaction during the course of the Diels-Alder reaction of an unsymmetrical dienophile with oxazole affected the structural isomeric distribution of the resulting products. On the basis of the above result, α^4-norpyridoxol has been synthesized by the Dields-Alder reaction of 5-ethoxy-4 methyloxazole with allyl alcohol or its derivatives. With the latter, acid hydrolysis of the adduct was necessary to obtain the title compound.

In the previous papers[3] we stated that α^4-norpyridoxol (I), 4-deoxypyridoxol (II) and their esters had the anticoccidial activity. For determination of the relationship between the structure and activity, some analogous pyridoxols[1,3b,4,5] modified at the 2, 3, 4 and 5 positions have been also synthesized and α^4-norpyridoxol and several ester derivatives were found to be the most desirable compounds.

The preparation of α^4-norpyridoxol (I) has already been reported by Perez-medina, *et al.*,[6] Yoshikawa, *et al.*[7] and us,[3b] and recently Chekhum, *et al.*[8] described a new synthetic

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2) Location: *Hiromachi 1-2-58, Shinagawa-ku, Tokyo.*
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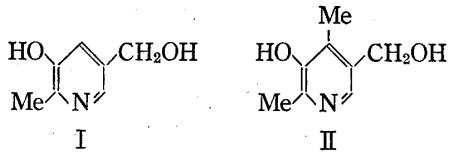


Chart 1

route to α^4-norpyridoxol by the application of the Diels-Alder reaction of 4-methyl-5-propoxyoxazole with ethoxycrotonolactone to α^4-norisopyridoxal, followed by reduction with $NaBH_4$. The present paper deals with an improved synthetic method of α^4-norpyridoxol by condensation of 5-ethoxy-4-methyloxazole with allylalcohol derivatives.

It is well known that the Diels-Alder reaction of oxazoles with the dienophiles with electron attracting substituents such as cyano, methoxycarbonyl, and carboxyl groups produced 4-substituted pyridinols.[9] On the other hand, Lutz, *et al.*[10] have shown that when isoprene is allowed to react with methyl vinyl ketone or acrolein in the presence of $SnCl_45H_2O$, mainly the 1,4-disubstituted adducts are obtained owing to the steric effect between the approaching isoprene molecule and the complexed carbonyl group co-ordinated with the Lewis acid.

Therefore we first investigated the steric effect of the dienophiles on the oxazole moiety in the Diels-Alder reaction.

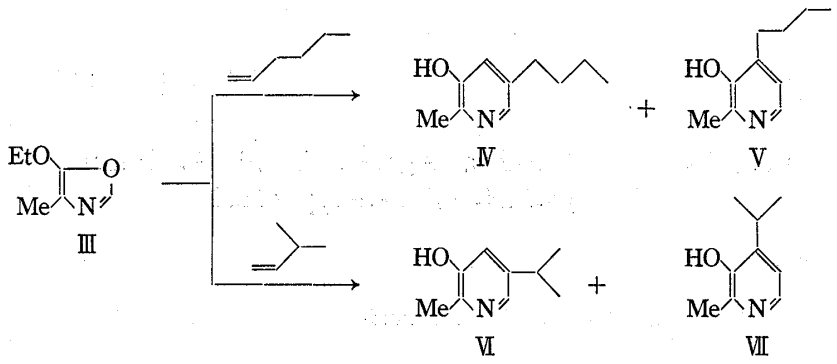
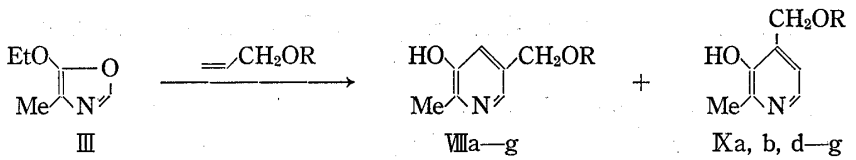


Chart 2

The reaction of 5-ethoxy-4-methyloxazole (III) with 1-hexene produced equal amount of the structurally isomeric products (IV and V) and the same condensation of the oxazole with 2-methyl-1-butene gave 5-isopropylpyridine (VI) and 4-isomer (VII) in 15.90 and 7.96% respective yields. These distributions of the resulting products may be reasonably explained by a consideration of the steric interaction between the ethoxy substituent on the oxazole ring and the isopropyl group of 2-methyl-1-butene. The latter causes the approaching dienophile to orient itself in such a manner that the isopropyl function does not lie above the ethoxy substituent.

On the basis of the above results, we investigated the reaction of the same oxazole derivative with allyl alcohol, allyl *t*-butyl ether, allyl benzyl ether, allyl phenyl ether, allyl tetrahydropyranyl ether, allyl cyclopentyl ether, allyl cyclohexyl ether and diallyl ether. The results obtained are summarized in Table I.



a: R=*t*-butyl
b: R=benzyl
c: R=phenyl
d: R=2-tetrahydropyranyl
e: R=cyclopentyl
f: R=cyclohexyl
g: R=allyl

Chart 3

9) T. Matsuo and T. Miki, *Chem. Pharm. Bull.* (Tokyo), **20**, 669 (1962).
10) E.F. Lutz and G.M. Bailey, *J. Am. Chem. Soc.*, **86**, 3899 (1964).

Table I. Reaction Products

Compound	mp (°C)	Yield (%)
VIIIa	208—210	61.0
IXa	oil	12.8
VIIIb	135—137	48.2
IXb	87— 90	16.3
VIIIc	193—194	23.8
VIIId	144	45.9
IXd	oil	8.6
VIIIe	155—156	36.1
IXe	63— 65	12.0
VIIIf	146	13.2
IXf	71— 73	4.3
VIIIg	102	67.9
IXg	127—128 (HCl)	13.0

The reaction of the oxazole (III) with allyl alcohol was effected on heating in a sealed tube at 180° to give α^4-norpyridoxol (I), 3-hydroxy-2-methylpyridine (X) and 4-allyloxymethyl-3-hydroxy-2-methylpyridine (IXg). The structure of the second compound (X) was deduced by nuclear magnetic resonance (NMR) spectroscopy indicating the presence of three aromatic protons at δ 7.05 (J=8.0 and 4.5 Hz), 7.24 (J=8.0 and 2.0 Hz) and 7.98 (J=4.5 and 2.0 Hz) and identified by infrared (IR) spectrum and by mixed melting point determination with the authentic sample prepared by Naito's method.[11] The route to this compound (X) might be assumed to take place *via* the retroaldol reaction of 3-hydroxy-4-hydroxymethylpyridine, produced by the Diels-Alder reaction of the oxazole and allylalcohol. The third compound (IXg) was considered to be a 4-substituted 3-pyridinol derivative by its NMR spectroscopy which indicated the presence of ortho-protons (J=6.0 Hz) and was identified by the comparison with the infrared and NMR spectra of authentic 4-allyloxymethyl-3-hydroxy-2-methylpyridine (IXg), synthesized from the oxazole (III) and diallylether.

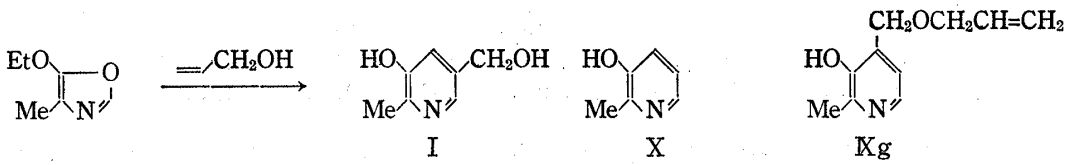


Chart 4

In view of the results shown in Table I, it may be concluded that in the reaction of this type of disubstituted oxazole with allyl alcohol derivatives the oxymethyl group is preferentially introduced at β-position of the pyridine ring. Such 5-substituted 3-pyridinols were readily converted to α^4-norpyridoxol in good yield by acid hydrolysis.

Experimental

Melting points were uncorrected. IR spectra were obtained with Perkin-Elmer 221 and JASCO IRA-2 spectrometers and NMR spectra were recorded on a Varian A 60 spectrometer using tetramethylsilane (TMS) as an internal standard and chemical shifts are given in δ values. The following abbreviations are used: b=broad, d=doublet, m=multiplet, s=singlet, t=triplet.

Diels-Alder Reaction with 1-Hexene——A mixture of 10 g of oxazole (III) and 30 g of 1-hexene was heated at 90° in a sealed tube for 4 hr. Removal of excess 1-hexene *in vacuo* gave a crystalline product, which was recrystallized from EtOAc to afford 1.8 g of 5-*n*-butyl-3-hydroxy-2-methylpyridine (IV), mp 118°. *Anal.* Calcd. for $C_{10}H_{15}ON$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.75; H, 9.21; N, 8.65. NMR (D_2O):

11) T. Naito, T. Yoshikawa, F. Ishikawa, S. Isoda, Y. Omura, and I. Takamura, *Chem. Pharm. Bull.* (Tokyo), **13**, 869 (1965).

0.95 (3H, t, J=6.0 Hz, C_5-$(CH_2)_3\underline{CH_3}$), 1.11—2.00 (4H, m, C_5-$CH_2\underline{CH_2}\underline{CH_2}CH_3$), 2.80 (2H, t, J=7.0 Hz, C_5-$\underline{CH_2}(CH_2)_2CH_3$), 2.64 (3H, s, C_2-Me), 7.86 (1H, d, J=2.0 Hz, C_4-H), 8.10 (1H, d, J=2.0 Hz, C_6-H). The mother liquor was chromatographed over silica gel to give 1.2 g of an additional product (IV) and 3.1 g of 4-*n*-butyl-3-hydroxy-2-methylpyridine (V) as an oil. *Anal.* Calcd. for $C_{10}H_{15}ON$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.52; H, 9.01; N, 8.35. NMR ($CDCl_3$): 0.88 (3H, t, J=6.0 Hz, C_4-$(CH_2)_3\underline{CH_3}$), 1.15—1.73 (4H, m, C_4-$CH_2\underline{CH_2}\underline{CH_2}CH_3$), 2.47 (3H, s, C_2-Me), 2.68 (2H, t, J=7.0 Hz, C_4-$\underline{CH_2}(CH_2)_2CH_3$), 6.97 (1H, d, J=5.0 Hz, C_5-H), 7.92 (1H, d, J=5.0 Hz, C_6-H).

Diels-Alder Reaction with 1-Isopentene——A mixture of 10 g of oxazole (III) and 20 ml of 1-isopentene was heated at 180° for 4 hr. After removal of excess isopentene, the residue was chromatographed over silica gel to yield 1.9 g of 3-hydroxy-5-isopropyl-2-methylpyridine (VI), which was recrystallized from EtOAc-petroleum ether to give a colorless solid, mp 141—142°. *Anal.* Calcd. for $C_9H_{13}ON$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.50; H, 8.60; N, 9.28. NMR (DMF-d_7): 1.18 (6H, d, J=7.0 Hz, C_5-CH$\underline{Me_2}$), 2.33 (3H, s, C_2-Me), 2.62—2.97 (1H, m, C_5-C$\underline{H}Me_2$), 7.05 (1H, d, J=2.0 Hz, C_4-H), 7.84 (1H, d, J=2.0 Hz, C_6-H). The second eluate (0.95 g) was 3-hydroxy-4-isopropyl-2-methylpyridine (VII), mp 129—130° on recrystallization from EtOAc-*n*-hexane. *Anal.* Calcd. for $C_9H_{13}ON$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.48; H, 8.59; N, 9.15. NMR (DMF-d_7): 1.16 (6H, d, J=7.0 Hz, C_4-CH$\underline{Me_2}$), 2.40 (3H, s, C_2-Me), 3.36 (1H, m, C_4-C$\underline{H}Me_2$), 6.93 (1H, d, J=5.0 Hz, C_5-H), 7.86 (1H, d, J=5.0 Hz, C_6-H).

Diels-Alder Reaction with Allyl Alcohol——A mixture of oxazole (III, 3 g) and allyl alcohol (10 g) was heated at 180° in a sealed tube for 3 hr. The mixture was concentrated into a small volume and chromatographed over silica gel. The first fraction eluted with EtOAc afforded 2-methyl-3-hydroxypyridine (X, 0.065 g), mp 150—152°, on recrystallization from EtOAc-*n*-hexane. *Anal.* Calcd. for C_6H_7ON: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.86; H, 6.49; N, 12.71. NMR (DMF-d_7): 2.40 (3H, s, C_2-Me), 7.05 (1H, d-d, J=8.0, 4.5 Hz, C_5-H), 7.24 (1H, d-d, J=8.0, 2.0 Hz, C_4-H), 7.98 (1H, d-d, J=4.5, 2.0 Hz, C_6-H), 8.98 (1H, b, OH). The second fraction eluted with EtOAc gave 4-allyloxymethyl-3-hydroxy-2-methylpyridine (IXg, 0.082 g) as an oil, which was converted into a hydrochloride, mp 127—128°. on recrystallization from EtOH-*n*-hexane. *Anal.* Calcd. for $C_{10}H_{14}O_2NCl$: C, 55.68; H, 6.54; N, 6.50. Found: C, 55.60; H, 6.61; N, 6.54. The third fraction eluted with the same solvent gave α^4-norpyridoxol (I, 0.783 g), mp 157—160° on recrystallization from MeCN. *Anal.* Calcd. for $C_7H_9O_2N$: C, 60.42; H, 6.52; N, 10.17. Found: C, 60.30; H, 6.41; N, 10.14.

Diels-Alder Reaction with Allyl *t*-Butyl Ether——A mixture of 2 g of oxazole (III) and 8 g of allyl *t*-butyl ether was heated at 180° in a sealed tube for 3 hr, cooled to give a crystalline product (VIIIa, 1.6 g), which was separated by filtration. The mother liquor was chromatographed on silica gel dry column eluting with EtOAc. The less-polar product was 5-*t*-butoxymethyl-3-hydroxy-2-methylpyridine (VIIIa, 0.32 g), which was recrystallized from EtOAc to give an analytical product, mp 208—210°. *Anal.* Calcd. for $C_{11}H_{17}O_2N$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.73; H, 8.76; N, 7.36. NMR (DMSO-d_6): 1.18 (9H, s, C_5-$CH_2OC\underline{Me_3}$), 2.31 (3H, s, C_2-Me), 4.33 (2H, s, C_5-CH_2), 7.08 (1H, d, J=2.0 Hz, C_4-H), 7.85 (1H, d, J=2.0 Hz, C_6-H). The more polar product was 4-*t*-butoxymethyl-3-hydroxy-2-methylpyridine (IXa, 0.4 g) as an oil. *Anal.* Calcd. for $C_{11}H_{17}O_2N$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.59; H, 8.75; N, 7.25. NMR (DMF-d_7): 1.27 (9H, s, C_4-$CH_2C\underline{Me_3}$), 2.42 (3H, s, C_2-Me), 4.60 (2H, s, C_4-CH_2), 7.14 (1H, d, J=5 .0 Hz, C_5-H), 7.96 (1H, d, J=5.0 Hz, C_6-H).

Diels-Alder Reaction with Allyl Benzyl Ether——A mixture of oxazole (III, 2.0 g) and allyl benzyl ether (20 g) was heated in a sealed tube at 180° for 2.5 hr. The mixture was chromatographed over silica gel eluting with benzene-EtOAc (1: 1) and (3: 7). The major product (1.78 g) was identified as 5-benzyloxymethyl-3-hydroxy-2-methylpyridine (VIIIb), which was recrystallized from EtOAc-*n*-hexane to give a colorless product, mp 135—137°. *Anal.* Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.10; H, 6.49; N, 6.15. NMR ($CDCl_3$): 2.53 (3H, s, C_2-Me), 4.45 and 4.50 (2H, each, s, C_5-$\underline{CH_2}O\underline{CH_2}Ph$), 7.26 (5H, m, Ph), 7.95 (1H, d, J=2.0 Hz, C_4-H), 9.33 (1H, d, J=2.0 Hz, C_6-H). The second product (0.6 g) was 4-benzyloxymethyl-3-hydroxy-2-methylpyridine (IXb), mp 87—90° on recrystallization from EtOAc-*n*-hexane. NMR ($CDCl_3$): 2.45 (3H, s, C_2-Me), 4.60 and 4.70 (2H, each, s, C_5-$\underline{CH_2}O\underline{CH_2}Ph$), 6.83 (1H, d, J=5.0 Hz, C_5-H), 7.35 (5H, m, Ph), 7.93 (1H, d, J=5.0 Hz, C_6-H).

Diels-Alder Reaction with Allyl Phenyl Ether——A mixture of oxazole (III, 2 g) and allyl phenyl ether (6 g) was heated in a sealed tube at 180° for 3 hr. The reaction mixture was chromatographed over silica gel, eluting with benzene-EtOAc (7: 3) and (6: 4) to give a crystalline product (VIIIc, 0.82 g). Recrystallization from EtOH gave a colorless product as plates, mp 193—194°. *Anal.* Calcd. for $C_{13}H_{13}O_2N$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.45; H, 6.02; N, 6.71. NMR (DMF-d_7): 2.39 (3H, s, C_2-Me), 5.10 (2H, s, C_5-CH_2), 6.90—7.40 (6H, m, Ph and C_4-H), 8.10 (1H, d, J=2.0 Hz, C_6-H).

Diels-Alder Reaction with Allyl Tetrahydropyranyl Ether——A mixture of oxazole (III, 6 g) and allyl tetrahydropyranyl ether (18 g) was refluxed for 4 hr, while distilling off the ethanol liberated. The reaction mixture was cooled to give a crystalline product (VIIId, 4.01 g). The filtrate was concentrated *in vacuo* and the residue was chromatographed over silica gel, eluting with EtOAc. The first fraction gave α^5-O-tetrahydropyranyl-α^4-nor pyridoxol (VIIId, 0.8 g), mp 144° on recrystallization from EtOAc. *Anal.* Calcd. for $C_{12}H_{17}O_3N$: C, 64.55; H, 7.68; N, 6.27. Found: C, 64.59; H, 7.65; N, 6.19. NMR ($CDCl_3$): 1.60 (6H, bs), 2.53 (3H, s, C_2-Me), 3.30—4.05 (2H, m), 4.70 (1H, m), 4.44 and 4.75 (2H, a pair of doublets, J=12.0 Hz,

C_5–CH_2), 7.26 (1H, d, J=2.0 Hz, C_4–H), 7.96 (1H, d, J=2.0 Hz, C_6–H). The second fraction gave α^4-O-tetrahydropyranyl-α^5-norpyridoxol (IXd, 0.9 g) as an oil. *Anal.* Calcd. for $C_{12}H_{17}O_3N$: C, 64.55; H, 7.68; N, 6.27. Found: C, 64.70; H, 7.59; N, 6.30. NMR (DMF-d_7): 1.30—2.00 (6H, b), 2.45 (3H, s, C_2–Me), 3.17-4.17 (2H, m), 4.77 (1H, m), 4.58 and 4.90 (2H, a pair of doublets, J=14 Hz, C_4–CH_2), 7.21 (1H, d, J=5.0 Hz, C_5–H), 8.02 (1H, d, J=5.0 Hz, C_6–H).

Diels-Alder Reaction with Allyl Cyclopentyl Ether——A mixture of oxazole (III, 2 g) and allyl cyclopentyl ether (6 g) was heated in a sealed tube at 180° for 3 hr. The reaction mixture was chromatographed over silica gel, eluting with EtOAc to give 5-cyclopentyloxymethyl-3-hydroxy-2-methylpyridine (VIIIe, 1.2 g), mp 155—156° on recrystallization from EtOAc–*n*-hexane. *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.48; H, 8.30; N, 6.71. NMR ($CDCl_3$): 1.50—1.80 (8H, m) 2.55 (3H, s, C_2–Me), 4.00 (1H, m), 4.44 (2H, s, C_5–CH_2), 7.25 (1H, d, J=2.0 Hz, C_4–H), 7.95 (1H, d, J=2.0 Hz, C_6–H). Further elution with EtOAc gave 4-cyclopentyloxymethyl-3-hydroxy-2-methylpyridine (IXe, 0.4 g), mp 63—65° on recrystallization from EtOAc–*n*-hexane. *Anal.* Calcd. for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.50; H, 8.19; N, 6.65. NMR ($CDCl_3$): 1.60—1.90 (8H, m), 2.47 (3H, s, C_2–Me), 4.10 (1H, m), 4.67 (2H, s, C_4–CH_2), 6.82 (1H, d, J=5.0 Hz, C_5–H), 7.90 (1H, s, OH), 7.98 (1H, d, J=5.0 Hz, C_6–H).

Diels-Alder Reaction with Allyl Cyclohexyl Ether——A mixture of oxazole (III, 3.0 g) and allyl cyclohexyl ether (9 g) was heated in a sealed tube at 180° for 3 hr. The reaction mixture was concentrated *in vacuo* and chromatographed over silica gel eluting with EtOAc. The first eluate was 5-cyclohexyloxymethyl-3-hydroxy-2-methylpyridine (VIIIf, 0.70 g), mp 146° on recrystallization from EtOAc–*n*-hexane. *Anal.* Calcd. for $C_{13}H_{19}O_2N$: C, 70.56; H, 8.67; N, 6.33. Found: C, 70.51; H, 8.59; N, 6.40. NMR ($CDCl_3$): 1.00—2.10 (10H, m). 2.56 (3H, s, C_2–Me), 3.33 (1H, m), 4.48 (2H, s, C_5–CH_2), 7.27 (1H, d, J=1.5 Hz, C_4–H), 7.97 (1H, d, J=1.5 Hz, C_6–H), 11.22 (1H, s, OH). The second eluate was 4-cyclohexyloxymethyl-3-hydroxy-2-methylpyridine (IXf, 0.23 g), mp 71—73° on recrystallization from EtOAc-*n*-hexane. *Anal.* Calcd. for $C_{13}H_{19}O_2N$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.58; H, 8.68; N, 6.43. NMR ($CDCl_3$): 1.03—2.13 (10H, m), 2.48 (3H, s, C_2–Me), 3.50 (1H, m), 4.77 (2H, s, C_4–CH_2), 6.80 (1H, d, J=5.0 Hz, C_5–H), 8.00 (1H, d, J=5.0 Hz, C_6–H).

Diels-Alder Reaction with Diallyl Ether——A mixture of oxazole (III, 4.0 g) and diallyl ether (40 ml) was heated at 190° in a sealed tube for 3 hr. After removal of the excess diallyl ether, the residue was chromatographed over silica gel. The first compound was 5-allyloxymethyl-3-hydroxy-2-methylpyridine (VIIIg, 3.83 g), mp 102°, which was converted into a hydrochloride, mp 135—136° on recrystallization from EtOH–*n*-hexane. *Anal.* Calcd. for $C_{10}H_{14}O_2NCl$: C, 55.68; H, 6.54; N, 6.50. Found: C, 55.71; H, 6.62; N, 6.55. NMR (D_2O): 2.64 (3H, s, C_2–Me), 4.16 (2H, d-t, J=5.0, 1.0 Hz, $O\underline{CH_2}CH=CH_2$), 4.71 (2H, s, C_5–CH_2), 5.17—5.55 (2H, m, $OCH_2CH=\underline{CH_2}$), 5.74—6.48 (1H, m, $OCH_2\underline{CH}=CH_2$), 7.89 (1H, d, J=2.0 Hz, C_4–H), 8.15 (1H, d, J=2.0 Hz, C_6–H). The second compound was 4-allyloxymethyl-3-hydroxy-2-methylpyridine (IXg, 0.736 g) as an oil, which was converted into a hydrochloride, mp 127—128° on recrystallization from EtOH–*n*-hexane. *Anal.* Calcd. for $C_{10}H_{14}O_2NCl$: C, 55.68; H, 6.54; N, 6.50. Found: C, 55.54; H, 6.55; N, 6.64. NMR (D_2O): 2.70 (3H, s, C_2–Me), 4.23 (2H, d-t, J=5.0, 1.0 Hz, $O\underline{CH_2}CH=CH_2$), 4.89 (2H, s, C_4–CH_2), 5.21—5.57 (2H, m, $OCH_2CH=\underline{CH_2}$), 5.78—6.41 (1H, m, $OCH_2\underline{CH}=CH_2$), 7.82 (1H, d, J=6.0 Hz, C_5–H), 8.21 (1H, d, J=6.0 Hz, C_6–H).

α^4-Norpyridoxol Hydrochloride (I)——a) A solution of *t*-butyl ether (VIIIa, 10 g) in 10% HCl (300 ml) was heated at 90—95° for 4 hr and the solvent was removed *in vacuo* to give a crystalline product, which was recrystallized from MeOH–ether to afford an analytically pure product (7.2 g), mp 165—167°. *Anal.* Calcd. for $C_7H_{10}O_2NCl$: C, 47.87; H, 5.74; N, 7.98; Cl, 20.19. Found: C, 47.85; H, 5.79; N, 8.04; Cl, 20.21. IR spectrum was identical with that of the authentic sample.

b) Tetrahydropyranyl ether (VIIId, 4.4 g) was dissolved in 10% HCl (45 ml), the solution was concentrated into dryness and the residue was recrystallized from MeOH–ether to afford a crystalline product (2.7 g), mp 165—167°. The IR spectrum was superimposable with that of the compound described above.

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