Reduction of *n*-(1,3-Dioxolan-2-yl)-1-methylpyridinium Ions: Molecular Structure of the 4-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-Borane Complex

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The reduction of the *n*-(1,3-dioxolan-2-yl)-1-methylpyridinium ions with sodium borohydride has been studied to prepare *N*-methylformylpiperidines. Deuterium oxide was used as the solvent in order to assign the protons in the nmr spectra. As a product of the reaction, the 4-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-borane complex, was isolated and crystallized. A X-ray study of this borane complex has been carried out.

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Introduction.

The synthesis of *N*-methylformylpiperidines has been outlined to prepare the spiro[1-methylpiperidine-*n*,3'-3*H*-indoles] which could have potential action as antidepressant drugs [1]. Thus, the synthesis of the *N*-methylformylpiperidines have been carried out from the commercially availables pyridinecarbaldehydes, which after acetalization with ethylene glycol and quarterisation with methyl iodide, were reduced by means of sodium borohydride in aqueous solution.

The mechanism of the reduction of pyridinium ions by sodium borohydride has been previously described [2] as producing a tetrahydropyridine which is indicating that sodium borohydride is reducing the C=N bond and also the C=C bond of the aromatic system. The type of products of the reaction, however, has been confirmed by many authors who have made the reduction of a variety of pyridinium ions into the corresponding tetrahydropyridines [3].

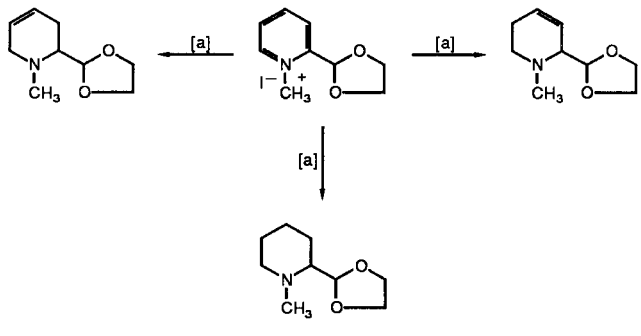
Borane complexes are formed during the reaction of the pyridinium ions with the sodium borohydride presumably by formation of the adduct of the reduced amine from the $C=N^+$ bond and the borohydride. The 4-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-borane complex has been obtained by isolation and careful crystallization. Its structure determination has been carried out by X-ray diffraction analysis.

Results and Discussion.

The *n*-pyridinecarbaldehydes (n = 2,3 and 4) were the starting products for the synthesis of *N*-methylformylpiperidines, which requires several steps: a) Pyridinecarbaldehydes with the formyl substituent on 2-, 3-, and 4-position were transformed into the *n*-(1,3-dioxolan-2-yl)pyridines to protect the aldehyde group. Then the treatment of the pyridine ring with methyl iodide allowed us to obtain the *n*-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide; b) 1-methylpyridinium salts were reduced by means of sodium borohydride in water at room temperature. Several reduction products were obtained which were dependent of the *n*-position of the 1,3-dioxolan-2-yl substituent on the pyridinium ring.

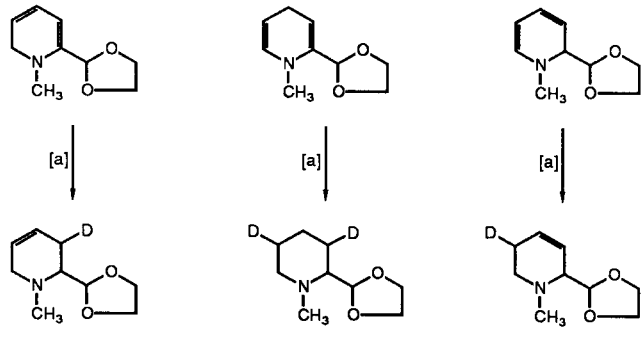
1) Reduction of 2-(1,3-dioxolan-2-yl)-1-methylpyridin-

Scheme 1



[a] Reagents: $NaBH_4/H_2O$.

Scheme 2



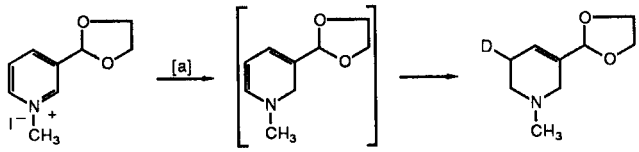
[a] Reagents: D_2O, H^+.

ium iodide with sodium borohydride gave three products, which can be interpreted according to the proposed mechanism [4] as an initial attack of a hydride ion: a) on the 6-position of the 1-methylpyridinium ring, giving 2-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine (55%); b) on the 2-position of the 1-methylpyridinium ring, giving 6-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine; c) on the 4-position of the 1-methylpyridinium ring, giving 2-(1,3-dioxolan-2-yl)-1-methylpiperidine, Scheme 1.

However as it is common in this type of reduction, the main product, 2-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine is generated as an amino-borane adduct which increases in relation to the free base when the reaction time increases.

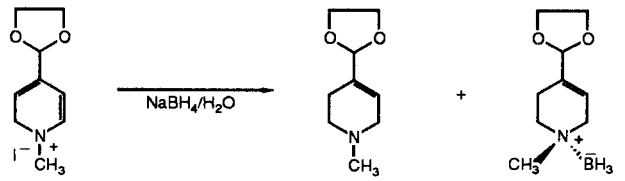
Evidence that the mechanism for the conversion of pyridinium ions to tetrahydropyridines by sodium borohydride involves the protonation of a 1,2-dihydropyridine intermediate has been presented [2]. In effect, when deuterium oxide was used as deuterioprotic solvent, several dihydropyridines as intermediates are possible for the 2-dioxolan derivatives as shown by means of the nmr spectra of each isolated product, Scheme 2. Moreover, evidence for the course of the protonation step is now understood by consideration of the carbanionic character of the carbon atoms conjugated with the nitrogen atom. Thus, the proton can attack at the center or terminal positions of the conjugated dienamines which can be correlated by Ingold's rule to the protonation of a conjugated dienamine [4]. Following that, weak acids leads to the kinetically-controlled product by proton attack at the central position of the enamine while the strong acids (or equilibrating conditions) give the product of thermodynamic control by attack of the proton at the terminal position.

Scheme 3



[a] Reagents; $NaBH_4/D_2O$.

Scheme 4



[a] Reagents; $NaBH_4/H_2O$.

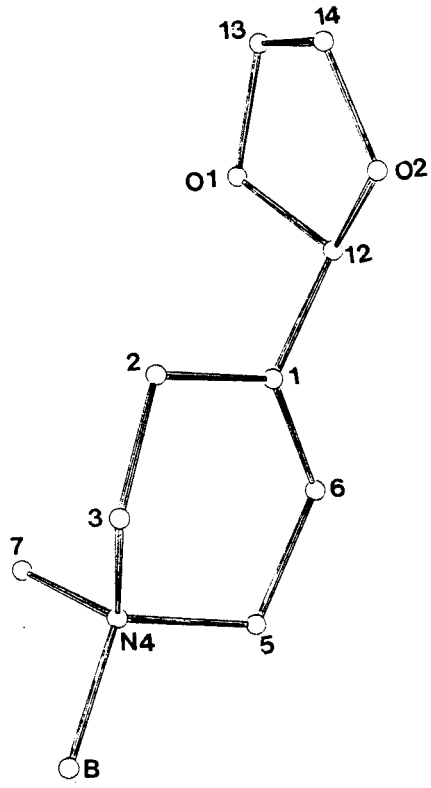


Figure 1. Molecular structure of 4-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine.

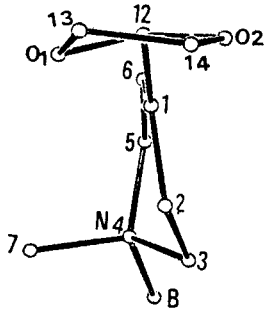


Figure 2. Projection of the molecule down the b axis.

On the other hand, the position of the substituent seems to direct the attack of the hydride ion on a defined position of the 1,2-dihydropyridinium ion. Thus, only a tetrahydropyridine is obtained by reduction with sodium borohydride of the 4-dioxolan pyridinium ion derivative. On the other hand, only the 5-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine was isolated by reduction with sodium borohydride of the 3-dioxolanpyridinium ion derivative, while the 2-dioxolanpyridinium ion derivative is reduced by the sodium borohydride to a mixture of 2-(1,3-

dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine (major) and 6-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine (minor). 2) On the other hand the reduction of the 3- or 4-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide with sodium borohydride only gives a tetrahydropyridine derivative, Scheme 2, together with its amino-borane adduct, which increases in proportion to the free base, with the reaction time, Scheme 3. 3) Reduction of the 4-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide with sodium borohydride was carried out in water at room temperature, giving only the 4-(1,3-dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine and its amino-borane adduct which, as occurs in the preceding reactions, increases when the reaction time increases, Table 1.

X-Ray Diffraction Analysis of the 4-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-Borane Complex.

Tables 2 and 3 give the atomic coordinates and bond lengths and angles respectively. The molecular shape is shown in Figure 1. The molecule consists of two heterocyclic rings fused through C(1)-C(12). The dihydropiperidine ring shows an amino-borane adduct moiety where the nitrogen atom exhibits a regular tetrahedral configuration of the ammonium ion type with C-N-B and C-N-C bond angles ranging between 108.2(2) to 110.5(2)°. The N-B ionic bond distance is 1.611(4)Å which agrees well with some N-B ionic bond lenghths reported [5] while C-N^+ bond distances C(3)-N(4) = 1.496(3), C(5)-N(4) = 1.494(3)Å for the cyclic methylenes and C(7)-N(4) = 1.489(3)Å for the methyl substituent, are within of the limits of the experimental error. The C(sp^3)-C(sp^2) bond distances C(1)-C(2) = 1.492(4), C(5)-C(6) = 1.490(3) and C(1)-C(12) = 1.494(3)Å show the same value within experimental error limits. C(1)-C(6) = 1.323(3)Å show the double bond of the dihydropiperidine ring. The 1,3-dioxolane ring, show the C-O bonds C(12)-O(1) = 1.407(3), C(12)-O(2) = 1.413(3), C(13)-O(1) = 1.398(4) and C(14)-O(2) = 1.390(4)Å, while the ethylene bridge C(13)-C(14) = 1.469(6)Å as normal values. The six membered ring shows a half-chair conformation $^1H_6$ [6] with the lowest asymmetric parameter C_2 C(6)-C(1) = 0.008. The five membered ring has a conformation closer to an envelope than a half-chair, its asymmetric parameter is C_n, O(1) = 0.005. The mean plane of both rings are nearly perpendicular to each other, the dihedral angle between them is 91.6(1)°. Figure 2 shows the molecule projection down the b axis. The packing of the molecules in the crystal is shown in Figure 3. There are not significant intermolecular contacts less than the sum of the Van der Waals radii.

Table 1

Reduction of 4-(1,3-Dioxolan-2-yl)-1-methylpyridinium Iodide with Sodium Borohydride; A (% of Free Base) and B (% of Amino-borane adduct)

time (minutes)	A	B
30	50	50
60	30	70
120	10	90

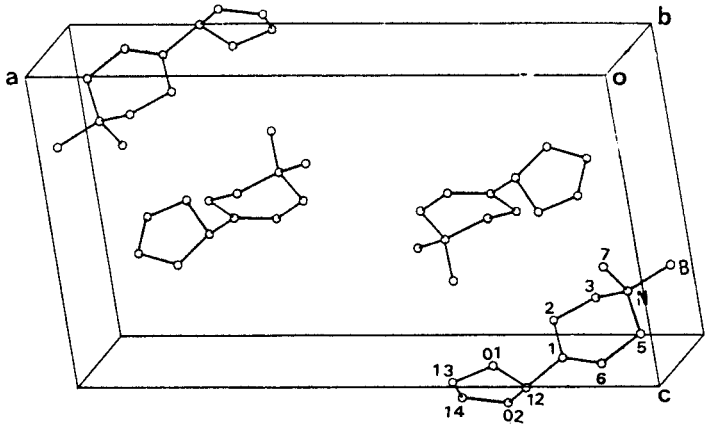


Figure 3. Packing of the molecules in the unit cell.

Table 2

Fractional Atomic Coordinates (e.s.d'.s in parenthesis)

ATOM	x	y	z
O1	0.3338(1)	−0.3549(0)	1.0383(2)
O2	0.3431(1)	−0.0896(4)	1.2016(2)
N4	0.1254(1)	0.1012(3)	0.8751(2)
B	0.0606(2)	0.2716(6)	0.8197(4)
C1	0.2344(1)	−0.0984(4)	1.0544(2)
C2	0.2559(1)	0.0918(4)	0.9663(3)
C3	0.1914(1)	0.2407(4)	0.9191(3)
C5	0.1033(1)	−0.0353(5)	0.9890(2)
C6	0.1655(1)	−0.1514(4)	1.0650(2)
C7	0.1424(2)	−0.0643(5)	0.7701(2)
C12	0.2935(1)	−0.2351(5)	1.1274(2)
C13	0.4062(2)	−0.3555(8)	1.0930(4)
C14	0.4132(2)	−0.1473(8)	1.1740(4)

EXPERIMENTAL

Melting points were determined by using a Reichert stage microscope and are uncorrected. Infrared spectra were recorded using a SP 1100 Phillips Pye Unicam Spectrophotometer. Nuclear Magnetic Resonance spectra were recorded at 200 Mz using a Bruker WM-200-SY spectrometer. Chemical shifts are given relative to internal tetramethylsilane. The assignment of the protons were carried out by means of deuteration during the hydrolysis stage of the reduction (see Schemes) and proton irradiation techniques. Elemental analysis were performed with a Model 240 Perkin Elmer analyzer.

Table 3

Bond Distances (A) and Angles (°) (e.s.d'.s in parenthesis)

Atoms		Atoms	
O1-C12	1.407(3)	C12-O1-C13	107.2(2)
O1-C13	1.398(4)	C12-O2-C14	108.8(3)
O2-C12	1.413(3)	C5-N4-C7	108.9(2)
O2-C14	1.390(4)	C3-N4-C7	109.9(2)
N4-B	1.611(4)	C3-N4-C5	108.2(2)
N4-C3	1.496(3)	B-N4-C7	109.1(2)
N4-C5	1.494(3)	B-N4-C5	110.5(2)
N4-C7	1.489(3)	B-N4-C3	110.2(2)
C1-C2	1.492(4)	C6-C5-C12	120.5(2)
C1-C6	1.323(3)	C2-C1-C12	117.8(2)
C1-C12	1.494(3)	C2-C1-C6	121.7(2)
C2-C3	1.511(3)	C1-C2-C3	111.3(2)
C5-C6	1.490(3)	N4-C3-C2	113.4(2)
C13-C14	1.469(6)	C4-C5-C6	113.2(2)
		C1-C6-C5	124.0(2)
		O2-C12-C1	112.0(2)
		O1-C12-C1	109.5(2)
		O1-C12-O2	106.5(2)
		O1-C13-C14	104.8(3)
		O2-C14-C13	106.0(3)

Preparation of the *n*-(1,3-Dioxolan-2-yl)pyridines.

A solution of 0.09 mole of the *n*-pyridinecarbaldehydes, 0.18 mole of the ethylene glycol and 0.10 mole of the *p*-toluenesulfonic acid was boiled during 4 hours, to remove water azeotropically. The mixture was cooled, made basic with aqueous sodium hydroxide and extracted with dichloromethane. The solvent was evaporated and the residual oil distilled under vacuum to give a colorless liquid with the following yields and spectral data:

2-(1,3-Dioxolan-2-yl)pyridine.

This compound had bp 146°/5 mm, 84% yield; ^{1}H nmr (deuteriochloroform): 8.61 (m, 1H, H-6), 7.70 (m, 1H, H-4), 7.53 (m, 1H, H-3), 7.27 (m, 1H, H-5), 5.84 (s, 1H, O-CH-O), 4.12 (m, 4H, O-(CH$_2$)$_2$-O); ir (film): 1090, 1030 and 980 (st C-O-O-C).

3-(1,3-Dioxolan-2-yl)pyridine.

This compound had bp 150°/1 mm, 87% yield; ^{1}H nmr (deuteriochloroform): 8.64 (m, 1H, H-2), 8.55 (m, 1H, H-6), 7.70 (m, 1H, H-4), 7.30 (m, 1H, H-5), 5.79 (s, 1H, O-CH-O), 4.05 (m, 4H, O-(CH$_2$)$_2$-O); ir (film): 1090, 1030 and 980 (st C-O-C-O-C).

4-(1,3-Dioxolan-2-yl)pyridine.

This compound had bp 120°/5 mm, 90% yield; ^{1}H nmr (deuteriochloroform): 8.60 (m, 2H, H-2, H-6), 7.34 (m, 2H, H-3, H-5), 5.76 (s, 1H, O-CH-O), 4.00 (m, 4H, O-(CH$_2$)$_2$-O); ir (film): 1090, 1030 and 990 (st C-O-C-O-C).

Preparation of the *n*-(1,3-Dioxolan-2-yl)-1-methylpyridinium Iodide.

To 0.08 mole of the *n*-(1,3-dioxolan-2-yl)pyridine was added dropwise a solution of 0.16 mole of methyl iodide in 50 ml of the diethyl ether, at 10-15°. The mixture was stirred for 10 hours and allowed to stand at 5° overnight. The solid was filtered off and washed with diethyl ether. The *n*-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide was purified by solution in methanol and precipitate with a mixture of the ethyl acetate-hexane to give a solid with the following yields and spectral data:

2-(1,3-Dioxolan-2-yl)-1-methylpyridinium Iodide.

This compound was obtained as an orange solid, mp 122-124°, 85% yield; ^{1}H nmr (deuteriochloroform): 9.06 (m, 1H, H-6), 8.63 (m, 1H, H-4), 8.19 (m, 1H, H-3), 8.13 (m, 1H, H-5), 6.47 (s, 1H, O-CH-O), 4.37 (s, 3H, CH$_3$), 4.09 (m, 4H, O-(CH$_2$)$_2$-O).

Anal. Calcd. for $C_9H_{12}INO_2$: C, 36.88; H, 4.12; N, 4.78. Found: C, 36.54; H, 4.01; N, 4.92.

3-(1,3-Dioxolan-2-yl)-1-Methylpyridinium Iodide.

The compound was obtained as a yellow solid, mp 183-185°, 90% yield; ^{1}H nmr (deuteriochloroform): 9.10 (m, 1H, H-2), 9.02 (m, 1H, H-6), 8.60 (m, 1H, H-4), 8.17 (m, 1H, H-5), 6.07 (s, 1H, O-CH-O), 4.38 (s, 3H, CH$_3$), 4.05 (m, 4H, O-(CH$_2$)$_2$-O).

Anal. Calcd. for $C_9H_{12}INO_2$: C, 36.88; H, 4.12; N, 4.78. Found: C, 36.61; H, 4.17; N, 4.81.

4-(1,3-Dioxolan-2-yl)-1-Methylpyridinium Iodide.

This compound was obtained as a yellow solid, mp 156-158°, 95% yield; ^{1}H nmr (deuteriochloroform): 9.00 (m, 2H, H-2, H-6), 8.12 (m, 2H, H-3, H-5), 6.08 (s, 1H, OCH=), 4.36 (s, 3H, CH$_3$), 4.02 (m, 4H, O-(CH$_2$)$_2$-O).

Anal. Calcd. for $C_9H_{12}INO_2$: C, 36.88; H, 4.12; N, 4.78. Found: C, 36.49; H, 4.01; N, 4.69.

Reduction of the *n*-(1,3-Dioxolan-2-yl)-1-methylpyridinium Iodide.

To 0.12 mole of sodium borohydride was added dropwise a solution of 0.06 mole of the *n*-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide in 50 ml of water at 10-15°. The mixture was stirred at room temperature during 30 minutes. The aqueous solution was extracted with dichloromethane. The organic solution was dried over magnesium sulfate and evaporated to give an oil, which was chromatographed on a silica gel column, eluting with chloroform-methanol (5:1), to provide several reduction products. The reduction of the 2-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide gave the following products:

2-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-Borane.

This compound was obtained as a yellow oil, 30% yield; ^{1}H nmr (deuteriochloroform): 5.70 (m, 3H, O-CH-O, HC=CH), 3.90 (m, 4H, O-(CH$_2$)$_2$-O), 3.20 (m, 3H, H-2, H-6), 2.65 (s, 3H, CH$_3$), 2.28 (m, 2H, H-3); ir (film): 2290, 2400 (st BH).

Anal. Calcd. for $C_9H_{16}BNO_2$: C, 59.05; H, 9.91; N, 7.65. Found: C,

2-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine.

This compound was obtained as a yellow oil, 25% yield; ^{1}H nmr (deuteriochloroform): 5.71 (m, 2H, HC=CH), 5.01 (d, 1H, O-CH-O, J = 5.1 Hz), 3.90 (m, 4H, O-(CH$_2$)$_2$-O), 2.9 (m, 1H, H-2), 2.63 (m, 2H, H-6), 2.49 (s, 3H, CH$_3$), 2.15 (m, 2H, H-3); ir (film): 1670 (st C=C).

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.78; H, 8.93; N, 8.27. Found: C, 63.46; H, 8.82; N, 8.12.

6-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine.

This compound was obtained as a yellow oil, 15% yield; ^{1}H nmr (deuteriochloroform): 5.95 (m, 2H, HC=CH), 4.90 (d, 1H, O-CH-O, J = 4.2 Hz), 3.90 (m, 4H, O-(CH$_2$)$_2$-), 2.9 (m, 1H, H-6), 2.83 (m, 2H, H-2), 2.50 (s, 3H, CH$_3$), 2.15 (m, 2H, H-3); ir (film): 1670 (st C=C).

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.78; H, 8.93; N, 8.27. Found: C, 63.46; H, 8.89; N, 8.36.

2-(1,3-Dioxolan-2-yl)-1-methylpiperidine.

This compound was obtained as a yellow oil in 20%; ^{1}H nmr (deuteriochloroform): 4.98 (d, 1H, O-CH-O, J = 3.5 Hz), 3.92 (m, 4H, O-(CH$_2$)$_2$-O), 2.38 (s, 3H, CH$_3$), 2.90 (m, 1H, H$_{eq}$-6), 2.19 (m, 1H, H-2), 2.0-1.4 (br, 7H, H$_{ax}$-6, CH$_2$ on positions 3, 4 and 5).

The reduction of the 3-(1,3-Dioxolan-2-yl)-1-methylpyridinium iodide gave the following products:

5-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-Borane.

This compound was obtained as a yellow oil, 28% yield; ^{1}H nmr (deuteriochloroform): 5.98 (m, 1H, HC=C), 5.13 (s, 1H, O-CH-O), 3.90 (m, 4H,

O-(CH_2)$_2$-O), 3.54 (m, 2H, H-6), 2.93 (t, 2H, H-2, J = 5.6 Hz), 2.48 (s, 3H, CH_3), 2.23 (m, 2H, H-3); ir (film): 2270, 2400 (st BH); ms: 70 eV): 182 (M^+, 4%), 169 (6%), 152 (4%), 138 (4%), 124 (33%), 96 (49%), 81 (26%).

Anal. Calcd. for $C_9H_{18}BNO_2$: C, 59.05; H, 9.91; N, 7.65. Found: C, 59.37; H, 9.78; N, 7.61.

5-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine.

This compound was obtained as a colourless oil, 54% yield; ^{1}H nmr (deuteriochloroform): 5.96 (m, 1H, HC=C), 5.18 (s, 1H, O-CH-O), 3.95 (m, 4H, O-(CH_2)$_2$-O), 2.97 (m, 2H, H-6), 2.52 (m, 2H, H-2), 2.38 (s, 3H, CH_3), 2.23 (m, 2H, H-3); ir (film): 1660 (st C=C).

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.87; H, 8.93; N, 8.27. Found: C, 63.72; H, 8.79; N, 8.14.

The reduction of the 4-(1,3-dioxolan-2-yl)-1-methylpyridinium iodide gave the following products:

4-(1,3-Dioxolan-2-yl)-1,2,3,6-tetrahydropyridine-Borane.

The compound was obtained as a colourless solid, mp 85-87°, 30% yield; ^{1}H nmr (deuteriochloroform): 5.83 (m, 1H, HC=C), 5.21 (s, 1H, O-CH-O), 3.97 (m, 4H, O-(CH_2)$_2$-O), 3.65 (m, 1H, H-6), 3.23 (m, 1H, H-6), 3.03 (m, 1H, H-2), 2.57 (s, 3H, CH_3), 2.30 (m, 3H, H-2 and CH_2-3); ir (film): 2280, 2400 (st BH); ms: (70 eV): 182 (M^+, 42%), 169 (15%), 152 (7%), 138 (6%), 124 (36%), 96 (100%), 81 (15%).

Anal. Calcd. for $C_9H_{18}BNO_2$: C, 59.05; H, 9.91; N, 7.65. Found: C, 58.98; H, 9.97; N, 7.63.

4-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine.

This compound was obtained as a yellow oil, 60% yield; ^{1}H nmr (deuteriochloroform): 5.87 (m, 1H, HC=C), 5.19 (s, 1H, O-CH-O), 3.94 (m, 4H, O-(CH_2)$_2$-O), 2.97 (m, 2H, H-6), 2.55 (m, 2H, H-2), 2.36 (s, 3H, CH_3), 2.22 (m, 2H, H-3; ir (film): 1670 (st C=C).

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.87; H, 8.93; N, 8.27. Found: C, 63.67; H, 8.86; N, 8.12.

X-Ray Diffraction Analysis of the 4-(1,3-Dioxolan-2-yl)-1-methyl-1,2,3,6-tetrahydropyridine-Borane Complex.

The following data was obtained: $C_9H_{18}BNO_2$, Mr = 183.06, monoclinic crystals, $P2_1/n$, a = 18.488 (1), b = 5.729 (1), c = 10.274 (4) Å, β = 94.91 (3)°, V = 1084.2 (1) Å^3, Z = 4, D_c = 1.12 g cm^{-3}, F(000) = 400, μ = 5.75 (1) cm^{-1}, transparent yellow needles, 0.18 x 0.23 x 0.15 mm, θmax = 65°. A four-circle automatic Pw 1100 diffractometer with graphite monochromated CuKα radiation (λ = 1.5418A) and $\lambda/2\theta$ scan were used to collect the intensities of 2049 independent reflections. Cell constants, were obtained by least-squares fit of 35 reflections with high angles, measured for both positive and negative Bragg angles. Two standard reflections, monitored every 90 minutes, showed no crystal decomposition. In reducing the data, Lorentz and polarization factors were applied, but no corrections for absorption were made. 1232 reflections were considered as observed with the criterion $I \geq 2\sigma(I)$.

The structure was solved using MULTAN [7]. The usual sequence of isotropic and anisotropic refinement was followed, after which all H atoms were located on difference maps. A weighting scheme of the type $w = w_1 \cdot w_2$ was used to prevent bias on $<w\Delta^2F>$ vs. $<Fo>$ and vs. $<\sin 2\theta/\lambda>$, with $w_1 = K/(a + b[Fo] + c[Fo]\Delta^2)^2$ and $w_2 = 1/(d + e \sin 2\theta/\lambda)$ [8]. Final full-matrix [9] anisotropic weighted refinement (isotropic fixed parameters for H atoms) gave the discrepancy indices R = 0.051, Rw = 0.054. Scattering factors for neutral atoms [10] were used.

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