SYNTHESIS AND STEREOCHEMISTRY OF SOME NEW 1,3-DIOXANE DERIVATIVES OBTAINED FROM 2-ACETYL AND 2,6-DIACETYLPYRIDINE

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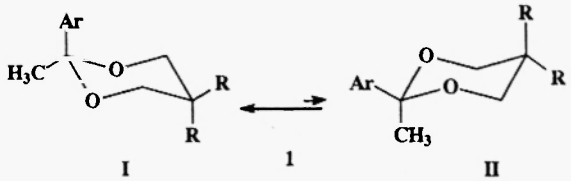
Abstract: The stereochemistry of new 1,3-dioxane derivatives obtained by the acetalization of 2-acetyl and 2,6-diacetylpyridine with several 1,3-propanediols have been investigated by NMR methods and by X-ray diffractometry. The anancomeric structure of the compounds and the axial orientation of the aromatic group in both type of derivatives was revealed.

INTRODUCTION

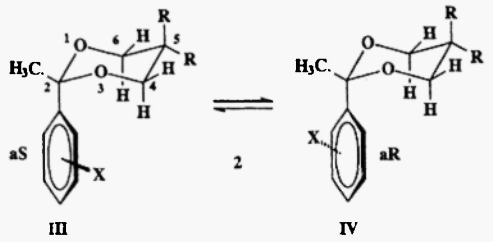
The studies on the stereochemistry of 2-aryl, 2-methyl-1,3-dioxane derivatives (**1**) show the high axial preference of the aromatic substituent (Scheme 1; equilibrium shifted towards conformer I).[1-7]



Scheme 1

The comparison of the A-values of methyl (A = free conformational enthalphy; A_{Me} = 16.64 kJ/mol)[2] and phenyl (A_{Ph} = 13.04 kJ/mol)[2] groups at position 2 of the 1,3-dioxane ring (? A = $A_{Me} - A_{Ph}$ = 3.60 kJ/mol) predicts the axial preference of the aromatic substituent. The thermodynamic measurements in 2-methyl, 2-phenyl-1,3-dioxanes showed a considerably higher preference of the methyl group for the equatorial position (? G^0 = 10.1 kcal/mol)[2] as it was obtained by the simple addition of the A-values of these substituents (? A). The axial aromatic ring prefers the orthogonal disposition, either in solid state and in solution.[4-11] The studies[5] on the stereochemistry of 1,3-dioxane compounds bearing disymmetric aromatic rings (**2**) revealed the axial chirality of the compounds (Scheme 2). The hindrance of the rotation of the aromatic ring at low temperature made possible to demonstrate the chirality of the molecules by the diastereotopicity of the homomorphic groups attached to prochiral centers (*e.g.* the low temperature spectra exhibit two signals for the axial protons at position 4 and 6 and two signals for the equatorial protons of the same positions). The stereochemical investigations on the 1,3-dioxane derivatives of 1,4-diacetylbenzene[7] revealed the axial orientation of

the aromatic rings for both heterocycles and its preference for the orthogonal rotamer. Some of these derivatives were versatile substrates in the synthesis of new macrocyclic cyclophanes.[12] The peculiar aspects of the stereochemistry of aromatic 1,3-dioxane derivatives and their structural pre-organization, that enables the macrocyclisation, motivates the synthesis and the stereochemistry investigation on new 1,3-dioxane derivatives obtained starting from 2-acetyl and 2,6-diacetylpyridine.

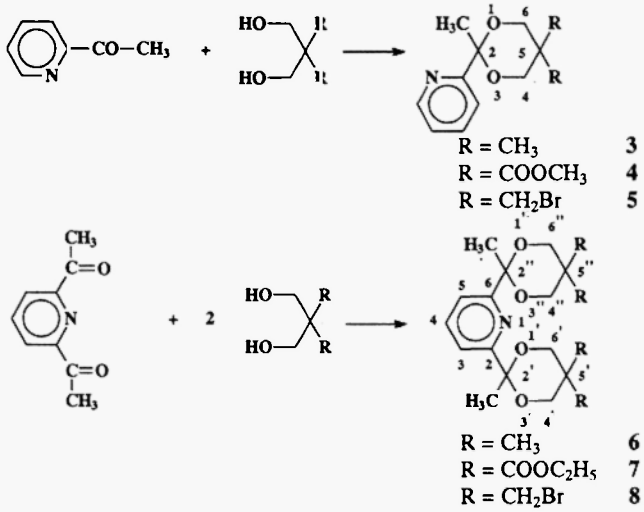


III IV

Scheme 2

RESULTS AND DISCUSSIONS

New 1,3-dioxane derivatives **3-9** have been obtained by the reaction of 2-acetylpyridine and 2,6-diacetylpyridine with several 1,3-propanediols (Scheme 3).

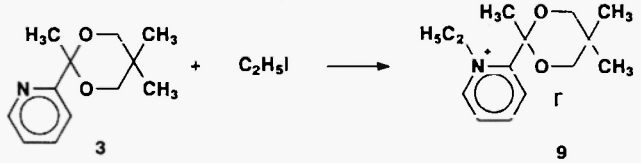


R = CH_3 **3**
R = $COOCH_3$ **4**
R = CH_2Br **5**

R = CH_3 **6**
R = $COOC_2H_5$ **7**
R = CH_2Br **8**

Scheme 3

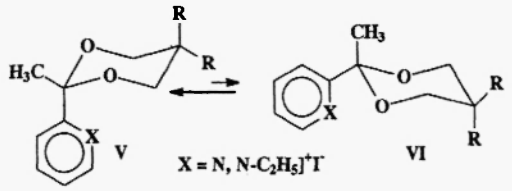
Compounds **3** and **6** were reacted with C_2H_5I, but the N-alkylation reaction underwent only in the case of compound **3** (Scheme 4).



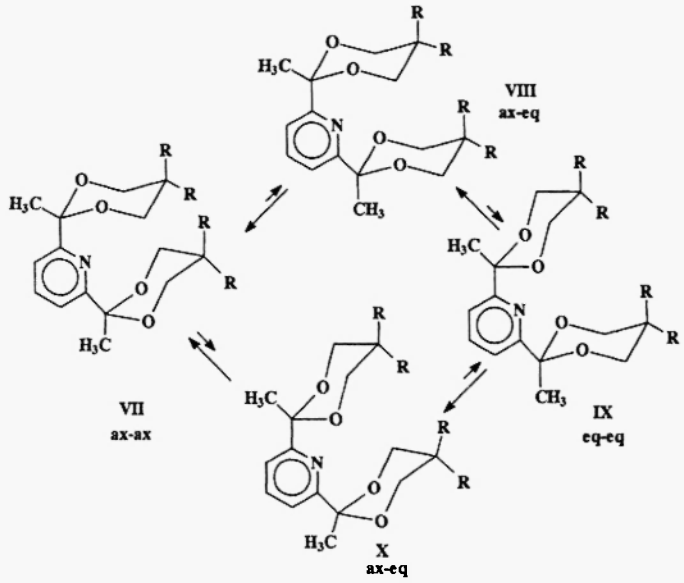
3 **9**

Scheme 4

All investigated compounds exhibit anancomeric 1,3-dioxane rings. The conformational equilibria are shifted towards the conformer showing the aromatic ring in axial orientation (structures V and VII; Schemes 5 and 6). The NMR spectra (Table 1) exhibit different signals for the equatorial and axial protons of the 1,3-dioxane rings ($\Delta\delta_{eq\text{-}ax}$ = 0.07-0.56 ppm) and for the axial and equatorial similar groups located at the alkyl part of the saturated heterocycles ($\Delta\delta_{ax\text{-}eq}$ = 0.14-0.83 ppm).



Scheme 5



Scheme 6

Table 1. ^{1}H NMR data (δ, ppm, $CDCl_3$) for compounds **3-9**

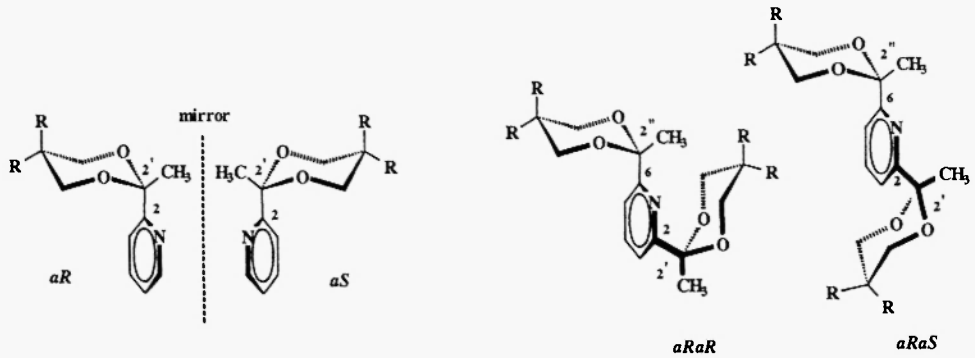
Compound	positions 5 (5',5''): CH_3, CH_2Br; OCH_2-			positions 4 (4',4''), 6 (6',6'')		
	axial	*equatorial*	*Δax-eq*	*equatorial*	*axial*	*Δeq-ax*
3†	1.25	0.62	0.63	3.49	3.42	0.07
4#	3.88	3.63	0.25	4.55	3.99	0.56
5•	3.96	3.13	0.83	3.91	3.63	0.28
6†	1.19	0.62	0.57	3.47	3.38	0.09
7#	1.29	1.15	0.14	4.50	3.98	0.52
	4.31	4.07	0.28			
8•	3.90	3.18	0.72	3.91	3.64	0.27
9†	1.19	0.77	0.42	3.62	3.44	0.18

† **5-CH_3**; • **5-CH_2Br**; # **5-$COO(CH_2)$-CH_3**

If the rotation of the aromatic ring is considered frozen the axis C^2-$C^{2'}$ in compounds **3-5** and **9** (Scheme 7) and the axes C^2-$C^{2'}$ and C^6-$C^{2''}$ in compounds **6-8** (Scheme 7), due to the disymmetry of the aromatic substituents, represent axes of chirality. For instance, the reference groups for the chiral axis (C^2-$C^{2'}$) in compounds **3-5** and **9** are N and CH (position 3) at the 2 end and the whole 1,3-dioxane ring and the methyl group at the other end (2') of the chiral axis.

The two chiral axes of the frozen structure of **6-8** determine the presence of two diastereoisomers: one with the same configuration of the chiral axes (*like*: *aRaR*, *aSaS*) and another one with different configurations of the chiral elements (*unlike*: *aRaS*).

The chirality of the frozen structures should be theoretically observed by the diastereotopicity of the homomorphic groups connected to prochiral elements (*e.g.* the axial or the equatorial protons of positions 4 and 6) for all investigated compounds and in addition by the presence of signals for two diastereoisomers in the case of compounds **6-8**.



3-5 **6-8**

Scheme 7

It was considered of high interest to investigate these compounds using variable temperature ^{1}H NMR experiments. The experiments were carried out with compounds **3**, **6** and **9**. The experiments with **9** failed due to the low solubility at low temperature of the product in all usual NMR solvents. The experiments with **3** and **6** ([D_8]-toluene) showed only light modifications of the shape of the spectra with the lowering of the temperature and the separation in the low temperature spectra (193 K) of the signals belonging to the different diastereoisomers or to the diastereotopic protons could not be observed. This peculiar situation is probably due to the insignificant modifications of the magnetic environment in the possible isomers and at the level of diastereotopic protons, despite the freezing of the rotation of the pyridine ring (it is to believe that the barrier of the rotation of the pyridine ring around its bond with the 1,3-dioxane ring is similar with that of other aromatic substituents).[5]

Structure of compound **8** was investigated in solid state by X-ray diffractometry. The ORTEP diagram shows the axial-orthogonal orientation of the aromatic ring for both 1,3-dioxane rings (Figure 1).

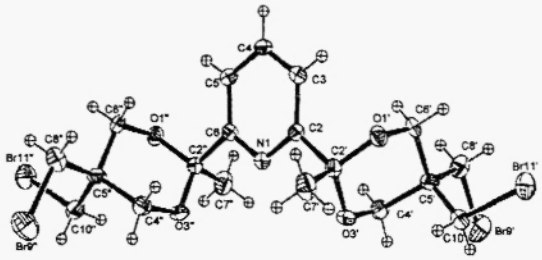


Figure 1. ORTEP diagram for compound **8.**

The 1,3-dioxane rings exhibit chair conformations and the methyl groups at position 2' and 2" are oriented on opposite directions. This arrangement corresponds to the *like* diastereoisomer (similar configuration for the two chiral axes; *e.g.* *aRaR* in the structure shown in Figure 1).

CONCLUSIONS

The good yields synthesis of new 1,3-dioxane derivatives of 2-acetyl- and 2,6-diacetyl-pyridine by acetalization with several 1,3-propanediols was performed using PTSA in excess. The stereochemistry investigations by NMR in solution, and by the molecular structure of compound **8** obtained by X-ray diffractometry in solid state revealed the axial orientation of the aromatic substituent and its orthogonal rotameric behaviour.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded at room temperature using $CDCl_3$ as solvent in 5 mm tubes on a Varian Gemini or Bruker Avance DPX 300 spectrometer equipped with a multinuclear head operating at 300 MHz for protons and 75 MHz for carbon atoms. Melting points were measured with a *Kleinfeld* melting point apparatus and are uncorrected.

X-ray Crystallographic Study: Crystal data and data-collection information are summarized in Table 2.

The sample was studied on an automatic diffractometer CAD4 NONIUS[13] with graphite monochromatized Mo-$K\alpha$ radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. After Lorenz and polarization

corrections[14] the structure was solved with SIR-97[15] which reveals the non hydrogen atoms of the compound. After anisotropic refinement a Fourier Difference reveals many hydrogen atoms. The whole structure was refined with SHELXL97[16] by the full-matrix least-square techniques.
Atomic scattering factors from International Tables for X-ray Crystallography.[17] ORTEP view was realized with PLATON98[18] and ORTEP-3 for windows.[19] All the calculations were performed on a Pentium NT Server computer.
The structural data were deposited at the Cambridge Crystallographic Data Center with the number CCDC-215375.

Table 2. Crystal data and data collection information for **8.**

Parameters	Values	Parameters	Values
Empirical formula	$C_{19}H_{25}Br_4NO_4$	Z	4
Formula weight	651.04	D_{calc} (g cm^{-3})	1.908
Temperature (K)	293(2)	Absorption coefficient (mm^{1})	7.128
Wavelength (A)	0.71069	F(000)	1272
Crystal system	monoclinic	Crystal size (mm)	0.22x0.20x 0.08
Space group	C2/c	? range for data collection (°)	1.37-27.02
Unit cell dimension		Reflections collected	2605
a (Å)	29.682(9)	Independent reflections	2476 [R_{int} = 0.1412]
b (Å)	6.391(8)	Data / restraints / parameters	2476/0/129
c (Å)	11.958(6)	Goodness-of-fit on F^2	0.988
a (°)	90	Final R indices [F^2>2s (F^2)]	R_1=0.0652, wR_2=0.1640
ß (°)	92.61	R indices (all data)	R_1=0.1500, wR_2=0.1981
? (°)	90	Largest difference	
Volume ($Å^3$)	2266(3)	peak and hole (e $Å^{-3}$)	1.249 and –1.600

***Compounds* 3-8 (*General Procedure*)**
Stoechiometric amounts of (0.1 mol or 0.2 mol) 1,3-diol, (0.1 mol) ketone or diketone and (0.12 mol) *p*-toluenesulfonic acid (20 % excess) were dissolved in 200 cm^3 toluene. The mixture was refluxed and reaction H_2O was removed by a Dean-Stark trap. When 80% of the H_2O was separated, after cooling at room temperature, PTSA was neutralised (under stirring 0.5 h) with (2 g) sodium acetate. The reaction mixture was washed twice with 100 cm^3 H_2O. After drying with Na_2SO_4 the solvent was removed and the compounds were purified by crystallisation from ethanol or by flash-chromatography. Compound **6** was previously succintelly described in literature, being isolated as side-product in the mono protection of the carbonyl groups of 2,6-diacetyl-pyridine.[20]

***2-(2'-Pyridyl)-2,5,5-trimethyl-1,3-dioxane* 3**
Solid, m.p. 38-39 °C. Yield: 60 %. Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.37; H, 8.29; N, 6.93. ^{1}H NMR δ ($CDCl_3$) 0.62 (s, 3H, 5-CH_3-*eq*)], 1.25 (s, 3H, 5-CH_3-*ax*), 1.58 (s, 3H, 2-CH_3-*eq*), 3.42 (d, J = 11.1 Hz, 2H, H_{ax}-4,6), 3.49 (d, J = 11.1 Hz, 2H, H_{eq}-4,6), 7.21-7.26 (m, 1H, 5'-H), 7.52 (d, J = 7.8 Hz, 1H, 3'-H), 7.73 [t (overlapped dd), J = J' = 7.8 Hz, 1H, 4'-H), 8.69 (d, J = 4.3 Hz, 1H, 6'H). ^{13}C NMR d ($CDCl_3$) 22.07 (5-CH_3-*eq*), 22.96 (5-CH_3-*ax*), 29.55 (2-CH_3-*eq*), 29.92 (C-5), 72.13 (C-4,6), 99.97 (C-2), 121.82 (C-5'), 122.63 (C-3'), 136.94 (C-4'), 149.64 (C-6'), 154.44 (C-2').
***2-(2'-Pyridyl)-2-methyl-5,5-dimethyloxycarbonyl-1,3-dioxane* 4**
Solid, m.p. 95-96 °C. Yield: 48 %. Anal. Calcd. for $C_{14}H_{17}NO_6$: C, 56.94; H, 5.80; N, 4.74. Found: C, 57.15; H, 7.97; N, 4.66. ^{1}H NMR δ ($CDCl_3$) 1.61 (s, 3H, 2-CH_3-*eq*)], 3.63 (s, 3H, 5-$COOCH_3$-*eq*), 3.88 (s, 3H, 5-$COOCH_3$-*ax*), 3.99 (d, J = 11.6 Hz, 2H, H_{ax}-4,6), 4.55 (d, J = 11.6 Hz, 2H, H_{eq}-4,6), 7.26 (m, 1H, 5'-H), 7.50 (d, J = 7.7 Hz, 1H, 3'-H), 7.76 [t (overlapped dd), J = J' = 7.8 Hz, 1H, 4'-H), 8.69 (m, 1H, 6'-H). ^{13}C NMR d ($CDCl_3$) 29.48 (2-CH_3-*eq*), 53.26 (5-$COOCH_3$-*eq*), 53.45 (C-5), 53.59 (5-$COOCH_3$-*ax*), 64.32 (C-4,6), 100.91 (C-2), 122.01 (C-5'), 123.38 (C-3'), 137.56 (C-4'), 150.20 (C-6'), 158.91 (C-2'), 167.80 (5-$COOCH_3$-*eq*), 168.87 (5-$COOCH_3$-*ax*).
***2-(2'-Pyridyl)-2-methyl-5,5-di(bromomethyl)-1,3-dioxane* 5** Colorless oil, subjected to column chromatography; dichloromethane (R_f=0.27). Yield: 44 %. Anal. Calcd. for $C_{12}H_{15}Br_2NO_2$: C, 39.48; H, 4.14; N, 3.84; Br, 43.78. Found: C, 39.39; H, 4.07; N, 3.99; Br, 43.61. ^{1}H NMR δ ($CDCl_3$) 1.59 (s, 3H, 2-CH_3-*eq*)], 3.13 (s, 2H, 5-CH_2Br-*eq*), 3.63 (d, J = 11.7 Hz, 2H, H_{ax}-4,6), 3.91 (d, J = 11.7 Hz, 2H, H_{eq}-4,6), 3.96 (s, 2H, 5-CH_2Br-*ax*), 7.27 (m, 1H, 5'-H), 7.49 (d, J = 7.6 Hz, 1H, 3'-H), 7.77 [dt (overlapped ddd), J = J' = 7.6 Hz, J'' = 1.4 Hz, 1H, 4'-H), 8.69 (m, 1H, 6'-H). ^{13}C NMR d ($CDCl_3$) 29.30 (2-CH_3-*eq*), 35.00 (5-CH_2Br-*eq*), 36.33 (5-CH_2Br-*ax*), 37.56 (C-5), 66.50 (C-4,6), 101.02 (C-2), 121.72 (C-5'), 123.21 (C-3'), 137.41 (C-4'), 149.96 (C-6'), 158.63 (C-2').
***2,6-Bis(2,5,5-trimethyl-1,3-dioxan-2-yl)pyridine* 6**
Solid, m.p.=217-218 °C.Yield: 58%. ^{1}H-NMR δ ($CDCl_3$) 0.62 [s, 6H, 5'(5")-CH_3-*eq*], 1.19 [s, 6H, 5'(5")-CH_3-*ax*)], 1.58 [s, 6H, 2'(2")-CH_3-*eq*], 3.38 [d, J = 11.3 Hz, 4H, H_{ax}-4'(4"),6'(6")], 3.47 [d, J = 11.3 Hz, 4H, H_{eq}-4'(4"),6'(6")], 7.44 [d, J = 7.9 Hz, 2H, 3,5-H], 7.73 [t, J = 7.9 Hz; 1H, 4-H]. ^{13}C-NMR δ ($CDCl_3$) 22.49 [5'(5")-CH_3-*eq*], 23.22

[5'(5")-CH_3-*ax*], 28.98 [2'(2")-CH_3-*eq*], 30.23 [C-5'(5")], 72.31 [C-4'(4"),6'(6")], 100.30 [C-2'(2")], 121.00 [C-3,5], 137.77 [C-4], 160.24 [C-2,6].

2,6-Bis(5,5-diethyloxycarbonyl-2-methyl-1,3-dioxan-2-yl)pyridine 7

Solid, m.p. = 120-121^{0}C. Yield: 60%. Anal. Calcd. for $C_{27}H_{37}NO_{12}$: C, 57.14; H, 6.57; N, 2.47. Found: C, 57.33; H, 6.41; N, 2.58. ^{1}H-NMR δ ($CDCl_3$) 1.15 [t, J = 7.1 Hz, 6H, 5'(5")-$COOCH_2CH_3$-*eq*], 1.29 [t, J = 7.1 Hz, 6H, 5'(5")-$COOCH_2CH_3$-*ax*], 1.56 [s, 6H, 2'(2")-CH_3-*eq*] 3.98 [d, J = 11.6 Hz, 4H, H_{ax}-4'(4"),6'(6")], 4.07 [q, J = 7.1 Hz, 4H, 5'(5")-$COOCH_2CH_3$-*eq*], 4.31 [q, J = 7.1 Hz, 4H, 5'(5")-$COOCH_2CH_3$-*ax*], 4.50 [d, J = 11.6 Hz, 4H, H_{eq}-4'(4"),6'(6")], 7.46 [d, J = 7.9 Hz, 2H, 3,5-H], 7.78 [t, J = 7.9 Hz, 1H, 4-H]. ^{13}C-NMR δ ($CDCl_3$) 14.19 [5'(5")-$COOCH_2CH_3$-*eq*], 14.40 [5'(5")-$COOCH_2CH_3$-*ax*], 28.51 [2'(2")-CH_3-*eq*], 53.62 [C-5'(5")], 62.14 [5'(5")-$COOCH_2CH_3$-*eq*], 62.27 [5'(5")-$COOCH_3CH_2$-*ax*], 64.22 [C-4'(4"),6'(6")], 100.73 [C-2'(2")], 121.31 (C-3,5), 138.42 (C-4), 159.18 (C-2,6), 167.54 [5',5"-$COOC_2H_5$-*eq*], 168.36 [5',5"-$COOC_2H_5$-*ax*].

2,6-Bis(5,5-dibromomethyl-2-methyl-1,3-dioxan-2-yl)pyridine **8**

Solid, m.p. = 196^{0}C. Yield: 45%. Anal. Calcd. for $C_{19}H_{25}Br_4NO_4$: C, 35.05; H, 3.87; N, 2.15; Br, 49.09. Found: C, 34.89; H, 3.92; N, 2.28; Br, 48.94.^{1}H-NMR δ ($CDCl_3$) 1.60 [s, 6H, 2'(2")-CH_3-*eq*] 3.18 [s, 4H, 5'(5")-CH_2-*eq*], 3.64 [d, J = 12.0 Hz, 4H, H_{ax}-4'(4"),6'(6")], 3.90 [s, 4H, 5'(5")-CH_2-*ax*], 3.91 [d, J = 12.0 Hz, 4H, H_{eq}-4'(4"),6'(6")], 7.46 [d, J = 7.9 Hz, 2H, 3,5-H], 7.81 [t, J = 7.9 Hz, 1H, 4-H]. ^{13}C-NMR δ ($CDCl_3$) 28.79 [2'(2")-CH_3-*eq*], 35.41 [5'(5")-CH_2-*eq*], 36.49 [5'(5")-CH_2-*ax*], 37.84 (C-5',5"), 66.62 (C-4',4",6'6"), 101.17 (C-2',2"), 121.26 (C-3,5), 138.50 (C-4), 159.41 (C-2,6).

1-Ethyl-2-(2',5',5'-trimethyl-1',3'-dioxan-2'-yl)-pyridinium iodide **9**

Solid, m.p. 172 °C. Yield: 85 %. Anal. Calcd. for $C_{14}H_{22}INO_2$: C, 46.29; H, 6.10; N, 3.86; I, 34.94. Found: C, 46.44; H, 6.01; N, 3.97; I, 35.11.^{1}H NMR δ ($CDCl_3$) 0.77 (s, 3H, 5'-CH_3-*eq*), 1.19 (s, 3H, 5'-CH_3-*ax*), 1.71 (t, J = 7.2 Hz, 3H, 1-CH_2-CH_3), 1.76 (s, 3H, 2'-CH_3-*ax*), 3.44 (d, J = 11.2 Hz, 2H, H_{ax}-4',6'), 3.62 (d, J = 11.2 Hz, 2H, H_{eq}-4',6'), 5.18 (2H, d, J = 7.2 Hz, 1-CH_2-CH_3), 8.19 (d, J = 7.9 Hz, 1H, 3-H), 8.28 (m, 1H, 5-H), 8.62 (m, 1H, 4-H), 9.70 (d, J = 6.0 Hz, 1H, 6-H). ^{13}C NMR δ ($CDCl_3$) 17.43 (1-CH_2-CH_3), 21.97 (5'-CH_3-*eq*), 22.42 (5'-CH_3-*ax*), 28.46 (2'-CH_3-*ax*), 30.10 (C-5'), 54.40 (1-CH_2-CH_3), 72.71 (C-4',6'), 105.78 (C-2'), 128.08, 128.99, 146.17, 149.40 (aromatic tertiary carbon atoms), 155.60 (aromatic quaternary carbon atom).

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Received on September 16, 2003.