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SELECTIVE SUBSTITUTION OF UNPROTONATED PYRIDINES BY ALKYL RADICALS

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Abstract—The reactions of dioxanyl and cyclohexyl radicals with 2- and 3-X-pyridines (X = CN, COMe, CO_2Me) give a single substitution product deriving by addition at the 5- and 6-position respectively; with 4-X-pyridines substitution occurs preferentially at the 3-position. If the reactions are carried out with protonated pyridines other positional isomers are obtained. From the synthetic point of view the two procedures are therefore complementary. The change in positional selectivity on passing from unprotonated to protonated aromatic substrates is discussed and interpreted on the basis of the different nature of the transition state of the addition step.

We have recently reported[1] that dioxanyl radicals react with 2,5-diacetylpyridine to give the *ipso* substitution products, 2-acetyl-5-dioxanylpyridine and 2-dioxanyl-5-acetylpyridine; similar results were obtained with the 2,4,5-triacetylpyridine. On the other hand, in the presence of sulphuric acid, the substitution occurs at the 2- and 4-positions. This change in positional selectivity on passing from unprotonated to protonated pyridines is interesting from the mechanistic point of view and can also find useful synthetic applications. In the present paper we report the results of the radical dioxanylation and cyclohexylation of cyano-, acetyl- and ethoxycarbonylpyridines under neutral conditions and in the presence of sulphuric acid. From the comparison of the results obtained in the two cases it is now possible to have a better knowledge of the factors controlling the selectivity of these homolytic aromatic substitution reactions.

RESULTS

In the reactions carried out under neutral conditions, the dioxanyl and cyclohexyl radicals were produced by hydrogen abstraction from the corresponding hydrocarbons; the abstracting species was the *t*-butoxy radical produced by thermal decomposition of the *t*-butylperoxyoxalate:

$$(Me_3COCO_2)_2 \rightarrow 2Me_3Co\cdot + 2CO_2$$

$$Me_3CO\cdot + RH \rightarrow Me_3COH + R\cdot$$

$$R\cdot = C_4H_7O_2\cdot,\ C_6H_{11}\cdot$$

In the reactions carried out in the presence of sulphuric acid the dioxanyl radical was produced from dioxane[2] and the cyclohexyl radical from cyclohexane carboxylic acid[3] according to the procedures described in the literature.

The reactions of dioxanyl radicals with 2-cyano-, **1**, 2-acetyl-, **2**, and 2-ethoxycarbonylpyridine, **3**, afforded the product of substitution at the 5 position **4**, **5** and **6** respectively, with the yields indicated in parentheses (Scheme 1). Similarly the cyclohexyl radicals gave products **7**, **8** and **9**. On the other hand, the reactions of dioxanyl radicals with the protonated substrates, **1–3**, afforded derivatives **10**, **11** and **12** respectively (Scheme 2). Only in the case of 2-ethoxycarbonylpyridine was the product of substitution at the 6 position, **13**, also formed in small amounts. In order to minimize the amount of polysubstitution products, these reactions were stopped at low conversions and reaction yields were therefore not determined. In the case of the cyclohexylation of **2** the expected product **14** was also accompanied by the products of substitution at the 6 position, **15**, and at the 4 and 6 positions, **16**.

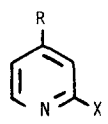
From the reaction of the 3-acetylpyridine **17** with dioxanyl radicals the only product obtained, in 34% yields, was the 3-acetyl-6-dioxanyl-pyridine **18**. The same product was also formed from protonated **17**; in this case, however, even at low conversions, the disubstituted product **19** was also present (Scheme 3).

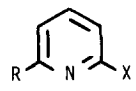
With 4-substituted pyridines, **20–22**, the alkylation reactions, under neutral conditions, were not completely selective, a mixture of the two possible isomers being obtained in every case (Scheme 4); the ratio between the

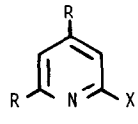
1, X = CN
2, X = COMe
3, X = CO_2Et

4, X = CN, R = $C_4H_7O_2$ (35%)
5, X = COMe, R = $C_4H_7O_2$ (35%)
6, X = CO_2Et, R = $C_4H_7O_2$ (50%)
7, X = CN, R = C_6H_{11} (37%)
8, X = COMe, R = C_6H_{11} (39%)
9, X = CO_2Et, R = C_6H_{11} (35%)

Scheme 1.





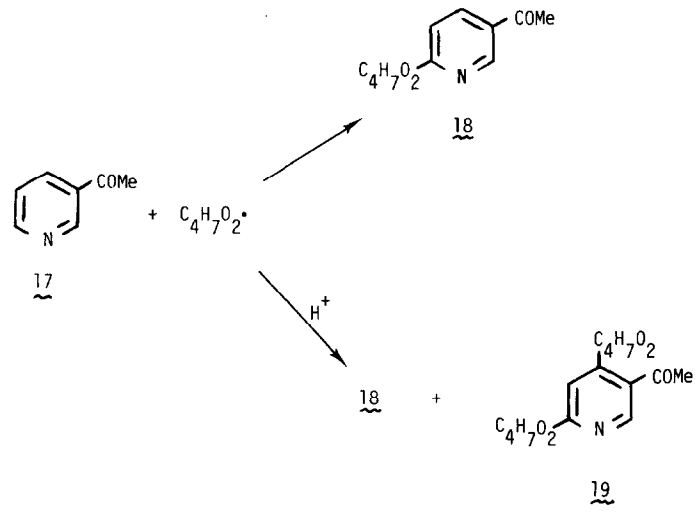


10, X=CN, R=$C_4H_7O_2$
11, X=COMe, R=$C_4H_7O_2$
12, X=CO_2Et, R=$C_4H_7O_2$
14, X=COMe, R=C_6H_{11}

13, X=CO_2Et, R=$C_4H_7O_2$
15, X=COMe, R=C_6H_{11}

16, X=COMe, R=C_6H_{11}

Scheme 2.



Scheme 3.

products of substitution at the 3 position and those at the 2 position was 85 : 15 in the dioxanylation and cyclohexylation of 4-cyanopyridine **20** and about 60 : 40 in all the other cases. Total reaction yields are reported in parentheses in Scheme 4. In the case of **22** the reaction with cyclohexyl radicals also afforded considerable amounts (14%) of the 2,5-dicyclohexyl-4-ethoxycarbonylpyridine **35**.

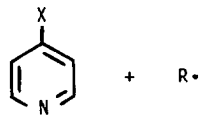
When the reactions of the 4-X-pyridine **20–22** with dioxanyl radicals were carried out in the presence of sulphuric acid, substitution occurred at the 2 position to give the products **23–25**; these compounds however were always accompanied by the products of bis substitution at the 2 and 6 positions, **36**, **38** and **39**. In the case of 4-cyanopyridine attack at the 5 position to give 2,5-didioxanyl-4-cyanopyridine **37** (13%) was also observed (Scheme 5). Similarily the cyclohexylation of **20** afforded **26** together with small amounts of **40**. Interesting results were obtained from the cyclohexylation of 4-acetylpyridine **21**. In this reaction, radical substitution at the 2 position to give **27** (17%) and *ipso* substitution at the 4 position to give the 4-cyclohexylpyridine **41** (9%) were in competition (Scheme 5). Small amounts of the 2,4-dicyclohexylpyridine **42** (5%) were also obtained; this product very likely originates from the *ipso* substitution of **27**. This peculiar behaviour of the 4-acetylpyridine is similar to that already observed with bridgehead radicals.[4,5]

Structural assignment of the products described above could be easily effected by proton NMR spectroscopy. Pertinent data are collected in Table 1. The values of the coupling constants were perfectly in agreement with those expected and were particularly useful to establish the substitution pattern of the various pyridine derivatives.

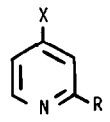
DISCUSSION

The results described in this paper demonstrate that alkyl radicals can effect selective substitutions both on protonated and on unprotonated pyridines; of particular interest is the fact that different isomers are obtained in the two cases.

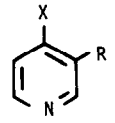
In the presence of sulphuric acid substitution occurs at the α and/or γ positions; the only exception is the formation of 2,5-didioxanyl-4-cyanopyridine **37**, as a by-product, in the reaction of dioxanyl radicals with 4-cyanopyridine. Radical addition occurs at these positions even if they are already occupied by an acetyl group. Interesting examples of *ipso* substitution are thus observed as in the case of 4-acetylpyridine (Scheme 5) and of the previously studied[1] 2,5-diacetylpyridine which give rise to the alkyldeacylation products. The positional



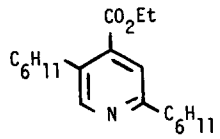
20, X=CN
21, X=COMe
22, X=CO_2Et



23, X=CN, R=$C_4H_7O_2$
24, X=COMe, R=$C_4H_7O_2$
25, X=CO_2Et, R=$C_4H_7O_2$
26, X=CN, R=C_6H_{11}
27, X=COMe, R=C_6H_{11}
28, X=CO_2Et, R=C_6H_{11}



29, X=CN, R=$C_4H_7O_2$ (33%)
30, X=COMe, R=$C_4H_7O_2$ (34%)
31, X=CO_2Et, R=$C_4H_7O_2$ (45%)
32, X=CN, R=C_6H_{11} (28%)
33, X=COMe, R=C_6H_{11} (40%)
34, X=CO_2Et, R=C_6H_{11} (40%)



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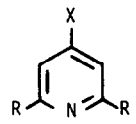
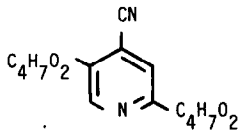
Scheme 4.



36, X=CN, R=$C_4H_7O_2$
38, X=COMe, R=$C_4H_7O_2$
39, X=CO_2Et, R=$C_4H_7O_2$
40, X=CN, R=C_6H_{11}



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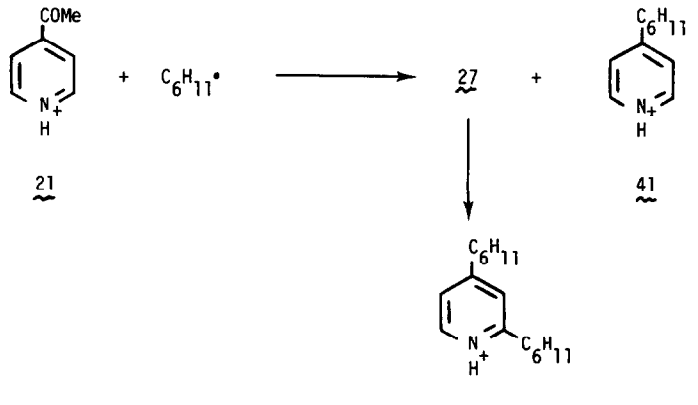


21 41 42

Scheme 5.

Table 1. Physical and NMR data of pyridine derivatives[a] formed from the reactions of 2-, 3-, and 4-cyano-, acetyl- and ethoxycarbonyl-pyridines with dioxanyl and cyclohexyl radicals

Pyridine Derivatives		Method of	Mp or Bp (°C)	Chemical Shifts (δ)[b]							Coupling Constants (Hz)				
Number	Substituents	Preparation	[P/mmHg·10^{-2}]	2	3	4	5	6	CH[c]	CH[d]	$J_{2,4}$ $J_{4,6}$	$J_{2,5}$ $J_{3,6}$	$J_{3,4}$ $J_{4,5}$	$J_{3,5}$	$J_{5,6}$
4	2-CN,5-$C_4H_7O_2$	A	94-6		7.9	7.7		8.65	4.75		2.1	0.5	7.8		
5	2-COMe,5-$C_4H_7O_2$	A	119-20		8.05	7.8		8.65	4.75		2.1	0.5	7.8		
6	2-CO_2Et,5-$C_4H_7O_2$	A	72-4		8.05	7.7		8.7	4.75		2.1	0.5	7.8		
7	2-CN,5-C_6H_{11}	A	101-3[1.5]		7.6	7.6		8.5		2.8-2.4		g			
8	2-COMe,5-C_6H_{11}	A	82-4 [1]		7.95	7.6		8.5		2.8-2.4	2.1	0.5	7.8		
9	2-CO_2Et,5-C_6H_{11}	A	45-7		8.0	7.6		8.5		2.8-2.4	2.1	0.5	7.8		
10	2-CN,4-$C_4H_7O_2$	B	109-10[3]		7.75[e]		7.55[e]	8.65	4.7			0.5		1.5	4.8
11	2-COMe,4-$C_4H_7O_2$	B	90-2		7.9[e]		7.45[e]	8.6	4.7			0.5		1.5	4.8
12	2-CO_2Et,4-$C_4H_7O_2$	B	69-70		8.1[e]		7.5[e]	8.7	4.75			0.5		1.5	4.8
13	2-CO_2Et,6-$C_4H_7O_2$	B	f		8.05	7.9	7.75						7.8	1.5	
14	2-COMe,4-C_6H_{11}	B	49-51		7.95		7.35	8.6		2.8-2.4		0.5		1.5	4.8
15	2-COMe,6-C_6H_{11}	B	f		7.85	7.65	7.3			3.0-2.6			7.8	1.5	
16	2-COMe,4,6-C_6H_{11}	B	f		7.7		7.15			2.9-2.4				1.5	
18	3-COMe,6-$C_4H_7O_2$	A,B	143-5	9.05		8.2	7.6		4.8		2.1	0.5	7.8		
19	3-COMe,4,6-$C_4H_7O_2$	B	108-10	9.0			7.9		5.2,4.8			g			
23	4-CN,2-$C_4H_7O_2$	A,B	93-4[h]		7.7		7.4	8.65	4.7			0.5		1.5	4.8
36	4-CN,2,6-$C_4H_7O_2$	B	125-7		7.6		7.6		4.75						
37	4-CN,2,5-$C_4H_7O_2$	B	150-2		7.65			8.75	4.95,4.75			g			
24	4-COMe,2-$C_4H_7O_2$	A,B	97-9 [4]		7.9		7.6	8.65	4.75			0.5		1.5	4.8
38	4-COMe,2,6-$C_4H_7O_2$	B	137-9		7.8		7.8		4.75						
25	4-CO_2Et,2-$C_4H_7O_2$	A,B	54-5		8.0		7.7	8.65	4.75			0.9		1.5	4.8
39	4-CO_2Et,2,6-$C_4H_7O_2$	B	132-4		8.0		8.0		4.75						
26	4-CN,2-C_6H_{11}	A,B	67-9[3]		7.4		7.35	8.7		3.0-2.6		0.9		1.5	4.8
40	4-CN,2,6-C_6H_{11}	B	67-8		7.1		7.1			3.0-2.6					
27	4-COMe,2-C_6H_{11}	A,B	76-7[3]		7.55		7.5	8.65		3.0-2.6		0.9		1.5	4.8
41	4-C_6H_{11}	B	f	8.45	7.05		7.05	8.45		2.7-2.3					
42	2,4-C_6H_{11}	B	f		6.95		6.85	8.35		2.9-2.2		0.5		1.5	4.8

28	4-CO_2Et,2-C_6H_{11}	A	62-3[8]		7.75	7.65	8.7		3.0-2.6	0.9	1.5	4.8
35	4-CO_2Et,2,5-C_6H_{11}	A	70[2.5]		7.35		8.6		3.3-2.95 2.85-2.5	g		
29	4-CN,3-$C_4H_7O_2$	A	84-6[1.5]	8.85		7.45	8.65	4.9		0.5		4.8
30	4-COMe,3-$C_4H_7O_2$	A	96-9	8.9		7.35	8.65	5.0		0.5		4.8
31	4-CO_2Et,3-$C_4H_7O_2$	A	51-3	8.9		7.6	8.6	5.25		0.5		4.8
32	4-CN,3-C_6H_{11}	A	44-5	8.65		7.4	8.55		3.1-2.6	0.5		4.8
33	4-COMe,3-C_6H_{11}	A	70-2[1]	8.65		7.2	8.5		3.1-2.7	0.5		4.8
34	4-CO_2Et,3-C_6H_{11}	A	79-81[5]	8.65		7.45	8.45		3.4-3.0	0.5		4.8
i	2,4-COMe,5-$C_4H_7O_2$	A	100-3		8.1		8.9	5.05		g		
i	2,5-COMe,4-$C_4H_7O_2$	B	103-5		8.3		8.9	5.1		g		
i	4,5-COMe,2-$C_4H_7O_2$	A	f		7.5		8.9	4.75		g		

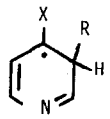
[a]Satisfactory elemental analyses were obtained for all new compounds. [b]The methyl of the COMe group gave a singlet at δ 2.7 when linked at the 2 position of the pyridine ring and at δ 2.6 when linked at the 3 or 4 positions. The ethyl of the CO_2Et group gave a quartet at δ 4.4 and a triplet at δ 1.4 with a J = 7 Hz. [c]Tertiary hydrogen of the dioxanyl group. This proton appeared as a doublet of doublet (J = 3 and 9 Hz); the remaining seven protons gave a multiplet in the δ 4.3–3.1 region. [d]Region of the broad absorption due to the tertiary hydrogen of the cyclohexyl group; the other ten protons gave a multiplet in the δ 2.2–1.1 region. [e]This proton was also coupled with the tertiary hydrogen of the dioxanyl group. [f]Oil. Bp not determined. [g]Not resolved. [h]See Ref. 2. [i]See Ref. 1.

selectivity observed in these reactions could be anticipated on the basis of previous observations. Thus from the extensive work of Minisci *et al.*,[6–8] it is now well documented that protonated 4-substituted pyridines are selectively substituted at the 2 position by nucleophilic radicals like the dioxanyl[2] and the cyclohexyl.[3] The preference for attack at the 6 position in the dioxanylation of 3-acetylpyridine in the presence of acid (Scheme 3) is in agreement with the selectivity observed in the *t*-butylation of protonated 3-substituted pyridines.[9] Moreover, the present knowledges on the factors controlling radical *ipso*-attack and *ipso*-substitution[10,4,5] can easily explain the alkyldeacylation reactions described above. The results observed with protonated 2-substituted pyridines fall into the same picture. The reaction occurs at the 4 position and only in some cases the 6-substituted and the 4,6-disubstituted compounds (Scheme 2) can be obtained as by-products. In every case therefore the radical substitution takes place at the α and/or γ positions indicating that also in these substrates, as in the case of the 3- and 4-substituted pyridines, the positional selectivity is governed by the positive nitrogen atom. Thus the whole of the results obtained with the protonated pyridines **1–3**, **17**, **20–22** and with the 2,5-diacetylpyridine[1] emphasize once again the importance of polar effects in these reactions so that the selectivity of the addition of the nucleophilic radicals is determined by the charge density distribution in the protonated substrates.

A quite different picture emerges from the radical alkylation of the same subtrates under neutral conditions. Clearly with the unprotonated pyridines polar effects cannot operate and other factors must control the positional selectivity.

The reactions of dioxanyl and cyclohexyl radicals with the 2-X-pyridines **1–3** give rise exclusively to the 5-substituted products **4–9** and the dioxanylation of 3-acetylpyridine **17** occurs at the 6 position (Scheme 3). In both cases therefore the addition occurs at the ring positions which are *para* to the electron-withdrawing substituents to give the intermediates **43** and **44**. These are the more stable intermediates which can be formed from **1–3** and **17** because the unpaired electron can be delocalized into the substituents X. A similar stabilization could also be obtained in the intermediates **45** and **46** formed by addition at the positions *ortho* to the substituents. However, products deriving from these two σ-complexes were not observed and this could be due to steric effects which are known to be important in homolytic aromatic substitutions.[11] Thus the steric effects and the stability of the intermediates act in the same direction and as a result very selective processes are realized. A similar interpretation can explain the addition of the dioxanyl radical at the *ipso* 2 and 5-positions of the 2,5-diacetyl- and 2,4,5-triacetylpyridine.[1]

The same effects can explain why the reactions with 4-substituted pyridines **20–22** are not selective. In this case, in fact, the more stable intermediate, **47**, is that deriving from the addition at the 3 position; steric effects however act in the opposite direction favouring the formation of **48**.



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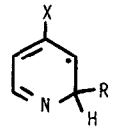


48

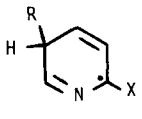
As a result, products deriving from both these intermediates are formed in ratios which are dependent on the nature of the radical R and of the substituent X; in every case, however, addition at the 3 position is favoured.

In the foregoing discussion the stability of the radical intermediates has been attributed to the capability of the substituent X to delocalize the unpaired electron. Very recently experimental[12] and theoretical[13] evidences have been accumulated on synergetic capto-dative stabilization of carbon radicals. These investigations demonstrated that a particular stability is associated with carbon radicals when a donor and an acceptor substituent are linked to the same radical centre. The intermediates **43** and **47** can be considered as capto-dative radicals and this stabilizing effect can be considered to operate also in the present cases.

Thus all the experimental results concerning the radical alkylation of the unprotonated pyridines **1–3**, **17**, **20–22**, as well as of the 2,4-diacetyl-, 2,5-diacetyl- and 2,4,5-triacetylpyridine,[1] can be explained assuming that the transition state of the addition step is similar to the σ-complexes and hence that the positional selectivity is governed by the stability of these intermediates.[14]

The change of the nature of the transition state of the addition step has therefore profound consequences on the selectivity of the homolytic aromatic substitution process. Selective substitutions can be obtained under two kinds of conditions: when the nature of the radical and of the substrate allows polar effects to operate or, if this cannot occur, when the structure of the aromatic substrate is such that the addition of the radical can afford a σ-complex intermediate of particular stability. This latter hypothesis can also explain the selective substitutions and *ipso* substitutions previously observed in the reactions of dioxanyl radicals with di- and triacetylpyridines[1] and in the reactions of methyl radicals with polynitrobenzenes[15] and nitrothiophene derivatives.[16]

Finally, from the synthetic point of view, the procedure described in the present paper with unprotonated pyridines can have considerable importance because it makes possible the synthesis of those isomers which cannot be obtained from the radical alkylation of the protonated pyridines.



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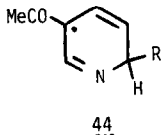

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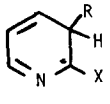

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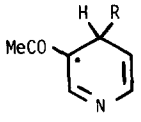

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EXPERIMENTAL

The synthesis of the di- and triacetylpyridines and the physical and NMR data of the products obtained from their reactions with dioxanyl radicals, which were not reported in the previous paper,[1] are described in this section. The 2- and 4-cyano-, acetyl-, ethoxycarbonylpyridines and the 3-acetylpyridine were commercial products. The *t*-butylperoxyoxalate was prepared as described in the literature.[17]

2,4-Diacetylpyridine and 2,4,5-triacetylpyridine. To a refluxing mixture of 4-acetylpyridine (2.4 g), pyruvic acid (3.4 g) and silver nitrate (0.1 g) in water (20 ml), a solution of potassium persulphate (5.3 g) in 20 ml of water was added dropwise.[3] Refluxing was continued for 2 hr. The cooled mixture was made alkaline with sodium hydroxide solution and extracted with chloroform. Evaporation of the solvent left a residue which was chromatographed on silica gel using a 7 : 3 mixture of light petroleum and ethyl ether as eluant. Small amounts (0.1 g) of *2,4,6-triacetylpyridine*, m.p. 105–6°, were first obtained; NMR, δ 8.55 (s, 2H), 2.8 (s, 6H), 2.65 (s, 3H). The following fractions contained the *2,4-diacetylpyridine* (1.2 g), m.p. 70–2°, NMR, δ 8.9 (dd, H_6, J = 4.8 and 0.9 Hz), 8.35 (dd, H_3, J = 1.5 and 0.9 Hz), 7.95 (dd, H_5, J = 4.8 and 1.5 Hz), 2.75 (s, 3H), 2.7 (s, 3H). Further elution afforded the *2,4,5-triacetylpyridine* (1.0 g), m.p. 79–81°, NMR, δ 9.05 (s, 1H), 8.1 (s, 1H), 2.8 (s, 3H), 2.7 (s, 3H), 2.6 (s, 3H).

2,5-Diacetylpyridine. This product was prepared from the 3-acetylpyridine (2.4 g) according to the procedure described above; the reaction was carried out in the presence of sulphuric acid (6 ml) and with ammonium peroxydisulphate. Pure *2,5-diacetylpyridine* (0.8 g), m.p. 103–5°, was obtained after column chromatography on silica gel; NMR, δ 9.1 (dd, H_6, J = 2.1 and 0.9 Hz), 8.3 (dd, H_4, J = 7.8 and 2.1 Hz), 8.05 (dd, H_3, J = 7.8 and 0.9 Hz), 2.8 (s, 3H), 2.7 (s, 3H).

General procedures for the radical dioxanylation and cyclohexylation of pyridine derivatives

Method A. To a stirred solution of the pyridine derivative (0.005 mols) in dioxane, or cyclohexane (25 ml), kept at 90°C, a solution of *t*-butyl peroxyoxalate (0.0125 mols) in dioxane, or cyclohexane (10 ml), was added dropwise. The decomposition of the peroxide was immediate. Stirring was continued for 1 hr. The course of the reactions was monitored by tlc and glc. The isomer ratios in the alkylations of the 4-substituted pyridines **20–22** were determined by glc analyses of the reaction mixtures prior to work up. Most of the dioxane, or cyclohexane was removed in vacuum; the residue was poured on water and extracted with ether. The organic layer was separated, dried and evaporated. The residue was chromatographed on silica gel using mixtures of light petroleum and diethyl ether as eluant; the ratio of the two solvents was indicated by the results of tlc analyses of the reaction mixtures.

Method B. The radical dioxanylations in the presence of sulphuric acid were carried out as described in the literature.[2] Dioxanyl radicals were produced from dioxane using ammonium peroxydisulphate. The cyclohexyl radical was instead generated by the oxidative decarboxylation of the cyclohexane carboxylic acid carried out with ammonium peroxydisulphate in the presence of silver nitrate; the procedure was that already described in the literature.[3] Reactions were carried out on 0.005 mols of pyridine derivatives.

The experiments carried out with methods A and B, the products obtained and the reaction yields have been described under Results section. Physical and NMR data of the reaction products are collected in the Table.

NMR spectra were recorded, in $CDCl_3$ solution, using a 90 MHz spectrometer, Varian EM 390. Glc analyses were carried out on a Hewlett-Packard 5830 chromatograph with a 20 in. 10% UCW 982 column.

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