Mesoionic Compounds. Part 10.[1] A Study of the Reactions of 3-(3-Pyridyl)sydnone with Some Nucleophilic Reagents [2]

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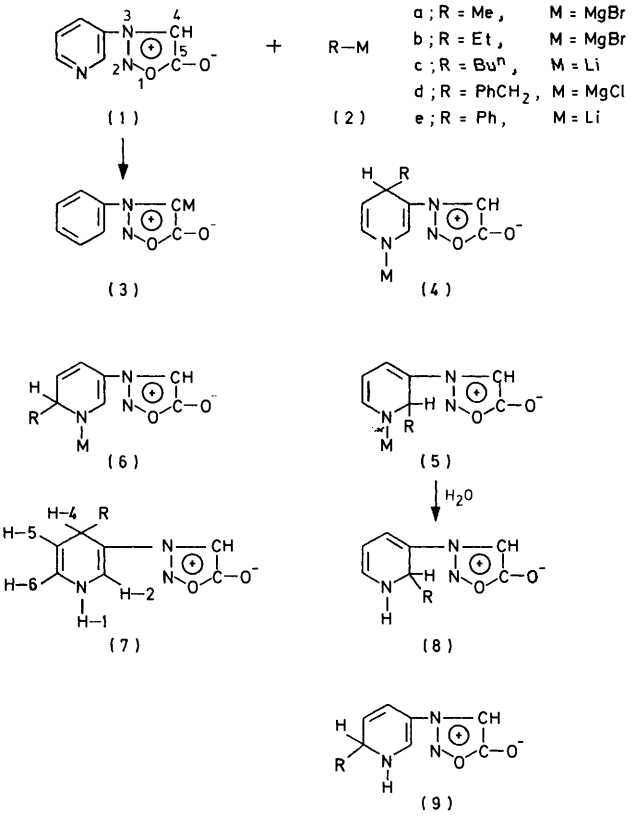
Nucleophilic addition of organo-magnesium and -lithium reagents to 3-(3-pyridyl)sydnone (1) afforded 4-substituted-3-(sydnon-3-yl)-1,4-dihydropyridines (7), accompanied by lesser amounts of the 1,2-dihydropyridine isomers (8). The mixtures were separated by t.l.c. and the isomers examined by u.v. spectroscopy. The structures of the pure dihydropyridines (7, R = Et, Bu^n, or $PhCH_2$) were further established by ^1H n.m.r. spectroscopy. Sodium borohydride in aprotic or protic solvents reduced (1) to 3-(sydnon-3-yl)-1,4-dihydropyridine (10) or 3-(sydnon-3-yl)-1,4,5,6-tetrahydropyridine (11) respectively. 1-Alkyl-3-(sydnon-3-yl)pyridinium iodides (12a and 12b) with potassium cyanide gave the respective 1-alkyl-4-cyano-3-(sydnon-3-yl)-1,4-dihydropyridines (13a) and (13b). Methylmagnesium bromide favoured formation of [3-(3-pyridyl)sydnon-4-yl]-magnesium bromide (3a) over dihydropyridine adducts (4a) and (5a) and was employed in the preparation of alcohols (14)—(23) which were dehydrated with trifluoroacetic acid to their respective (3-pyridyl)sydnon-3-yl-substituted alkenes (27)—(31).

THE direct lithiation of 3-phenylsydnone and conversion of the 4-lithiated intermediate to 3-phenylsydnone-4-carboxylic acid [3] has been found to be not applicable to 3-(3-pyridyl)sydnone (1). Our attempt to do so produced a yellow solid which, we assumed, was a lithiated 3-(3-pyridyl)sydnone formed by nucleophilic addition of n-butyl-lithium [4-6] to (1), perhaps *via* a charge-transfer complex,[7] which on hydrolysis yielded the product. Identification of this yellow compound and further study on the reactions of (1) with other nucleophilic reagents is the subject of this paper.

Nucleophilic substitutions and additions to pyridine derivatives by organometallic reagents to afford substituted pyridines [8] and dihydropyridines,[9] respectively, have been reviewed. In 1930, Ziegler and Zeiser [10] described the formation of 2-n-butylpyridine by elimination of lithium hydride from the intermediate 2-n-butyl-1-lithio-1,2-dihydropyridine adduct obtained by treating pyridine with n-butyl-lithium. Subsequent studies [4] assumed reactions between pyridine derivatives and organometallic reagents led to such intermediate 1,2-dihydropyridine adducts prior to hydrolysis. Later reports [4-6] conclusively established these adduct structures by ^1H n.m.r. spectroscopy and reaction with benzophenone to yield alcohols.[6] In some cases,[11] the 2-substituted-1-lithio-1,2-dihydropyridines were actually isolated. Reactions of 3-pyridyl ketones with Grignard reagents, however, were reported [12,13] to yield mainly 1,4-dihydropyridines and some addition to the carbonyl group.

With the 3-substituted-pyridine (1), 1,2-, 1,4-, and 1,6-dihydropyridylsydnone adducts (7)—(9) (Scheme 1) were possible when treated with organometallic reagents (2a—e). However, in our study of these reactions none of the 1,6-dihydropyridine isomers (9a—e) were detected. The crude products from the reactions of (1) with (2a—e) were separated by t.l.c. and the components, eluted from the plate, were examined by u.v. spectroscopy (Table 1). The addition of n-butyl-lithium (2c) to (1) gave mainly the 1,4-dihydropyridine adduct (7c) instead of the 1,2-isomer, as reported [14,15] for other substituted pyridines, together with some contamination by the corresponding 1,2-isomer (8c) and (1). A substantial amount of (1) was found accompanying the crude isomer mixtures (7b,8b) and (7d,8d). This may be the result of a slower rate of formation of the dihydro-isomers because of the decreased reactivity of the Grignard reagents relative to organolithium compounds, the reaction then favouring formation of (3). However, our efforts to purify the phenyl analogues (7e,8e) by recrystallization always produced a mixture of these dihydropyridine isomers and, likewise, the methyl



SCHEME 1

TABLE 1

U.v. spectra of the t.l.c.-separated dihydropyridylsydnones

Compound	R	R_F Value [a]	$\lambda_{max.}$/nm Band I (200—240 nm)	Band II (250—300 nm)	Sydnone absorption	Band III (300—450 nm)
1,4-Isomers						
(7a)	Me	0.17			294	375
(7b)	Et	0.19	225 [b]		298	375
(7c)	Bu^n	0.23	225 [b]		295	380
(7d)	$PhCH_2$	0.21			306	387
(7e)	Ph	0.18			306	381
1,2-Isomers						
(8a)	Me	0.35	225		285	440
(8b)	Et	0.44	225	270	290	440
(8c)	Bu^n	0.45	225 [b]	270	290 [b]	440
(8d)	$PhCH_2$	0.43		275 [c]	306	462 [d]
(8e)	Ph	0.41		254	294	445

[a] R_F on 20 × 20 cm Kodak fluorescence alumina t.l.c. plates. EtOAc–C_6H_6 ratio 3 : 1, elution with Spectrograde methanol. [b] Shoulder. [c] Slight shoulder. [d] Very low intensity, doubtful.

analogues (7a,8a) constantly afforded a mixture with additional contamination from (1). The infrared and ultraviolet data for the purified dihydropyridylsydnones (7b—d) are in Table 2.

The typical sydnone ring absorption was observed in the 285—306 nm region of the u.v. spectrum. The 1,4-dihydropyridine moiety normally displays [8] two absorption maxima in the regions 200—240 and 300—400 nm. Sometimes the former band is not reported.[14,16-18] Our 1,4-dihydropyridylsydnones (7b,7c) also showed two absorption maxima (*cf.* Tables 1 and 2, Bands I and III). Band I was absent in the t.l.c. samples of (7a, d, and e) but appeared in the purified sample of (7d) (*cf.* Table 2). The 1,2-dihydropyridine group usually displays [14] three absorption maxima. In addition to Bands I and III of the 1,4-isomers a third band (Band II) appears in the 250—300 nm region. All the 1,2-dihydropyridylsydnones showed this third absorption except (8a). Band I was also missing in the spectra of (8d) and (8e). Band III, the most intense absorption in dihydropyridines,[18] undergoes bathochromic shifts by substitution at the 3- and/or 5-positions with electron-withdrawing groups. For example the 278 nm absorption of the parent 1,4-dihydropyridine [19] is shifted 76, 98, and 114 nm by CN, CO_2Et, and CO_2Me, respectively, in 3,5-disubstituted analogues.[18,20] In our study, we have found the electron-withdrawing sydnone ring at the 3-position of 1,4-dihydropyridine to cause a red shift of 120 nm (*cf.* Experimental section). This shift is less for the substituted 1,4-dihydropyridylsydnones (7a—c) (97—109 nm) and greater for the 1,2-isomers (8a—e) (162—167 nm). These variations in absorption maxima in the same region have been attributed [18] to non-bonded repulsion between substituents in the 2- or 4-position and an adjacent chromophore in the 3-position.

The ^1H n.m.r. spectra for the 1,4-isomers (7b—d) were consistent with reported values for 3-substituted-1,4-dihydropyridines.[5,21-23] The chemical shifts at δ 3.80—4.10 (multiplet or quartet) were from H-4 coupling with H-5, the latter appearing as a pair of doublets resulting from an additional spin-coupling to H-6 (δ 4.60—4.67, $J_{5,4}$ 5, $J_{5,6}$ 7.5 Hz). Another pair of doublets at δ 6.13—6.25 represents H-6 coupled to H-5 and H-1 ($J_{1,6}$ 4—5 Hz). Similarly, a doublet at δ 7.29—7.33 ($J_{1,2}$ 3—6 Hz) results from coupling of H-2 with H-1, the latter appearing as a multiplet (δ 8.20—8.27). On addition of [$^2H_4$]methanol, the H-1 signal disappeared while that for H-2 became a singlet and that for H-6 a doublet. Such coupling patterns of NH protons with adjacent 2- and/or 6-protons have also been described elsewhere.[18,19,24] The sydnone-CH appeared as a singlet (δ 7.20—7.29). The Bu^n group of (7c) exhibited a triplet at δ 0.38 and a broad multiplet at δ 1.33. The Et group of (7b) gave a triplet at δ 0.83 and a multiplet at 1.40. The $PhCH_2$ group of (7d) absorbed at δ 2.83 and 7.29.

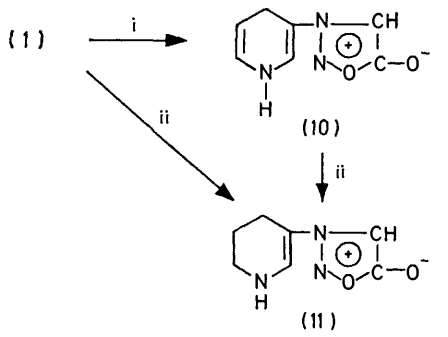
Reductions of pyridine and pyridinium salts with sodium borohydride to afford dihydropyridine derivatives have been reviewed.[25] Those with electron-withdrawing substituents in the 3-position gave 1,4-dihydropyridines in aprotic solvents and tetrahydropyridines in protic

TABLE 2

I.r. and u.v. spectra of purified dihydropyridylsydnones

Compound	$\lambda_{max.}$/μm Sydnone C–H	Sydnone C=O	Dihydropyridine N–H	Dihydropyridine C=C–N	Dihydropyridine C=C	$\lambda_{max.}$/nm (log ε) Band I (200—240)	Band II (250—300)	Sydnone absorption	Band III (300—400)
(7b)	3.20	5.85	3.02	5.95	6.13	225 [a] (3.80)		307 (3.54)	387 (3.86)
(7c)	3.17	5.79	3.00	5.95	6.10	225 [b] (3.83)		307 (3.56)	387 (3.92)
(7d)	3.20	5.85	3.00	6.00	6.12	225 (3.88)		307 (3.56)	373 (3.70)

[a] Shoulder on 206 nm (4.02) peak. [b] Shoulder.



SCHEME 2 *Reagents:* i, $NaBH_4$ in THF; ii, $NaBH_4$ in EtOH

solvents,[21] whereas such 3,5-disubstituted derivatives yielded 1,2- and 1,4-dihydropyridines in both protic and aprotic solvents.[26]

Nucleophilic reduction of (1) with sodium borohydride in tetrahydrofuran gave 3-(sydnon-3-yl)-1,4-dihydropyridine (10). This structural assignment was based on spectral data (*cf.* Experimental section) consistent with that found for other 3-substituted-1,4-dihydropyridines.[21]

Sodium borohydride reduction of (1) in ethanol[27] gave 3-(sydnon-3-yl)-1,4,5,6-tetrahydropyridine (11). The dihydropyridine (10) also reduced to (11) in ethanol. Spectral data for (11) are similar (*cf.* Experimental section) to those reported for other 3-substituted 1,4,5,6-tetrahydropyridines.[22,24] The ^1H n.m.r. spectrum of compound (10) showed a triplet at δ 3.38 (J 4.0 Hz) which indicated the protons at position 4 are non-equivalent as previously demonstrated [23] for 1,4-dihydronicotinamide.

The quaternary salts 1-methyl-3-(sydnon-3-yl)pyridinium iodide (12a) and its 1-ethyl analogue (12b) were readily prepared from (1) by a modification of the procedure used to obtain *N*-methyl-3-cyanopyridinium iodide.[20]

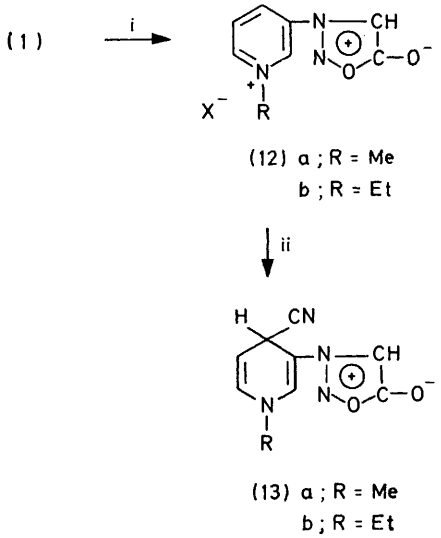
The reactions of 3-substituted pyridinium ions with nucleophiles usually occur with formation of the corresponding 1,2-, 1,4-, or 1,6-dihydropyridine.[28] The reactions of the pyridinium ion with nucleophiles of low ionization potential were believed to proceed *via* a charge-transfer complex [7] and the orientation of the cyano-group in the product supported this mechanism.[16,29] In some cases, cyano-addition reactions have been shown to be reversible,[30] the cyanide ion attacking initially at the 6-position of the pyridinium ion.[31,32] The generality of this pathway has been questioned since it was shown by ^1H n.m.r. spectroscopy that the addition of cyanide occurred mainly at the 4-position.[5]

The quaternary salts (12a) and (12b) reacted with potassium cyanide to give stable 1,4-isomers, namely 4-cyano-1-methyl-3-(sydnon-3-yl)-1,4-dihydropyridine (13a) and its ethyl analogue (13b) (*cf.* Scheme 3). The i.r. spectra (see Experimental section) of (12a) and (12b) showed a carbonyl absorption at higher frequency (5.70 μm) compared to the same absorption in (1).[33] This is believed to be due to the lower electron density of the pyridinium ion.[34] The u.v. spectra (*cf.* Experimental section) of (13a) and (13b) show absorption maxima at 360—365 nm which correspond to the 1,4-dihydropyridine isomers.[35] Assignment of a 1,2-dihydropyridine structure was inconsistent with the u.v. data since the maximum wavelength for these isomers is known [36] to occur at considerably longer wavelengths than those observed for our compounds.

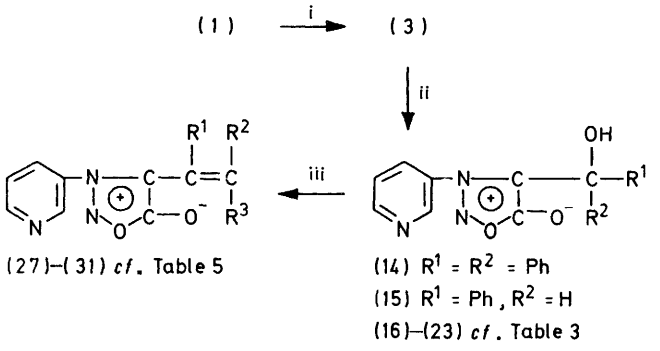
The ^1H n.m.r. spectrum of (12b) showed all protons to have higher chemical shifts than in (1). The assignments conform to the general pattern established by previous workers for 3-acetyl- and 3-carboxy-pyridinium salts.[34,37,38] The close similarities between the coupling constants and chemical-shift values of (13a) and (13b) and 4-cyano-3-substituted-1,4-dihydropyridines [39-41] clearly support our assignment of a 1,4-dihydro-structure to these compounds.

The final part of this study was directed to the reaction conditions which would minimize nucleophilic addition of organometallic reagents to the pyridine ring of (1), *i.e.* formation of (7) and (8), and favour formation of the 4-metallated derivatives (3) (M = Li or MgBr), which could be used for the preparation of 3-(3-pyridyl)-sydnonyl-substituted alkenes as shown in Scheme 4.

Reaction of (1) with methylmagnesium bromide, ethylmagnesium bromide, or n-butyl-lithium followed by treatment of the respective metallated intermediates (3) with benzophenone or benzaldehyde afforded stable, readily isolable, crystalline diphenyl-[3-(3-pyridyl)sydnon-4-yl]methanol (14) or phenyl-[3-(3-pyridyl)sydnon-4-yl]methanol (15). The reaction of (4c) with benzophenone as described for solutions in pyridine of phenyllithium [42] and n-butyl-lithium [6] was not observed. Instead, in each case, the alcohols (14) and (15) were accompanied by formation of the respective dihydropyridines (7) and (8) (*cf.* Scheme 1). Naturally, these by-products decreased the yield of alcohols relative to that obtained with 3-phenylsydnone under similar conditions.[43] We found methylmagnesium bromide gave the highest yields of alcohol, *i.e.* very little contamination by (7a,8b), whereas increased amounts of



SCHEME 3 *Reagents:* i, MeI or EtI; ii, KCN



SCHEME 4 *Reagents:* i, Bu^nLi, EtMgBr, or MeMgBr; ii, $R^1-\overset{\overset{O}{\|}}{C}-R^2$ with variable substituents R^1 and R^2 corresponding to assignment given for alcohols (14)—(23) in Table 3, H_2O; iii, CF_3CO_2H

(7b or c) accompanied alcohol formation. We therefore employed methylmagnesium bromide in extending this reaction to the preparation of the alcohols (16)—(23) [*cf.* Tables 3 and 4 and data in Supplementary Publication No. SUP 22599 (4 pp.) *] using a variety of aldehydes and ketones. The pure alcohols (16) and (20)—(23) were all dehydrated by trifluoroacetic acid at room temperature to afford (3-pyridyl)sydnon-3-yl-substituted alkenes (27)—(31) (*cf.* Table 5 and data in SUP 22599).

TABLE 3

Reaction of (3-pyridyl)sydnon-3-ylmagnesium bromide with carbonyl compounds

Product	Substituents R^1	R^2	Cryst. solvent [a]	M.p. (°C)	Yield (%) [b]
(14)	Ph	Ph	A	197—199	55.5
(15)	Ph	H	A	143—145	54.1
(16)	Ph	Me	A	185—186	58.4
(17)	*o*-Cl·C_6H_4	H	B	122—124	57.0
(18)	*p*-MeO·C_6H_4	H	B	106—108	54.1
(19)	*p*-Me·C_6H_4	H	B	118—120	48.5
(20) [c]	Me	Me	B	144—146	51.9
(21)	Et	Et	B	145—146	55.5
(22)	$-CH_2[CH_2]_2CH_2-$		A	150—152	42.1
(23)	$-CH_2[CH_2]_3CH_2-$		A	177—178	46.3

[a] Solvents: A, THF–pentane; B, benzene–hexane, the alkane added to the cloud-point of the boiling solvent. [b] Based on (1). [c] Prepared previously by M. Sorm and S. Nespurek, *Coll. Czech. Chem. Comm.*, 1975, **40**, 3459.

TABLE 4

Microanalyses for pyridylalcohols

Alcohol	Molecular formula	Found (Required) (%) C	H	N
(14)	$C_{20}H_{15}N_3O_3$	69.4 (69.55)	4.45 (4.4)	12.05 (12.15)
(15)	$C_{14}H_{11}N_3O_3$	62.3 (62.45)	4.05 (4.12)	15.5 (15.6)
(16)	$C_{15}H_{13}N_3O_3$	63.55 (63.60)	4.6 (4.6)	15.1 (14.85)
(17)	$C_{14}H_{10}N_3O_3Cl$ [a]	55.45 (55.35)	3.45 (3.3)	14.0 (13.85)
(18)	$C_{15}H_{13}N_3O_4$	60.05 (60.2)	4.3 (4.4)	14.1 (14.05)
(19)	$C_{15}H_{13}N_3O_3$	63.4 (63.60)	4.65 (4.65)	15.0 (14.85)
(20)	$C_{10}H_{11}N_3O_3$	54.4 (54.3)	4.95 (5.0)	18.85 (19.0)
(21)	$C_{12}H_{15}N_3O_3$	57.95 (57.8)	6.1 (6.05)	16.9 (16.85)
(22)	$C_{12}H_{13}N_3O_3$	58.3 (58.3)	5.2 (5.3)	16.75 (17.0)
(23)	$C_{13}H_{15}N_3O_3$	59.95 (59.75)	5.65 (5.8)	16.15 (16.1)

[a] Found: Cl, 11.87. Required: 11.67%.

EXPERIMENTAL

Melting points were determined on a Mel-Temp melting point apparatus. I.r. spectra were measured on a Perkin-Elmer Infracord 137 using KBr discs. U.v. spectra were obtained with either a Bausch and Lomb 505 or Cary Model 14 recording spectrophotometer for solutions in methanol. N.m.r. spectra were obtained in [$^2H_6$]DMSO [except for compound (12b) (D_2O)] on a Varian A60A instrument and chemical shifts are reported as p.p.m. (δ) downfield from internal tetramethylsilane. Microanalyses were performed by Childer's Microanalytical Laboratory, Milford, New Jersey, or Schwarzkopf Microanalytical Laboratory, Woodside, New York.

n-Butyl-lithium was purchased from Matheson, Coleman, and Bell and assayed as 1.66M by double titration.[44] Methylmagnesium bromide (Ventron Corp., Mass.) and ethylmagnesium bromide (Matheson, Coleman, and Bell) were assayed as 2.0M by direct titration of an aliquot in water against standardized hydrochloric acid using phenolphthalein as indicator.[45] The phenyl-lithium (2.0M) and benzylmagnesium chloride (1.20M) from Ventron Corp. were used directly with manufacturer's assay.

TABLE 5

(3-Pyridyl)sydnon-3-yl alkenes

Alkene	Substituents R^1	R^2	R^3	Cryst. solvent [a]	M.p. (°C)	Yield (%) [b]	Formula	Found (Required) (%) C	H	N
(27)	Ph	H	H	B	118—120	70.2	$C_5H_{11}N_3O_2$	67.75 (67.9)	4.35 (4.2)	15.65 (15.85)
(28)	Me	H	H	A	93—95	41.6	$C_{10}H_9N_3O_2$	59.3 (59.1)	4.6 (4.45)	20.4 (20.7)
(29)	Et	Me	H	A	83—85	38.0	$C_{12}H_{13}N_3O_2$	62.55 (62.35)	5.9 (5.65)	18.0 (18.15)
(30)	$-CH_2CH_2CH_2-$		H	B	131—133	60.0	$C_{12}H_{11}N_3O_2$	62.65 (62.85)	5.15 (4.85)	18.1 (18.35)
(31)	$-CH_2[CH_2]_2CH_2-$		H	B	133—135	52.1	$C_{13}H_{13}N_3O_2$	64.2 (64.2)	5.45 (5.4)	17.1 (17.25)

[a] Solvents: A, THF–pentane; B, EtOH–H_2O. [b] Based on alcohol precursor.

* For details of the Supplementary Publications scheme see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

Tetrahydrofuran (Fisher, ACS grade) was dried over molecular sieve (type 4A, Linde Air Products). All ketones and aldehydes (Fisher Certified, ACS grade) were used without further purification. 3-(3-Pyridyl)sydnone was prepared as previously described.[33]

All reactions with organometallic reagents were performed under nitrogen. It is essential that these reagents are added slowly to a solution in THF of the sydnone at the designated temperatures.

4-*Methyl*-3-(*sydnon*-3-*yl*)*dihydropyridines* (7a) *and* (8a).—To a solution of 3-(3-pyridyl)sydnone (1) (1.63 g, 0.01 mol) in tetrahydrofuran (50 ml) was added methylmagnesium bromide (20 ml, 0.04 mol) at 0° and after stirring for 3 h the mixture was poured into 10% ammonium chloride solution (100 ml) and stirred for 0.5 h. The separated aqueous layer was extracted with benzene (2 × 100 ml) and the extracts were combined with the organic layer, dried ($MgSO_4$) and filtered, and the filtrate was evaporated *in vacuo*. The crude solid residue, after washing with cold benzene (25 ml), gave a mixture (0.72 g) of the 1,2-dihydro-isomer (8a) as major component, a considerable amount of (1), and very little of the 1,4-dihydro-isomer (7a), as shown by the u.v. spectra of the t.l.c.-separated components (*cf.* Table 1). The mixture became tacky after exposure to air for 1 day and decomposed on heating in benzene.

4-*Ethyl*-3-(*sydnon*-3-*yl*)-1,4-*dihydropyridine* (7b).—A solution of (1) (1.63 g, 0.01 mol) in tetrahydrofuran (50 ml) was treated with ethylmagnesium bromide (20 ml, 0.04 mol) at 0°. After stirring for 3 h, the mixture was poured into 10% ammonium chloride solution (100 ml) and stirred for an additional 0.5 h. The aqueous layer was separated and extracted with benzene (2 × 100 ml). The extracts were combined with the organic layer, dried ($MgSO_4$), and filtered, and the filtrate was evaporated *in vacuo* to afford a solid mixture of (7b), (8b), and (1). Washing with cold benzene (25 ml) removed (8b) and (1) and the remaining (7b) was recrystallized from benzene to afford the pure *product* (7b) (0.59 g), m.p. 146—148° (decomp.) as an amorphous yellow-orange powder (Found: C, 56.05; H, 5.7; N, 21.55. $C_9H_{11}N_3O_2$ requires C, 55.95; H, 5.75; N, 21.75%). Long periods of exposure to air caused decomposition.

4-*n*-*Butyl*-3-(*sydnon*-3-*yl*)-1,4-*dihydropyridine* (7c).—To a solution of (1) (1.63 g) in tetrahydrofuran (50 ml) was added n-butyl-lithium (24 ml, 0.04 mol) at −20° and after stirring for 4 h the mixture was poured into 10% ammonium chloride solution (100 ml) and stirred for a further 0.5 h. The separated aqueous layer was washed with benzene (2 × 100 ml) and the extracts were combined with the organic layer, dried ($MgSO_4$), and filtered, and the filtrate was evaporated *in vacuo* to afford a mixture of (7c), (8c), and (1). After washing with cold benzene (25 ml) and then with hot benzene (20 ml) the pure dihydro-isomer (7c) (1.07 g) was isolated as an amorphous yellow powder, m.p. 148—149° (decomp.) which decomposed on long exposure to air (Found: C, 59.8; H, 6.85; N, 19.2. $C_{11}H_{15}N_3O_2$ requires C, 59.7; H, 6.85; N, 19.0%).

4-*Benzyl*-3-(*sydnon*-3-*yl*)-1,4-*dihydropyridine* (7d).—To a solution of (1) (1.63 g) in tetrahydrofuran (50 ml) was added benzylmagnesium chloride (33.3 ml, 0.0 4mol) at 0° and after stirring for 3 h the mixture was poured into 10% ammonium chloride solution (100 ml) and stirred for 0.5 h. The separated aqueous layer was extracted with benzene (2 × 100 ml) and the extracts were combined with the organic layer, dried ($MgSO_4$), and filtered. The filtrate was evaporated *in vacuo* to afford a red oil which crystallized on refrigeration to afford a mixture of (7d) and (8d). Dissolution in tetrahydrofuran and treatment with pentane to the cloud-point gave, after refrigeration, the pure *benzyl compound* (7d) (0.25 g), m.p. 129—131° (decomp.) (Found: C, 66.05; H, 5.6; N, 15.55. $C_{14}H_{13}N_3O_2$ requires C, 65.85; H, 5.15; N, 16.45%). In some preparations, the red oil would not crystallize and was stirred two days in hexane (250 ml) to afford only an amorphous powder which turned very tacky on exposure to air.

4-*Phenyl*-3-(*sydnon*-3-*yl*)*dihydropyridines* (7e) *and* (8e).—A solution of (1) (1.63 g) in tetrahydrofuran (50 ml) was treated with phenyl-lithium (20 ml, 0.04 mol) at −20°. After stirring for 3 h, the mixture was poured into 10% ammonium chloride solution (100 ml) and stirred for 0.5 h. The aqueous layer was separated and extracted with benzene (2 × 100 ml). The extracts were combined with the organic layer, dried ($MgSO_4$), and filtered, and the filtrate was evaporated *in vacuo* to afford a solid. Washing with warm benzene (20 ml) gave a mixture of the 1,2- and 1,4-dihydropyridine isomers (7e) and (8e) (1.35 g) as shown by the u.v. spectra of the t.l.c.-separated components (*cf.* Table 1). The product decomposed on long exposure to air.

3-(*Sydnon*-3-*yl*)-1,4-*dihydropyridine* (10).—A solution of (1) (1.63 g, 0.01 mol) in tetrahydrofuran (75 ml) was treated with sodium borohydride (1.13 g, 0.03 mol) and refluxed for 16 h. The solvent was removed at reduced pressure and the residue treated with water (50 ml) and stirred for 0.5 h at room temperature. The crude solid was collected and washed with cold tetrahydrofuran (10 ml) to afford the *product* (0.66 g), m.p. 192—193° (decomp.) (from acetone). The orange solid decomposed on long exposure to air (Found: C, 50.99; H, 4.44; N, 25.34. $C_7H_7N_3O_2$ requires C, 50.91; H, 4.27; N, 25.44%), i.r. $\lambda_{max.}$ 3.20 and 13.19 (sydnone CH), 5.85 (C:O), 3.05 (NH), 5.89 (C:C), and 6.12 μm (NC:C); u.v. $\lambda_{max.}$ (log ε) 233 (3.75), 315 (3.33), and 398 (3.92) nm; δ 3.38 (2 H, t, $J_{4,5}$ 4.0 Hz, H-4), 4.83 (1 H, m, $J_{5,6}$ 8.0, $J_{5,4}$ 4.0 Hz, H-5), 6.17 (1 H, d, $J_{6,5}$ 8.0 Hz, H-6), 7.27 (1 H, s, sydnone CH), 7.42 (1 H, s, H-2), and 8.42br (1 H, s, NH).

3-(*Sydnon*-3-*yl*)-1,4,5,6-*tetrahydropyridine* (11).—(a) *From compound* (1). Using the same quantities as for the preparation of (10) but using 50 ml of absolute ethanol as solvent the mixture was refluxed for 20 h. The residue, after evaporation of the solvent *in vacuo*, was dissolved in water (50 ml) and extracted with chloroform (2 × 75 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The crude product was washed with cold ether (10 ml) to afford the pure *tetrahydropyridine* (0.234 g), m.p. 156—158° (decomp.) (Found: C, 50.3; H, 5.6; N, 25.4. $C_7H_9N_3O_2$ requires C, 50.3; H, 5.45; N, 25.15%), i.r. $\lambda_{max.}$ 3.00 (NH), 3.20 and 13.80 (sydnone CH), 5.85 (C:O), and 6.12 μm (C:C); u.v. $\lambda_{max.}$ (log ε) 216 (3.80), 305 (3.90), and 359 nm (4.23); δ 1.90 (2 H, m $J_{5,4}$ 6.0, $J_{5,6}$ 5.0 Hz, H-5), 2.62 (2 H, t, $J_{4,5}$ 6.0 Hz, H-4), 3.22 (2 H, t, $J_{6,5}$ 5.0 Hz, H-6), 6.62br (1 H, NH), 7.02 (1 H, s, sydnone CH), and 7.52 (1 H, t, H-2).

(b) *From compound* (10). In absolute ethanol (50 ml), compound (10) (1.65 g, 0.01 mol) was reduced by sodium borohydride (1.134 g, 0.03 mol) by refluxing for 4 h, evaporating the solvent *in vacuo*, and treating the residue with water (50 ml). Extraction with chloroform (2 × 100 ml) and evaporation of the dried ($MgSO_4$) combined extracts afforded the crude product which, upon washing with cold

ether (15 ml), gave the pure tetrahydropyridine (11) (1.01 g), mixed m.p. 155—158°.

1-*Methyl*-3-(*sydnon*-3-*yl*)*pyridinium Iodide* (12a).—Methyl iodide (8.4 ml, 0.14 mol) was added to a solution in tetrahydrofuran (100 ml) of (1) (3.26 g, 0.02 mol) and refluxed for 36 h. Evaporation of the solvent gave cream needles (4.1 g), m.p. 194—195° (decomp.) (from acetonitrile) (Found: C, 31.7; H, 2.65; N, 14.05; I, 41.75. $C_8H_8N_3O_2I$ requires C, 31.5; H, 2.65; N, 14.05; I, 41.6%), i.r. $\lambda_{max.}$ 3.30 and 13.74 (sydnone CH), 5.70 (C:O), 6.60, 6.73, and 6.85 μm (pyridinium C:C); u.v. $\lambda_{max.}$ (log ε) 245sh (3.97), 265sh (3.78), and 322 (3.44).

1-*Ethyl*-3-(*sydnon*-3-*yl*)*pyridinium Iodide* (12b).—This compound was prepared by the same procedure as that described for (12a) but using ethyl iodide (9.6 ml, 0.12 mol) which yielded yellow *needles* (2.04 g), m.p. 163—165° (decomp.) (from ethanol) (Found: C, 33.95; H, 3.15; N, 13.45; I, 39.85. $C_9H_{10}N_3O_2I$ requires C, 33.85; H, 3.2; N, 13.15; I, 39.75%), i.r. $\lambda_{max.}$ 3.30 and 13.80 (sydnone CH), 5.70 (C:O), 6.60, 6.70, and 6.83 (pyridinium C:C); u.v. $\lambda_{max.}$ (log ε) 245sh (3.90), 265sh (3.73), and 322 (3.42); δ(D_2O) 1.80 (3 H, t, CH_3), 4.93 (2 H, q, *J* 7.0 Hz, CH_2), 7.83 (1 H, s, sydnone CH), 8.58 (1 H, q, $J_{5.4}$ 8.0, $J_{5.6}$ 6.0 Hz, H-5), 9.20 (1 H, d, H-4), 9.43 (1 H, d, H-6), and 9.93br (1 H, s, H-2).

4-*Cyano*-1-*methyl*-3-(*sydnon*-3-*yl*)-1,4-*dihydropyridine* (13a).—A solution of (12a) (1.83 g, 0.006 mol) in water (100 ml) at 0° was treated with aqueous potassium cyanide (6 g in 100 ml), cooled to 0°, and stirred 15 min. The precipitate was collected and washed with ice–water followed by ether to give yellow-brown *needles* (0.79 g), m.p. 153—154° (decomp.) (from acetonitrile–ether). At decomposition point the compound rises rapidly in the capillary tube (Found: C, 52.85; H, 3.9; N, 27.25. $C_9H_8N_4O_2$ requires C, 52.95; H, 3.95; N, 27.45%), i.r. $\lambda_{max.}$ 3.20 and 13.71 (sydnone CH), 5.75 (C:O), 4.50 (C≡N), 5.94 (C:C–N), and 6.25 μm (conjugated C:C); u.v. $\lambda_{max.}$ (log ε) 239 (3.82), 260sh (3.60), 330 (3.49), and 365 nm (3.49); δ 3.23 (3 H, s, NCH_3), 5.17 (1 H, s, H-4),* 5.17 (1 H, q, H-5),* 6.50 (1 H, d, H-6), 7.37 (1 H, s, H-2), and 7.77 (1 H, s, sydnone CH).

4-*Cyano*-1-*ethyl*-3-(*sydnon*-3-*yl*)-1,4-*dihydropyridine* (13b).—Treatment of (12b) as above gave brown *needles* (0.69 g), m.p. 133—134° (decomp.) (from acetonitrile–ether). On decomposition, the sample rose rapidly in the capillary tube (Found: C, 54.7; H, 4.55; N, 25.45. $C_{10}H_{10}N_4O_2$ requires C, 55.05; H, 4.6; N, 25.7%), i.r. $\lambda_{max.}$ 3.24 and 13.78 (sydnone CH), 5.77 (C:O), 4.50 (C≡N), 6.00 (C=C–N), and 6.30 (conjugated C:C); u.v. $\lambda_{max.}$ (log ε) 240 (3.81), 260sh (3.61), 330 (3.46), and 360 nm (3.46); δ 1.20 (3 H, t, CH_3), 3.45 (2 H, q, *J* 7.0 Hz, CH_2), 5.17 (1 H, s, H-4),* 5.17 (1 H, q, H-5),* 6.50 (1 H, t, H-6), 7.37 (1 H, d, H-2), and 7.77 (1 H, s, sydnone CH).

The following procedures illustrate the general method employed in the preparation of the alcohols and alkenes listed in Tables 3—5.

Methylphenyl-[3-(3-*pyridyl*)*sydnon*-4-*yl*]*methanol* (16).—To a solution of (1) (4.89 g, 0.03 mol) in tetrahydrofuran (150 ml), methylmagnesium bromide (30 ml, 0.06 mol) was added dropwise at 0—5°. After stirring for 1 h, acetophenone (7.02 ml, 0.06 mol) was added at 0—5° and the mixture was stirred for an additional 2 h, poured into 20% aqueous ammonium chloride (300 ml), and acidified to pH 6 with acetic acid. The separated aqueous layer was extracted with benzene (3 × 250 ml), and the extracts were combined with the organic layer, dried ($MgSO_4$), filtered, and evaporated *in vacuo* to afford a red oil which crystallized on refrigeration † to give the *alcohol* (4.96 g), m.p. 185—186° (from tetrahydrofuran–pentane).

1-[3-(3-*Pyridyl*)*sydnon*-4-*yl*]-1-*phenylethylene* (27).—A mixture of (16) (0.80 g, 0.003 mol) and trifluoroacetic acid (4 ml) was stirred at room temperature for 4 h and then poured into ice–water (200 ml) and neutralized with solid sodium carbonate. The precipitated alkene ‡ was filtered off and dissolved in boiling ethanol. Water was added to the cloud-point to afford the pure *alkene* (0.53 g), m.p. 118—120°.

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* Absorptions overlapped making splitting pattern and assignment difficult to ascertain.

† The dihydropyridine contaminants were removed by washing with THF–benzene (2 : 1 v/v, *ca.* 20 ml).

‡ The crude alkenes (28) and (29) were isolated by extraction with chloroform (2 × 100 ml), drying ($MgSO_4$), filtration, and evaporation *in vacuo* to an oil which solidified.

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