Synthetic Applications of *N*–*N* Linked Heterocycles. Part 16.[1] Reactions between Carbanions Derived from Carbon Acids with pK_a 7—14 and *N*-(2,6-Dimethyl-4-oxopyridin-1-yl)pyridinium Tetrafluoroborate: Synthesis of 4-Substituted Pyridines, and Observation of Pyridine Ring-opening Reactions

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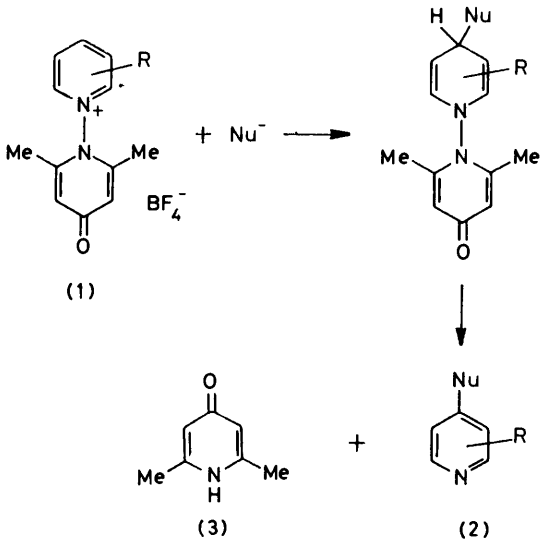
Carbanions, derived from carbon acids (5) lying in the pK_a range 7—14, add regiospecifically to the pyridinium γ-position in *N*-(2,6-dimethyl-4-oxopyridin-1-yl)pyridinium tetrafluoroborate (4) to yield 1,4-dihydro-adducts (6). While some intermediates could be fragmented successfully to give 4-substituted pyridines (7), others reverted under similar conditions to the carbon acids (5), due apparently to the presence of traces of water. Anions derived from malononitrile and ethyl cyanoacetate, however, gave ring-opened products (9) resulting from attack at the pyridinium α-position, and while the cyano-ester gave predominantly a 1,4-adduct at −30 °C, this reverted to the ring-opened compound at room temperature. An explanation for this abnormal behaviour is offered.

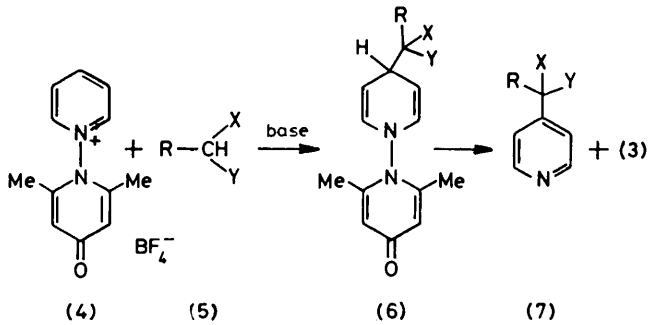
THE *N*-(2,6-dimethyl-4-oxopyridin-1-yl)pyridinium salts (1) have proved to be versatile intermediates for the regiospecific synthesis in high yields of a wide range of 4-substituted pyridines (2),[2] *via* attack by appropriate nucleophiles (Scheme 1). The reaction has been successful with nitrogen,[3] sulphur,[4] and phosphorus nucleophiles,[5] as well as with a variety of carbanions.[3,6] However, though lithium enolates of ketones (pK_a 16—20)



SCHEME 1

gave α-(4-pyridylalkyl)ketones in excellent yields,[6c] lithium derivatives of esters and nitriles (pK_a *ca.* 24) gave poor results, due apparently to competing deprotonation of the pyridone methyl groups in the salts (1),[6d,†] and thus indicating an upper limit to the pK_a of carbon acids useful in this reaction. At the lower end of the pK_a scale, cyanide [6a] (pK_a 9.3) and nitromethide [3] (pK_a 8—10) ions have been added successfully. We now report the reactions between the salt (4) and carbanions derived from carbon acids (5) bearing two activating groups (pK_a 7—14), the traditional active-methylene and -methine compounds. It was hoped that addition of these anions (Scheme 2) would lead to the dihydro-intermediates (6), which on fragmentation would yield the 4-substituted pyridine derivatives (7), a class of compounds of which very few examples are known.

Thus, previous preparations of pyridines of this type have been (*a*) by displacement of halide [7] or ether [8] substituents at the γ-position of pyridines by the appropriate carbanions; (*b*) by acylation of 4-pyridylacetonitrile; [9] (*c*) by conversion of the condensation product from a 4-pyrone and an active methylene com-



	R	X	Y		R	X	Y
a;	Ph	H	NO_2	i;	Me	CN	CO_2Et
b;	H	COMe	COMe	j;	H	CO_2Me	CO_2Me
c;	H	COMe	CO_2Et	k;	H	CO_2Et	CO_2Et
d;	Pr^n	COMe	CO_2Et	l;	Pr^n	CO_2Et	CO_2Et
e;	$PhCH_2$	COMe	CO_2Et	m;	$PhCH_2$	CO_2Et	CO_2Et
f;	H	CN	CN	n;	$[CH_2]_2OCO$		COMe
g;	H	CN	CO_2Et	o;	$[CH_2]_2CO$		CO_2Me
h;	Me	CN	CO_2Me	p;	H		$SO_2[CH_2]_3SO_2$

SCHEME 2

† Support for this suggestion was provided by the successful preparation of α-(4-pyridyl)-esters and -nitriles, by the reaction of the same carbanions with tritylpyridinium salts.[6d]

pound to a pyridine with formamide;[10] and (*d*) by treatment of a pyridine *N*-oxide with methyl 3-aminobut-2-enoate in the presence of benzenesulphonyl chloride.[11] The only other example, in addition to (*d*) above, in which regiospecific attack occurred at the 4-position of a pyridine having no 2- or 4-substituents, involved the reaction between active methylene anions and 1-methyl-3-nitropyridinium iodide, to give the dihydro-adducts (8).[12]

RESULTS

Generally, addition of a solution of the carbon acid (5) in 1M ethanolic sodium ethoxide * to a suspension of an equivalent amount of the pyridinium salt (4) in acetonitrile at 25 °C, gave a solution containing the corresponding dihydro-intermediate (6) in moderate to high yield. Reactions were carried out at 0 °C when results at 25 °C were unsatisfactory. Phenylnitromethane (5a) gave a high yield of intermediate (6a) using methanol as the solvent, by analogy with other nitroalkanes reported earlier.[3] However, this solvent was found to be unsatisfactory when using carbon acids of higher pK_a. Results, giving the reaction conditions, the pK_a of the carbon acids,† and yields of products are shown in Table 1. Since a number of

TABLE 1

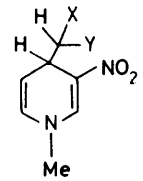
Preparation of dihydro-intermediates (6) from the salt (4)

C–H Acid	pK_a	Conditions: Solvent	Base	Temperature (°C)	Intermediate (6) Yield (%)
(5a)	6.8 [a]	MeOH	NaOMe	25	84
(5b)	8.9 [b]	MeOH	NaOMe	25	*c*
(5b)	8.9	MeCN	NaOEt	0	43
(5c)	10.7 [d]	MeCN	NaOEt	0	34
(5d)	11.5 [e]	MeCN	NaOEt	25	28
(5e)	11.5 [e]	MeCN	NaOEt	25	65
(5f)	11.2 [f]	MeCN	NaOEt	0	*g*
(5g)	12.0 [e]	MeCN	NaOEt	25	*h*
(5g)	12.0	MeOH	NaOMe	−20	34 [i]
(5g)	12.0	MeCN	NaOEt	−30	47 [j]
(5h)	13.0 [e]	MeCN	NaOMe	25	75
(5i)	13.0 [e]	MeCN	NaOEt	25	78
(5j)	13.3 [e]	MeCN	NaOMe	0	56
(5k)	13.3 [f]	MeCN	NaOEt	25	90
(5l)	14.0 [e]	MeCN	NaOEt	25	55
(5m)	14.0 [e]	MeCN	NaOEt	25	75
(5n)	11.5 [e]	MeCN	NaOEt	25	84
(5o)	11.5 [e]	MeCN	NaOMe	25	79
(5p)	12.6 [k]	MeCN	NaOEt	0	51

[a] V. M. Belikov, S. G. Mairanovskii, Ts. B. Korchemnaya, S. S. Novikov, and V. A. Klimova, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1960, 1675 (*Chem. Abstr.*, 1961, **55**, 8325i). [b] M. Laloi and P. Rumpf, *Bull. Soc. Chim. Fr.*, 1961, 1645. [c] Identified from ^{1}H n.m.r. spectrum, but too unstable to be isolated. [d] M. L. Eidinoff, *J. Am. Chem. Soc.*, 1945, **67**, 2072. [e] Estimated value. [f] R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 1953, **75**, 2439. [g] Compound (9a) only isolated (91%). [h] Compound (12c) only isolated (90%). [i] Product isolated as methyl ester; compound (9c) also present (19%). [j] Compound (9b) present, but not isolated. [k] E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Lett.*, 1962, 515.

dihydro-intermediates (6) were too unstable to be isolated, they were characterised by their i.r. and ^{1}H n.m.r. spectra, yields being computed, if necessary, using integrals of the latter. I.r. spectra showed two bands in the ranges 1 630—1 643 and 1 543—1 588 cm^{-1}, and one between 1 670 and 1 681 cm^{-1}, characteristic, respectively, of the pyridone and the dihydropyridine rings, in addition to peaks consistent with the groups in the 4-substituent. ^{1}H N.m.r. spectroscopic data, which are entirely consistent with those reported in earlier parts of this series, are displayed in Table 2, and physical and microanalytical data for stable intermediates (6) are given in Table 3.

When the reaction was attempted using malononitrile (5f) or ethyl cyanoacetate (5g), however, the 1 : 1 adducts isolated in high yield proved to be compounds (9a) and (9b), formed apparently by addition of the carbanions to the pyridinium 2-position, followed by ring-opening. No trace of the 1,4-adducts (6f) or (6g) was found. At −30 °C, however, the reaction with the cyanoester (5g) gave a mixture containing the desired intermediate (6g) together with a small amount the ring-opened material (9b), the former being converted entirely to the latter on stirring the mixture at room temperature. The product (9b) was also formed in quantitative yield when the pyridinium salt (4) was stirred in an excess of the ester (5g) at 25 °C, using triethylamine as the base. Use of the sodium salts of the methyl substituted cyanoesters (5h) and (5i) in acetonitrile, however, led only to the 1,4-adducts (6h) and (6i). Thus ring-opened products (9) were observed only for carbon



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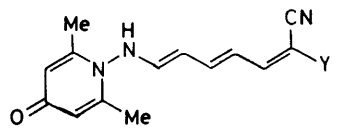
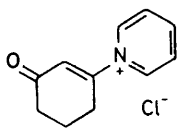


(9) a; Y = CN
b; Y = CO_2Et
c; Y = CO_2Me



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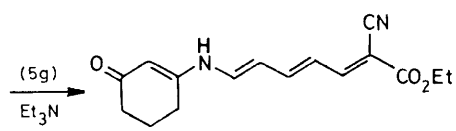


(11)

acids (5) having R = H and X = CN. An analogous ring-opened compound (11) was isolated in 79% yield by Tamura and co-workers [13] from a reaction between the ester (5g) and the pyridinium salt (10).

Decomposition of the intermediates (6) to the 4-substituted pyridines (7) was attempted using free-radical conditions, in analogy with the earlier successful preparations of α-(4-pyridyl)-ketones,[6c] and -esters and -nitriles.[6d] The use of carbon tetrachloride in the presence of azoisobutyronitrile was the most satisfactory, either under reflux (Method A) or with irradiation from a tungsten lamp (Method B), there being little to choose between the two sets of conditions. However, for intermediate (6a) and for the unstable intermediates (6b—e) and (6g), the major reaction was reversal to the carbon acid (5) with co-production of a dark red mass, resulting presumably from ring-opening of the pyridinium residue. In earlier work,[6c,d] analogous reversals were suppressed by scrupulous elimination of water from the reaction medium. Here, attempts to remove traces of water resulted only in the undesired

* Methanolic sodium methoxide was used with compounds (5h), (5j), and (5o) to prevent ester exchange.

† Estimated in many cases from reported values for analogous compounds. No correction has been made for the solvent.

TABLE 2

^{1}H N.m.r. data (δ) [a] for the dihydro-intermediates (6)

Compound	Pyridone ring H-2′, H-6′	Pyridone ring H-3′, H-5′	Dihydropyridine ring H-2, H-6	Dihydropyridine ring H-3, H-5	Dihydropyridine ring H-4	4-Substituent
(6a)	2.13 [b] 2.19	6.05	6.01	4.43	4.28	7.46 (5 H, m), 5.29 (1 H, d)
(6b)	2.23 [b] 2.20	6.07	5.97	4.58	3.87	2.20 (6 H, s)
(6c)	2.25	6.05	6.00	4.64	3.81	4.21 (2 H, q), 3.53 (1 H, d), 2.25 (3 H, s), 1.28 (3 H, t)
(6d)	2.19 [b] 2.25	6.06	6.03	4.76	3.91	4.28 (2 H, q), 2.25 (3 H, s), 1.85 (2 H, m), 1.25 (3 H, t; 2 H, m), 0.91 (3 H, t)
(6e)	2.15	6.05	6.01	4.80	3.89	7.20 (5 H, m), 4.12 (2 H, q), 3.18 (2 H, s), 2.24 (3 H, s), 1.16 (3 H, t)
(6g)	2.24	6.11	6.22	4.72	4.03	4.33 (2 H, q), 3.50 (1 H, s), 1.37 (3 H, t)
(6h)	2.22 [b] 2.26	6.08	6.21	4.66	3.75	3.88 (3 H, s), 1.58 (3 H, s)
(6i)	2.22 [b] 2.26	6.07	6.22	4.65	3.78	4.30 (2 H, q), 1.56 (3 H, s), 1.33 (3 H, t)
(6j)	2.24	6.04	5.98	4.69	3.95	3.75 (6 H, s), 3.41 (1 H, s)
(6k)	2.24	6.10	5.96	4.71	3.80	4.21 (4 H, q), 3.36 (1 H, s), 1.27 (6 H, t)
(6l)	2.24	6.04	5.94	4.70	3.90	4.18 (4 H, q), 1.90 (2 H, m), 1.26 (6 H, t; 2 H, m), 0.93 (3 H, t)
(6m)	2.19 [b] 2.26	6.09	6.01	4.88	3.93	7.21 (5 H, m), 4.11 (4 H, q), 3.31 (2 H, s), 1.16 (6 H, t)
(6n)	2.23	6.07	6.13	4.50	4.08	4.25 (2 H, m), 2.60 (2 H, m), 2.36 (3 H, s)
(6o)	2.24	6.05	6.03	4.60	4.11	3.67 (3 H, s), 2.5—1.9 (6 H, m)
(6p) [c]	2.12 [b] 2.20	5.91	6.33	4.70	4.40	5.15 (1 H, d), 3.40 (4 H, m), 2.03 (2 H, m)

[a] In $CDCl_3$. [b] Two separate signals indicating restricted rotation about the N–N bond. [c] In $(CD_3)_2SO$.

TABLE 3

Physical and analytical data for dihydro-intermediates (6) [a]

Compound	M.p. (°C)	Crystal form	Found (%) C	Found (%) H	Found (%) N	Formula [b]	Requires (%) C	Requires (%) H	Requires (%) N
(6a)	153—154	Needles	67.4	5.8	12.8	$C_{19}H_{19}N_3O_3$	67.6	5.7	12.5
(6h)	164—165	Plates	64.6	5.8	13.3	$C_{17}H_{19}N_3O_3 \cdot 0.25H_2O$	64.2	6.2	13.2
(6i)	131—132	Plates	66.0	6.6	13.1	$C_{18}H_{21}N_3O_3$	66.0	6.5	12.8
(6k)	82	Needles	60.3	6.8	7.0	$C_{19}H_{24}N_2O_5 \cdot H_2O$	60.3	6.9	7.4
(6l)	104—105	Prisms	64.0	7.3	7.1	$C_{22}H_{30}N_2O_5 \cdot 0.5H_2O$	64.2	7.3	6.8
(6m)	115.5—116.5	Prisms	69.4	6.5	6.3	$C_{26}H_{30}N_2O_5$	69.3	6.7	6.2
(6n)	130—131	Plates	63.3	5.9	8.4	$C_{18}H_{20}N_2O_4 \cdot 0.67H_2O$	63.5	6.3	8.2
(6o)	144—145	Plates	65.3	6.4	7.7	$C_{19}H_{22}N_2O_4 \cdot 0.5H_2O$	64.9	6.6	8.0
(6p)	189—190	Prisms	49.1	5.3	7.4	$C_{16}H_{20}N_2O_5S_2 \cdot 0.33H_2O$	49.2	5.3	7.2

[a] Compounds (6b—e), and (6g) were too unstable for satisfactory analyses to be obtained. [b] Residual water in some compounds, found near δ 2.4 in the n.m.r. spectra, could not be removed without causing decomposition.

reverse reaction. Conditions for successful decompositions, together with yields of products (7), are given in Table 4. Yields refer to crude isolated products, which from their ^{1}H n.m.r. spectra, however, (Table 5) were found to be essentially pure. Since most products were oils, they were characterised by their i.r. and ^{1}H n.m.r. spectra, and as

TABLE 4

Decomposition of intermediates (6) to pyridines (7) [a]

Intermediate	Method [b]	Time/h	Product	Yield (%)
(6h)	A	16	(7h)	39
(6i)	A	16	(7i)	84
(6k)	A	16	(7k)	75
(6k)	B	40	(7k)	83
(6l)	A	16	(7l)	87
(6l)	B	40	(7l)	84
(6m)	A	18	(7m)	86
(6m)	B	47	(7m)	74
(6n)	A	17	(7n)	63
(6o)	A	17	(7o)	86

[a] For intermediates (6a—e) and (6g), reversal to the C–H acid (5) was the major reaction. [b] Method A: reflux in CCl_4 in the presence of azoisobutyronitrile. Method B: irradiate in CCl_4 with 500-W tungsten lamp in the presence of azoisobutyronitrile.

TABLE 5

^{1}H N.m.r. data (δ) [a] for 4-substituted pyridines (7)

Compound	H-2, H-6	H-3, H-5	4-Substituent
(7a) [b]	8.81	7.58	7.80 (2 H, m), 7.60 (3 H, m)
(7h)	8.70	7.46	3.83 (3 H, s), 1.92 (3 H, s)
(7i)	8.66	7.45	4.26 (2 H, q), 1.94 (3 H, s), 1.28 (3 H, t)
(7j) [c]	8.60	7.34	4.62 (1 H, s), 3.77 (6 H, s)
(7k)	8.63	7.65	4.60 (1 H, s), 4.25 (4 H, q), 1.28 (6 H, t)
(7l) [c]	8.45	7.26	4.16 (4 H, q), 2.16 (2 H, m), 1.23 (6 H, t; 2 H, m), 0.93 (3 H, t)
(7m)	8.46	7.13	7.11 (3 H, m), 6.80 (2 H, m), 4.19 (4 H, q), 3.51 (2 H, s), 1.18 (6 H, t)
(7n) [c]	8.60	7.29	3.74 (2 H, m), 2.58 (2 H, m), 2.42 (3 H, s)
(7o)	8.56	7.35	3.72 (3 H, s), 2.6—1.9 (6 H, m)

[a] In $CDCl_3$. [b] Detected only, in admixture with a large excess of phenylnitromethane (5a). [c] Compounds characterised only by i.r. and ^{1}H n.m.r. spectra (see text).

TABLE 6

Physical and analytical data for 4-substituted pyridines (7) and their picrate derivatives

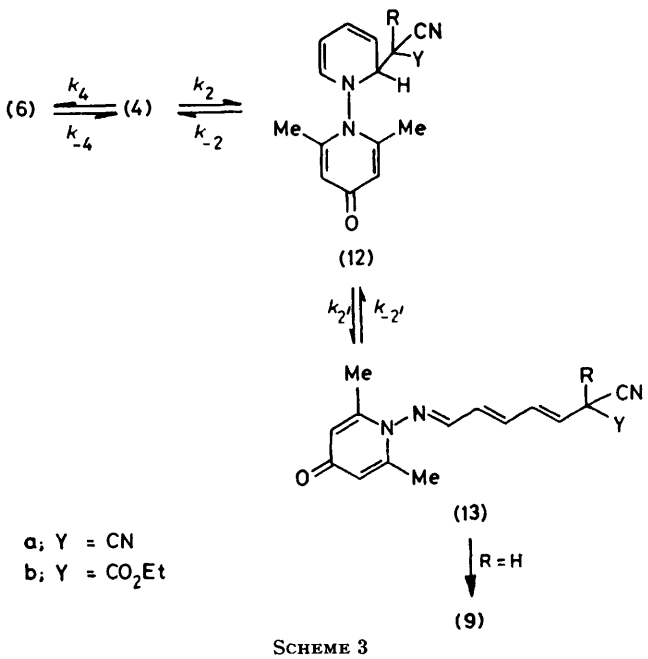
			Picrate derivative [a]						
			Found (%)				Requires (%)		
Compound	M.p. (°C)	Crystal form	C	H	N	Formula	C	H	N
(7h)	139.5—140.5	Needles	46.0	3.3	16.9	$C_{16}H_{13}N_4O_9$	45.8	3.1	16.7
(7i)	129—131	Prisms	47.4	3.6	16.1	$C_{17}H_{15}N_4O_9$	47.1	3.5	16.2
(7k)	122—123	Prisms	46.4	4.0	11.8	$C_{18}H_{18}N_4O_{11}$	46.4	3.9	12.0
(7m)	113—114	Prisms	53.8	4.2	10.4	$C_{25}H_{24}N_4O_{11}$	54.0	4.3	10.1
(7o) [b]	89—91	Prisms	61.5	6.5	6.1	$C_{12}H_{13}NO_3 \cdot 0.75H_2O$	61.9	6.3	6.0

[a] Recrystallised from 95% EtOH. [b] All data are for the free base, not the picrate derivative.

picrates (Table 6), though for pyridines (7j), (7l), and (7n), attempts to prepare crystalline derivatives were unsuccessful, and identification was by spectra alone. Thus all pyridines had in common a prominent i.r. band near 1 600 cm^{-1}, in addition to bands characteristic of the 4-substituent.

DISCUSSION

Although 1,4-dihydro-intermediates (6) could be prepared from most of the carbon acids (5) studied, the synthetic route is hampered in some cases by the competing formation of ring-opened adducts (9) and in general by the instability of the intermediates (6) towards loss of the carbon-acid fragment during attempted decomposition to the products (7). The former observation can be accommodated by reference to Scheme 3.



SCHEME 3

The reversibility of formation of the intermediates (6) is established by the conversion of the intermediate (6g) to the compound (9b) on stirring its solution at room temperature. Since the adduct (6g) is observed only at low temperatures, its formation appears to be kinetically controlled, whereas the product (9b) is evidently thermodynamically more stable. Thus, though k_{-4} and k_2 are likely to be very much smaller than k_4 in this reaction, the 1,2-adduct (12), when formed, can relieve its considerable steric strain *via* electrocyclic ring-opening to give the polyene (13) which, in turn, when R = H, would undergo a prototropic shift to yield the products (9). These, being push-pull systems, should lie in a potential energy well. For the cases where R = Me, the prototropic shift is not possible, and since only the 1,4-adducts (6h) or (6i) were isolated, it is apparent that intermediates (13) are thermodynamically less stable than the adducts (6). What is not clear is why ring-opened compounds form so easily when X = CN, but not in other cases studied. Anions derived from carbon acids having lower pK_a values, and both smaller and larger steric constraints (*e.g.* $MeNO_2$,[3] and $PhCH_2NO_2$) gave only the 1,4-adducts. Perhaps the course of the reaction is determined both by the strength of the C–C bond formed between the carbanion and the pyridinium 4-position (measured by k_{-4}), and by the steric constraint to attack at the pyridinium 2-position (measured by k_2).

Formation of carbon acids (5) during attempted fragmentation of the intermediates (6) is possible only if a proton source is present. When this is water, co-generated hydroxide ion will attack the pyridinium moiety yielding coloured polymeric products, as has been reported previously.[6d]

Thus, this synthetic route to the pyridines (7) can probably be made more general both by preparing and by decomposing the intermediates (6) under strictly non-protic conditions.

EXPERIMENTAL

The pyridinium salt (4) was prepared as described previously;[6c] the carbon acids (5) were re-distilled before use. I.r. spectra were recorded on a Perkin-Elmer model 577 spectrophotometer, using polystyrene in calibration, and ^1H n.m.r. spectra as solutions in $CDCl_3$ on a Perkin-Elmer R-20 spectrometer, using $SiMe_4$ as internal reference.

Preparation of Intermediate (6a) *in* MeOH.—To a stirred suspension of the pyridinium salt (4) (0.001 mol) in MeOH (8 ml) was added dropwise a solution of phenylnitromethane (0.002 mol) in methanolic NaOMe (2 ml; 1M). All the solid dissolved to give a yellow solution. After 30 min the solvent was removed *in vacuo* at 25 °C, the residue was triturated with water (10 ml), and the mixture extracted with $CHCl_3$ (4 × 15 ml). The $CHCl_3$ extract was dried ($MgSO_4$), the solvent was evaporated *in vacuo*, and the residue recrystallised by dissolution in CH_2Cl_2 and re-precipitation by slow addition of hexane.

Preparation of Intermediates (6) *in* MeCN.—To a stirred suspension of the salt (4) (0.001 mol) in dry MeCN (8 ml) was added dropwise a solution of the appropriate carbon acid (5) (0.0012 mol) in ethanolic NaOEt (or methanolic NaOMe as appropriate) (1.2 ml; 1M) at the stated temperature (Table 1). After 10 min the solvent was removed *in vacuo* at the same temperature, the residue was extracted with $CHCl_3$ (3 × 15 ml), and the extracts dried ($MgSO_4$). Removal of the solvent *in vacuo* gave a yellow or brown gum, which was triturated with ether, and the resulting solid was recrystallised as for intermediate (6a). Where the gum failed to crystallise [(6b—e)] the ^1H n.m.r. spectrum was recorded directly. Yields and spectroscopic and analytical data are given in Tables 1, 2, and 3, respectively.

In the case of $CH_2(CN)_2$, the product (9a) precipitated directly from the reaction mixture after 15 min, and was recrystallised from Me_2CO; m.p. 229—230 °C; δ($CDCl_3$) 9.38 (1 H, br), 7.73 (1 H, d, *J* 10 Hz), 6.88 (2 H, d, *J* 12 Hz), 6.41 (2 H, s), 5.83 (1 H, t, *J* 12 Hz), 5.15 (1 H, d, *J* 10 Hz), and 2.25 (6 H, s).

Isolation of Compound (9b).—To a stirred suspension of the salt (4) (0.0038 mol) in $EtOCOCH_2CN$ (5 ml) was added dropwise Et_3N (0.58 ml; 0.00042 mol) during 5 min. After stirring for 1 h, the dark solution was poured into a mixture of water (45 ml) and EtOH (5 ml), the yellow precipitate was triturated, and the mixture filtered. The residue was recrystallised from aqueous EtOH (2 : 1) to give *compound* (9b), 95%, m.p. 140 °C (decomp.) (Found: C, 64.1; H, 6.1; N, 13.4. $C_{17}H_{19}N_3O_3 \cdot 0.25H_2O$ requires C, 64.2; H, 6.2; N, 13.2%); $\nu_{max.}$ 3 000—2 500(vbr), 2 208, 1 705, 1 630, 1 580, and 1 525 cm^{-1}; δ[$(CD_3)_2SO$] 7.58 (1 H, d, *J* 6.2 Hz), 7.48 (1 H, d, *J* 6.4 Hz), 7.17 (1 H, dd, *J* 6.2, 6.4 Hz), 6.46 (2 H, s), 5.85 (1 H, t, *J* 6.4 Hz), 5.07 (1 H, t, *J* 6.2 Hz), 4.12 (2 H, q, *J* 6.9 Hz), 2.28 (6 H, s), and 1.19 (3 H, t, *J* 6.9 Hz).

Decomposition of Dihydro-intermediates (6).—*Method A*. The intermediate (6) was suspended in dry CCl_4 (30 ml) and refluxed together with azoisobutyronitrile (0.01 g) for 16—18 h. The mixture was cooled, filtered, and the filtrate extracted with HCl (20 ml; 2M). The acid layer was adjusted to pH 8 with solid K_2CO_3, extracted with CCl_4 (3 × 15 ml), and the organic phase dried ($MgSO_4$) and evaporated. The residual oils [pyridines (7)] were dissolved in 2M HCl (5 ml), picric acid was added, and the precipitated picrates were recrystallised from 95% EtOH. Attempts to form picrates from pyridines (7j), (7l), and (7n) failed; spectra are recorded in Table 5.

Method B. As for Method A, except the mixture was stirred at 25 °C and irradiated with a 500-W tungsten lamp for 40—47 h. The products (7) were isolated as above.

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