PREPARATION AND REACTIONS OF 1-CYANOMETHYL-2,4,6-TRISUBSTITUTED PYRIDINIUM YLIDS[1]

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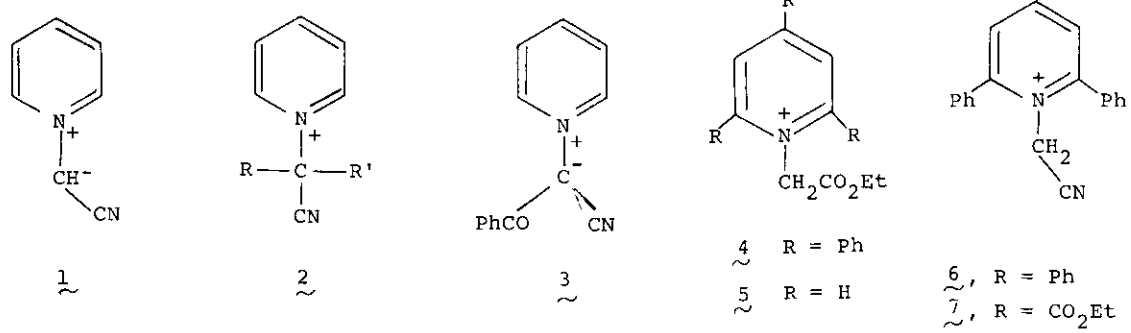
Abstract -- Aminoacetonitrile with pyrylium forms pyridiniums which are acylated to solvatochromic ylids. Pyrolysis of ylid (10a) (R = p-toluoyl) gives 3-cyano-2,4,6-triphenylpyridine. 1-Cyanomethyl-pyridinium (6) gives tetrahydroindolizines with α,β-unsaturated carbonyl compounds.

Cyanomethylpyridinium chloride, readily available from chloroacetonitrile and pyridine,[2] gives ylid (1) with base.[3] Subsequent reactions with electrophiles have given mono- and di-substituted products (2).[3] Ylid (1) has also been used in heterocycle synthesis,[4] and reductions,[5] e.g. (3) gives $PhCOCH_2CN$.



1 2 3 4 R = Ph; 5 R = H 6, R = Ph; 7, R = CO_2Et

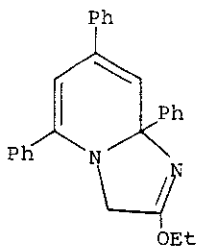
Scheme 1

In previous work,[6] we studied the reactions of 1-ethoxycarbonylmethyl-2,4,6-triphenylpyridinium (4). The reactivity of the ethoxycarbonyl in (4) was considerably influenced by the adjacent phenyl rings, as compared to the parent (5). We now report on the cyano analogue (6) for which the stereoelectronic considerations should be very different.

We prepared the 2,4,6-triphenylpyridinium salt (6) from aminoacetonitrile and 2,4,6-triphenylpyrylium.[7] Treatment of salt (6) with ethanolic sodium ethoxide rapidly forms the diazobicyclo-

nonane (8). If sodium hydroxide was used in MeOH or EtOH, then the corresponding esters (cf. 4) were readily produced: in the case of isopropanol, the intermediate imino ester (9) was isolated. These results underline the near normal reactivity of the cyano group in (6) as contrasted to the unreactivity of CO_2Et in (4).[6]

Formation and Reaction of Ylids.- The pyridinium (6) reacts readily with a variety of electrophiles under basic conditions to form the substituted ylids (10), isolated as deeply coloured crystalline materials of high melting point (Table 1).



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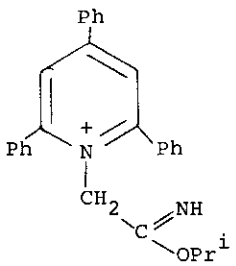

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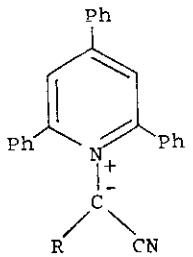

10 (For designation of R see Table 1)

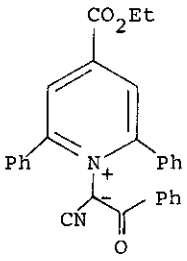

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Table 1. Preparation of Pyridinium Ylids[a]

Compd. no.	R	Method of Preparation	Cryst. Solvent	M.p. (°C)	Yield (%)	Found (%) C	H	N	Analysis Mol. Formula	Required (%) C	H	N
(10a)	$COC_6H_4CH_3$-p	A	$PhCH_3$	240	71	85.3	5.2	6.0	$C_{33}H_{24}N_2O$	85.3	5.2	6.0
(10b)	COPH	A	$PhCH_3$	235	73	84.9	4.8	6.1	$C_{32}H_{22}N_2O$	85.3	4.9	6.2
(10c)	COC_6H_4Cl-p	A	$PhCH_3$	274	63	78.9	4.2	5.8	$C_{32}H_{21}ClN_2O$	79.2	4.4	5.8
(10d)	$COCH_3$	A	EtOH	258	56	80.1	6.0	6.3	$C_{29}H_{26}N_2O_2$[b]	80.2	6.0	6.5
(10e)	CONHPh	B	$PhCH_3$	197	75	82.4	5.0	8.9	$C_{32}H_{23}N_3O$	82.6	5.0	9.0
(10f)	CSNHPh	B	$PhCH_3$	177	63	79.4	4.8	8.6	$C_{32}H_{23}N_3S$	79.8	4.8	8.7
(10g)	CO_2Et	B	Et_2O	224	41	80.1	5.2	6.7	$C_{28}H_{22}N_2O_2$	80.4	5.3	6.7
(11)	COPh	C	$PhCH_3$	210	68	77.4	4.9	6.2	$C_{29}H_{22}N_2O_3$	78.0	5.0	6.3

[a] Crystal form: prisms. [b] Contains EtOH of crystallization as confirmed by nmr and ir.

The deep colour of these ylids derives from a band around 500 nm of $\varepsilon \cong 1000$, the wavelength of which is sensitive to the solvent (Table 2): highest in $PhCH_3$ and decreasing through CH_2Cl_2 to EtOH. Kröhnke[8] observed increasing colour as the hydration of ylids decreased. A uv study of the toluoyl ylid (10a) in various solvents (Table 3) showed the Kosower correlation[9] of the λ_{max} of such ylids with Z values (Figure) indicating that these λ_{max} are charge transfer bands.[10]

The proton nmr spectra of the ylids (Table 4) support the structures assigned. The β-protons of the pyridine ring give rise to a sharp singlet near 8.0 ppm. The 15 protons of the 2-,4- and 6-phenyl groups appear as multiplets at 7.8-7.1 ppm whereas the aromatic protons of the N-substituent usually appear as a separated signal at 7.4-6.6 ppm.

Table 2. UV and IR Spectra of Pyridinium Ylids

Compd. no.	UV in EtOH $\lambda_{max.}$	log. ξ	UV in CH_2Cl_2 $\lambda_{max.}$	log. ξ	UV in $PhCH_3$ $\lambda_{max.}$	log. ξ	IR in nujol NH(m)	C=N (v.s.)
(10a)~	452	2.98	502	3.16	536	3.14		2160
(10b)~	448	2.92	496	3.06	532	2.94		2160
(10c)~	444	3.00	492	3.14	526	3.03		2160
(10d)~	446	2.85	504	3.03	536	3.02		2160
(10e)~	516	3.13	544	3.38	580	3.06	3400	2140
(10f)~	512	2.78	564	3.03	596	2.92	3160	2160
(10g)~	490	2.96	544	3.38	568	3.15		2160
(11)~	-	-	562	3.05	-	-		2150

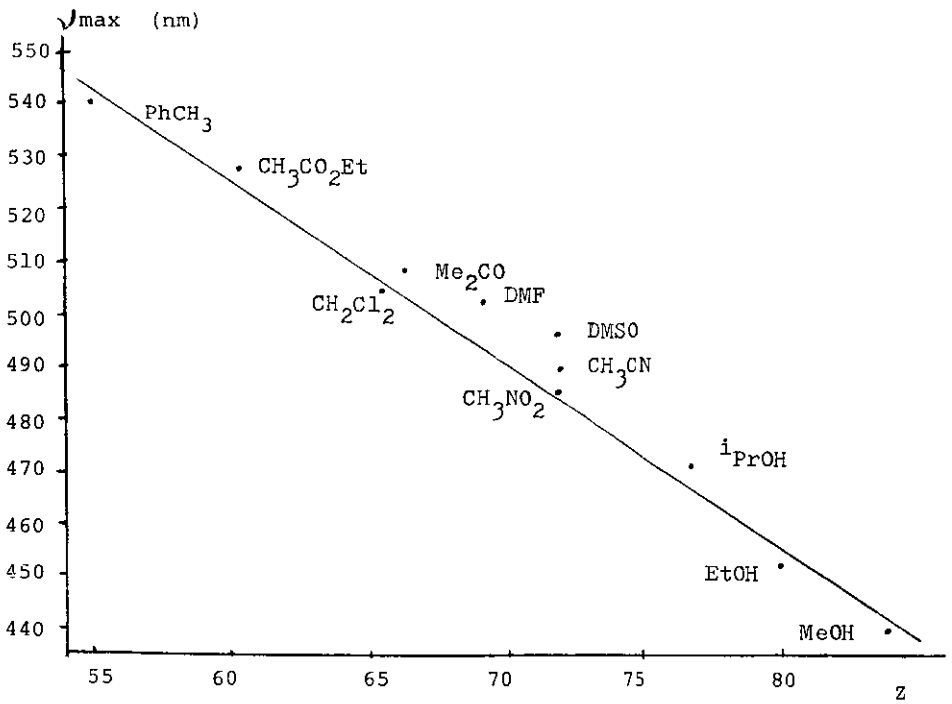


Figure. Solvent effect on uv. spectrum of 1-(p-toluoyl-cyanomethyl)-2,4,6-triphenylpyridinium ylid (10a).

Table 3. Solvent Effect on UV Spectrum of Ylid (10a).

Solvent	MeOH	EtOH	^{i}PrOH	CH_3CN	CH_3NO_2	Me_2SO	DMF	Me_2CO	CH_2Cl_2	CH_3CO_2Et	$PhCH_3$	CCl_4
$\lambda_{max.}$ (nm)	440	452	470	488	484	494	500	506	502	524	536	545
Z[a]	83.6	79.6	76.3	71.3	71.2	71.1	68.4	65.5	64.7	59.4	54.0[b]	-

[a] C. Reichardt, "Solvent Effects in Organic Chemistry", Weinheim, New York, 1979.

[b] Z for $PhCH_3$ not available; value shown is for PhH.

Table 4. ^{1}H NMR[a] of Pyridinium Ylids.

Compd. No.	Pyridinium Ring: 3,5 H (s, 2 H)	Pyridinium Ring: Other Aromatics (m, 15 H)	N-Substituent Signals: Aromatic	N-Substituent Signals: Aliphatic
(10a)	8.00	7.95 - 7.45	7.45-6.70 (m, 4 H)	2.20 (s, 3 H)
(10b)	8.00	7.80 - 7.30	7.15 (s, 5 H)	-
(10c)	8.00	7.90 - 7.30	7.10 (s, 4 H)	-
(10d)	7.95	7.90 - 7.20	-	1.60 (s, 3 H)
(10e)	7.95	7.90 - 7.30	7.30-6.60 (m, 5 H)	-
(10f)	7.90	7.85 - 7.15	7.15-6.70 (m, 5 H)	-
(10g)	7.95	7.90 - 7.40	-	3.80 (q, 2 H, J = 7) 0.85 (t, 3 H, J = 7)[b]
(11)	8.46	7.90 - 7.30 (10 H)	7.16 (s, 5 H)	4.50 (q, 2 H, J = 7)[b] 1.43 (t, 3 H, J = 7)[b]

[a] $CDCl_3$ as solvent, δ in ppm and J in Hz. [b] For CO_2Et group.

Table 5. ^{13}C NMR[a] of Pyridinium Ylids (10)

Cpd. No.	C=O/C=S (s)	Pyridinium Ring carbon signals C-2,6(s)	C-4(s)	C-3,5(a)	Other aromatic carbon signals	Carbanionic carbon signals (s)
(10a)	178.9	160.6	155.4	125.2	138.9 136.2 134.0 133.3 131.8 130.1 129.7 128.1 127.6 126.8 124.0	87.3
(10b)	179.0	160.7	155.6	125.3	139.2 134.0 133.3 132.7 131.9 130.8 130.3 129.7 129.0 128.6 128.1 127.6 127.5 126.8 123.8	87.5
(10c)	177.6	160.6	155.6	125.2	137.6 134.7 133.9 133.2 132.0 131.6 130.3 129.6 129.1 128.1 128.0 127.6 126.7 124.7 123.5	87.3
(10d)	180.1	160.2	155.1	125.1	133.8 133.3 131.7 130.1 129.5 128.0 127.8 127.4 124.0	86.6
(10e)	163.4	161.4	154.9	125.3	140.0 134.3 133.9 131.8 130.1 129.7 128.4 128.3 127.6 121.2 118.4	74.2
(10f)	180.9	161.4	155.7	125.4	140.0 133.9 133.2 132.0 130.3 129.6 128.5 128.0 127.7 123.9 123.7 121.3	87.5
(10g)	166.1	161.1	154.9	125.3	134.2 133.9 131.8 130.1 129.7 128.5 128.3 128.2 127.6	73.0

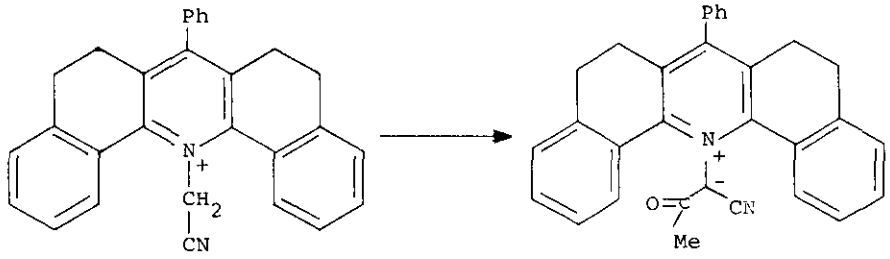
[a] $CDCl_3$ as solvent, TMS as internal reference, δ in ppm.

Footnotes: Aliphatic Carbon Signals (10a) 21.1(q), (10d) 23.0(q), (10g) 58.2(t), 14.9(q)

All the ylids show a strong νC≡N at ca. 2160 cm^{-1} (Table 2), but no νC=O above 1600 cm^{-1}. This indicates that the major canonical form carries a negative charge at the oxygen atom. However the C=O group carbon shows up characteristically in the ^{13}C spectra at 166-181 ppm (Table 2) as do the α- and γ-pyridine carbon rings (near 161 and 156 ppm, respectively) while the β-pyridine ring carbon occurs in the benzenoid aromatic multiplet. The α-carbon of the 1-substituent also occurs at 73-87 ppm in the ^{13}C nmr spectrum.

Other Pyridinium Ylids.- The 4-ethoxycarbonylpyridinium ylid (11) (Table 1) was readily prepared from the corresponding 1-cyanomethyl-4-ethoxycarbonylpyridinium (7) and benzoyl chloride at 0°C. In this ylid the charge transfer band shifts to 562 nm (cf., 10a λ_{max} in CH_2Cl_2 at 496 nm), presumably due to the electron withdrawing effect of the 4-ethoxycarbonyl group.

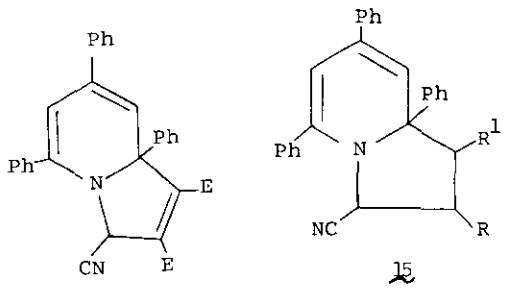
The N-cyanomethyldibenzo[c,h]acridinium triflate (12) from the corresponding xanthylium salt,[11,12] reacted with acetic anhydride in the presence of NEt_3 to give ylid (13) (76%) as crimson prisms of high mp (254°C). λ_{max} for this compound is 504 nm in CH_2Cl_2 indicating extensive charge delocation.



12 Scheme 3 13

Reaction with DMAD.- 1-Cyanomethyl-2,4,6-triphenylpyridinium (6) reacted readily with DMAD at room temperature under mildly basic conditions to give adduct (14) isolated in 76%; cf. ref.[13] for a similar result.

A range of α,β-unsaturated carbonyl compounds reacted similarly to afford the tetrahydroindolizines (15) (Table 6). Similar reactions have been previously reported and their spectra extensively discussed,[14] and the present compounds showed similar spectra characteristics.



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For designation of R and R' See Table 6.

Scheme 4

Pyrolysis.- At 250°C, 1-(p-toluoylcyanomethyl)-2,4,6-triphenylpyridinium ylid (10a, R = p-MeC_6H_4CO) gave 3-cyano-2,4,6-triphenylpyridine (49%) together with p-methylacetephenone (17%), instead to the expected ketene. The cyano compound was identified spectrally (see experimental). The mechanism of this reaction, which involves a 1,4-cyanoshift, is unknown.

Table 6. Preparation of Tetrahydroindolizines (15)

Adduct	R	R^1	Cryst.[a] form	M.p. (°C)	Yield (%)	Found (%) C	H	N	Mol. formula	Required (%) C	H	N
(15a)	H	CO_2Et	pl	172	63	80.9	5.8	6.3	$C_{30}H_{26}N_2O_2$	80.7	5.9	6.3
(15b)	H	CN	pr	209	65	84.0	5.3	10.5	$C_{28}H_{21}N_3$	84.2	5.3	10.5
(15c)	Ph	COPh	pr	205	63	86.6	5.4	5.1	$C_{40}H_{30}N_2O$	86.6	5.5	5.1
(15d)	$C_6H_4CH_3$-p	COPh	ne	194	60	86.5	5.6	4.9	$C_{41}H_{32}N_2O$	86.6	5.7	4.9
(15e)	Ph	COC_6H_4F-p	pr	203	60	83.9	5.0	4.9	$C_{40}H_{29}FN_2O$	83.9	5.1	4.9
(15f)	Ph	CHO	pr	115	45	84.9	5.4	5.7	$C_{34}H_{26}N_2O$	85.3	5.5	5.9
(15g)	Ph	CHO	pr	111	62	83.2	5.7	6.8	$C_{29}H_{24}N_2O$	83.6	5.8	6.7

[a] pl=plates, pr=prisms, ne=needles, all crystallized from 95% EtOH.

Table 7. ^{1}H NMR Spectral Data[a] of Tetrahydroindolizines (15)

Adduct	CHO (s)	Aromatic (m)	6,8 H (s)		3H	1H	2H	Others
(15a)	-	7.8-7.0 (15H)	6.30	6.00	4.64 (t, J=7)	3.50 (t, J=8)	2.52 (t, J=8)	4.12 (m, 2 H) 1.16 (t, 3 H, J=6)
(15b)	-	8.0-7.0 (15H)	6.32	6.30	5.08 (dd, J=4,8)	3.88 (t, J=7)	3.1-2.2 (m)	
(15c)	-	8.0-6.8 (25H)	6.50	6.08	4.84 (d, J=10)	4.64 (d, J=14)	4.46 (dd, J=8,12)	
(15d)	-	8.0-6.7 (24H)	6.48	6.06	4.82 (d, J=5)	4.60 (d, J=16)	4.42 (dd, J=8,12)	2.16 (s, 3 H)
(15e)	-	8.0-7.0 (24H)	6.50	6.04	4.80 (d, J=5)	4.62 (d, J=16)	4.44 (dd, J=8,12)	
(15f)	9.70	8.0-7.0 (20H)	4.58	5.90	4.56 (d, J=7)	3.85 (d, J=10)	4.02 (dd, J=10,18)	
(15g)	9.80	7.9-7.0 (15H)	6.37	5.75	4.23 (d, J=7)	3.19 (d, J=10)	2.9 (m)	1.21 (d, 3 H, J=6)

[a] δ in ppm, J in Hz, and solution $CDCl_3$ except compound (15b) in acetone -d_6

EXPERIMENTAL

Melting points were obtained on a Kofler hot stage apparatus, and are uncorrected. Ir spectra were run using NaCl plates on a Perkin-Elmer 257 grating spectrophotometer as solutions in $CHBr_3$. ^1H Nmr spectra were obtained on a Perkin-Elmer 60 MHz R-12 spectrometer. ^{13}C nmr spectra were run on a JEOL FX-100 machine operating at 25.05 MHz as 0.1 M solutions in $CDCl_3$: spectra were assigned using off resonance decoupling to establish multiplicity. Uv data were collected on a Unicam SP 800 A spectrophotometer as ca. 9×10^{-4} solutions.

1-Cyanomethyl-2,4,6-triphenylpyridinium Tetrafluoroborate.- To 2,4,6-triphenylpyrylium BF_4^-[7] (1 g, 2.5 mM) in CH_2Cl_2 (10 ml) was added a mixture of NEt_3 (0.7 ml, 5 mM) and aminoacetonitrile hydrochloride (0.2 g, 2.5 mM). After stirring at 25°C for 5 h, HOAc (0.5 ml) was added and the organic layer separated, dried ($MgSO_4$) and evaporated to give an oil which, after trituration with Et_2O and H_2O, crystallised from abs EtOH to give the pyridinium BF_4^- (0.6 g, 60%), needles, mp 209-210°C (Found: C, 68.7; H, 4.3; N, 6.4. $C_{25}H_{19}BF_4N_2$ requires C, 69.2; H, 4.4; N, 6.5%); δ($CDCl_3$/TFA) 8.15 (s, 2 H), 8.4-8.5 (m, 15 H), 4.7 (s, 2 H); $\bar{\nu}$ ($CHBr_3$) 1630s, 1600s, 1050b.

Similarly was prepared: 14-cyanomethyl-7-phenyl-5,6,8,9-tetrahydrodibenzo[c,h]acridinium trifluoromethanesulphonate (from 7-phenyl-5,6,8,9-tetrahydrodibenzo[c,h]xanthylium $CF_3SO_3^-$) (63%), yellow plates from MeOH, mp 213°C (Found: C, 65.6; H, 4.2; N, 5.1. $C_{20}H_{23}FN_2O_3S$ requires C, 65.7; H, 4.2; N, 5.1%); δ($CDCl_3$) 8.5-7.0 (m, 13 H), 4.1 (s, 2 H), 3.1-2.5 (m, 8 H); $\bar{\nu}$ ($CHBr_3$) 1603s, 1590s, 1250b, 1026b.

2-Ethoxy-4,6,8-triphenyl-3,5,7-dehydrodiazabicyclononane (8).- 1-Cyanomethyl-2,4,6-triphenyl-pyridinium BF_4^- (1g, 2.5 mM) was stirred in NaOEt/EtOH (10%, 10 ml) for 5 min. The resulting green solid was filtered off and extracted into pet. ether (60-80°C). Slow solvent evaporation afforded green needles of the bicyclononane (70%), mp 138-139°C (Found: C, 82.5; H, 6.2; N, 7.1. $C_{27}H_{23}N_2O$ requires C, 82.8; H, 5.9; N, 7.2%); δ($CDCl_3$) 7.0-7.8 (m, 15 H), 5.6 (d, 1 H, J = 2 Hz), 5.8 (d, 1 H, J = 2 Hz), 4.0 (q, 4 H, J = 7 Hz), 4.1 (s, 2 H), 1.2 (t, 3 H, J = 7 Hz); $\bar{\nu}$ ($CHBr_3$) 1660 (s).

Reactions of 1-Cyanomethyl-2,4,6-triphenylpyridinium Tetrafluoroborate with Alcohols.- The pyridinium tetrafluoroborate (6a) (1 g, 2.3 mM) was stirred with aqueous NaOH (33%, 0.5 ml) in alcohol (20 ml) for 1 h at 20°C. The reaction was quenched with HBF_4 (40%, 3 ml). Solvent was removed at 50°C/0.5 mmHg. The residue was washed with H_2O and recrystallised from the corresponding alcohol to give:

(a) 1-Ethoxycarbonylmethyl-2,4,6-triphenylpyridinium tetrafluoroborate as needles (0.7 g, 63%), mp 205°C (lit.[6] mp 201-203°C).

(b) 1-Methoxycarbonylmethyl-2,4,6-triphenylpyridinium tetrafluoroborate as prisms (0.65 g,

60%), mp 190°C (lit.[6] mp 191-193°C).

(c) 1-Isopropoxyiminomethyl-2,4,6-triphenylpyridinium tetrafluoroborate as prisms (0.45 g, 40%), mp 126°C (Found: C, 67.6; H, 5.4; N, 5.6. $C_{28}H_{27}N_2O$ requires C, 68.0; H, 5.5; N, 5.7%); δ[$(CD_3)_2CO$/TFA] 8.55 (s, 2 H), 8.4-7.4 (m, 15 H), 6.00 (s, 2 H), 5.1 (m, 1 H), 1.3 (d, 6 H, J = 6 Hz); $\bar{\nu}$ ($CHBr_3$) 3300 (m), 1675 (s), 1630 (s), 1560 (m), 1050 (s).

Reaction of 1-Cyanomethylpyridinium Salts with Electrophiles (cf. Table 1). Method A.- To 1-cyanomethyl-2,4,6-triphenylpyridinium BF_4^- (0.5 g, 1.2 mM) and the electrophile (1.2 mM) in CH_2Cl_2 (10 ml) and H_2O (7 ml) was added with stirring aqueous KOH (33%, 3 ml) at 25°C. The resulting dark red solution was stirred for 1 h, the organic layer collected, washed with H_2O (2 x 20 ml), dried ($MgSO_4$) and evaporated to give a red solid, which was washed with Et_2O (50 ml) and H_2O (20 ml) and crystallised from suitable solvent (Table 1).

Method B.- As above but to the 1-cyanomethylpyridinium BF_4^- and electrophile in CH_2Cl_2 was added aqueous NaOH (33%, 3 ml).

Method C.- As for Method B but reaction conducted at 0°C. After stirring for 1 h, the resulting dark red solution was worked up as described in Method A.

1-Cyanomethyl-4-ethoxycarbonyl-2,6-diphenylpyridinium Tetrafluoroborate (7b).- To 4-ethoxycarbonyl-2,6-diphenylpyrylium BF_4^-[15] (1 g, 2.5 mM) in CH_2Cl_2 (10 ml) was added a mixture of aminoacetonitrile hydrochloride (0.24 g, 2.5 mM) and NEt_3 (0.5 g, 5 mM). After stirring at 25°C for 2 h, AcOH (0.3 g, 5 mM) was added and solution stirred 2 h. Evaporation gave an oil which was triturated with Et_2O and H_2O to give the pyridinium BF_4^- (0.6 g, 55%), prisms from EtOH, mp 225°C (Found: C, 61.4; H, 4.5; N, 6.4. $C_{22}H_{19}BF_4N_2O_2$ required C, 61.4; H, 4.5; N, 6.5%); δ ($CDCl_3$/TFA) 8.45 (s, 2 H), 7.75 (s, 10 H), 5.20 (s, 2 H), 4.50 (q, 2 H, J = 8 Hz), 1.40 (t, 3 H, J = 8 Hz); $\bar{\nu}$ ($CHBr_3$) 1730 s, 1630 s, 1600 s, 1050 b.

14-(1'-Acetyl cyanomethyl)-7-phenyl-5,6,8,9-tetrahydrodibenzo[c,h]acridinium Ylid (13).- Acridinium $CF_3SO_3^-$ (12) (0.55 g, 1 mM) was mixed with acetic anhydride (10 ml) and NEt_3 (0.2 ml) and heated at 100°C for 4 h. H_2O (50 ml) was added and the mixture heated at 100°C for further 2 h. The product was extracted into CH_2Cl_2 (2 x 20 ml), dried ($MgSO_4$) and evaporated to give the ylid (76%), red prisms from toluene, mp 254-256°C (Found: C, 84.0; H, 5.6; N, 6.1. $C_{31}H_{24}N_2O$ requires C, 84.5; H, 5.5; N, 6 4%); δ($CDCl_3$) 8.0-8.3 (2 H, m), 7.2-7.7 (11 H, m), 2.4-2.9 (8 H, m), 1.9 (3 H, s); $\bar{\nu}$ ($CHBr_3$) 2940 m, 1604 m, 1582 m, 1390 m, 770 m, 752 m.

Reaction of 1-Cyanomethylpyridinium BF_4^- with DMAD.- A mixture of 1-cyanomethyl-2,4,6-triphenylpyridinium BF_4^- (0.4 g, 0.93 mM), and DMAD (0.14 g, 0.98 mM) in CH_2Cl_2 (10 ml) was stirred with aq. K_2CO_3 (16%, 50 ml) for 10 h. The organic layer was collected, dried ($MgSO_4$) and evaporated: the residue was recrystallised from pet. ether (100-120°C) and $PhCH_3$ (20%) to

give prisms of the bicyclic compound (14), (0.32 g, 76%), mp 192-194°C (Found: C, 76.4; H, 4.9; N, 5.7. $C_{28}H_{24}N_2O_4$ requires C, 76.2; H, 5.0; N, 5.7%); δ ($CDCl_3$) 7.2-7.8 (15 H, m), 7.4 (1 H, d, J = 1 Hz), 7.3 (1 H, d, J = Hz), 4.5 (1 H, s), 3.7 (3 H, s), 3.2 (3 H, s); $\bar{\nu}$ ($CHBr_3$) 1740 (s), 1695 (s), 1630 (m), 1610 (m), 1245 (s), 1197 (s).

Preparation of Tetrahydroindolizines (15).- 1-Cyanomethyl-2,4,6-triphenylpyridinium tetrafluoroborate (1 g, 2.3 mM) was stirred with the dipolarophile (3.4 mM) and aqueous NaOH (33%, 6 ml) in dichloromethane (10 ml) for 1 h at 20°C. The organic layer was washed with H_2O (2 x 20 ml). Evaporation at 100°C/0.5 mmHg and recrystallisation of the residue from EtOH (95%) gave the tetrahydroindolizines (Table 6).

Pyrolysis of Pyridinium Ylid (10a).- Ylid (10a) (2 g, 4.3 mM) was heated at 250°C/0.05 mmHg for 3 h. p-Methylacetophenone (0.1 g, 17%) was collected in a liquid nitrogen trap. (^{1}H nmr and ir spectra were identical to those quoted.[16]) The black residue was recrystallised from EtOAc, passed through a column (alumina/EtOAc), and again recrystallisation (from EtOH) to give 3-cyano-2,4,6-triphenylpyridine as white prisms (0.7 g, 49%), mp 200-203°C (Found: C, 86.6; H, 4.8; N, 8.0. $C_{24}H_{16}N_2$ requires C, 86.7; H, 4.9; N, 8.4%); δ ($CDCl_3$) 7.8 (s, 1 H), 8.3-7.4 (m, 15 H); $\bar{\nu}$ ($CHBr_3$) 2220 (m), 1600 (m), 1570 (s), 1585 (s); ^{13}C nmr δ ($CDCl_3$) 162.4 (s), 159.0 (s), 137.7 (s), 137.4 (s), 136.7 (s), 130.5-127.5 (m), 118.5 (d); M^+ 332.

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