Synthesis and Thermal Reaction of 2,2-Diacyl-*N*-(1-pyridinio)vinylaminides: Formation of Pyrazolo[1,5-*a*]pyridines and Isoxazoles

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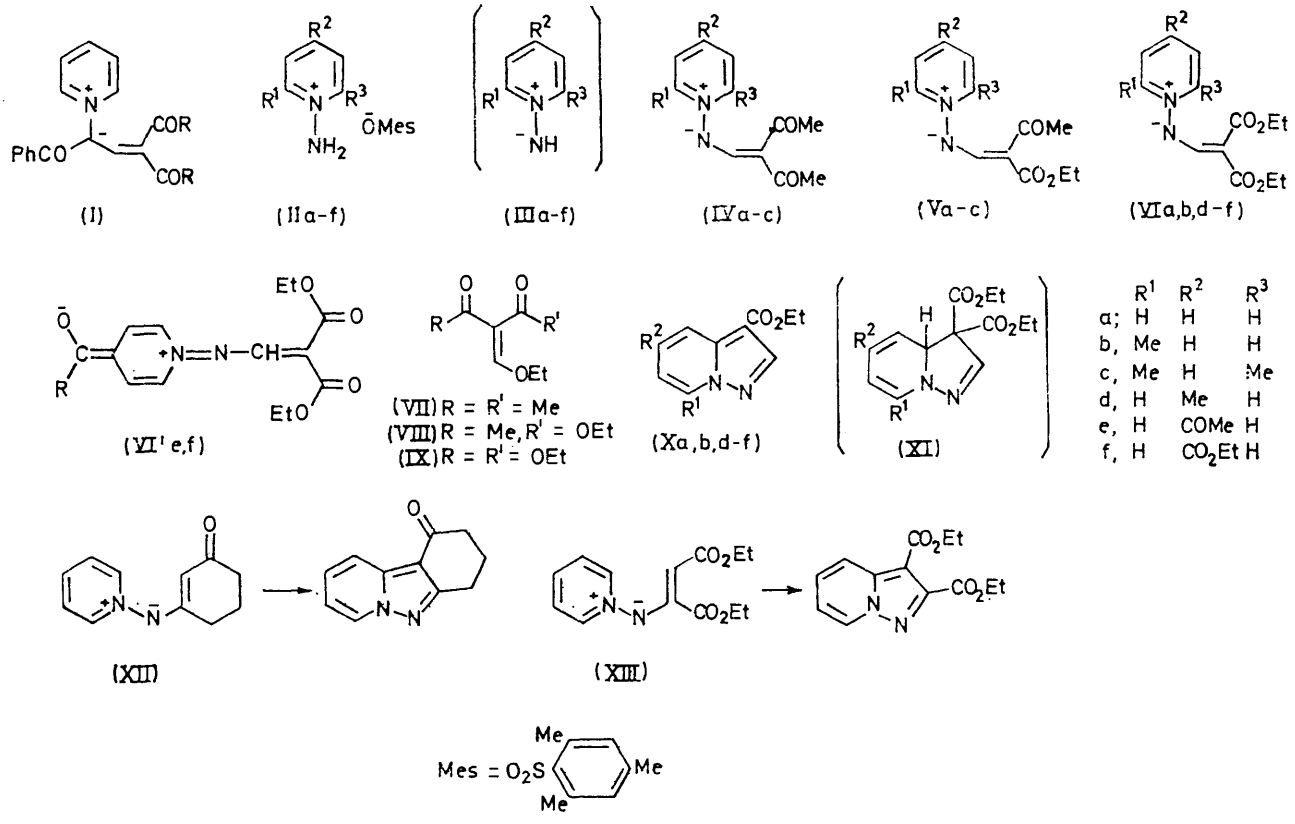
2,2-Diacyl-*N*-(1-pyridinio)vinylaminides have been prepared by the reaction of pyridine *N*-imides with 1,1-diacyl-2-ethoxyethylenes. Refluxing the bisethoxycarbonylvinylaminides (VIa, b, and d—f) in xylene afforded the ethyl pyrazolo[1,5-*a*]pyridine-3-carboxylates (Xa, b, and d—f); however the diacetylvinylaminides (IVa—c) and the acetyl(ethoxycarbonyl)vinylaminides (Va—c) are thermally labile and, upon heating in benzene, undergo N–N bond cleavage to give isoxazole derivatives [(XV) and (XVI)] in high yields.

We have previously described [1] the synthesis of pyridinium 3,3-diacylallylides (I) and their conversion into indolizine derivatives. We have now prepared the related 2,2-diacyl-*N*-(1-pyridinio)vinylaminides and examined their thermochemical behaviour.

malonate (IX) [5] was also found to react with a variety of pyridine *N*-imides to give 2,2-bisethoxycarbonyl-*N*-(1-pyridinio)vinylaminides (VIa, b, and d—f).

The spectral data of these compounds are summarised in Tables 1 and 2. In general, these compounds



The aminides (IVa—c) were synthesised by the reaction of 3-ethoxymethylenepentane-2,4-dione (VII) [2] with pyridine *N*-imides (IIIa—c), which were prepared by treatment of the *N*-aminopyridinium mesitylenesulphonates [3] (IIa—c) with Amberlite IRA-410 ion-exchange resin. Use of ethyl 2-(ethoxymethylene)-acetoacetate (VIII) [4] instead of (VII) gave rise to the hygroscopic 2-acetyl-2-ethoxycarbonyl-*N*-(1-pyridinio)vinylaminides (Va—c). Diethyl ethoxymethylene-

showed three u.v. absorption maxima, with that of longest wavelength at 383—395 nm. The exceptions are the 2,6-lutidine derivatives (IVc and Vc), which have the longest wavelength maximum at 354—355 nm, presumably a result of steric inhibition of coplanarity of the pyridine ring and the conjugated system. The introduction of a carbonyl group at the 4-position of the pyridine ring (VIe and VIf) produced a large batho-

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chromic shift (*ca.* 60 nm) of the longest wavelength maximum due to increased conjugation [see (VI'e) and (VI'f)]. The i.r. spectra showed a polarised carbonyl absorption band for all compounds examined. The

TABLE 1

I.r.[a] and u.v.[b] spectra for the diacylvinylaminides

Compound	$\nu_{max.}$/cm^{-1}	$\lambda_{max.}$/nm	log ε
(IVa)	1570	257sh	3·98
		279	4·24
		391	4·14
(IVb)	1575	261sh	4·08
		279	4·28
		383	4·10
(IVc)	1605	278	4·34
	1585	297	4·31
		354	3·67
(Va)	1660	246[c]	
	1590	280	
		389	
(Vb)	1660	250[c]	
	1590	283	
		379	
(Vc)	1660	250[c]	
	1580	299	
		355	
(VIa)	1670	238	4·22
	1620	278	4·21
		395	4·23
(VIb)	1690	239	4·15
		280	4·20
		386	4·04
(VId)	1655	249·5	4·18
	1605	277·5	4·16
		385	4·17
(VIe)	1670	235·5	4·15
	1640	286·5	4·15
		461·5	4·26
(VIf)	1695	230·5sh	4·50
	1675	287	4·25
	1635	457	4·34
(XVII)	2170	218	4·06
	1650	277	4·16
		394	4·18

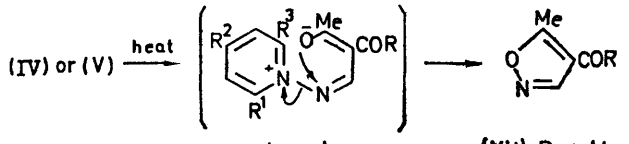
[a] In KCl. [b] In EtOH. [c] Precise extinctions were not determined since the compound was very hygroscopic.

n.m.r. spectra of compounds (IIIa—c) showed a sharp singlet at τ *ca.* 7·5 due to two acetyl methyl groups. Similarly for compounds (VIa, b, and d—f) the signal due to the methylene protons of two ethoxycarbonyl groups appeared as only one quartet. These data suggest that rapid rotation is possible around the polarised carbon–carbon double bond.[6] The olefinic proton singlet appeared at low field (τ *ca.* 1·1—1·6). This may be a result of a combined anisotropic, mesomeric, and inductive effects of the two acyl groups, along with an electronegative effect of the aminide nitrogen atom.

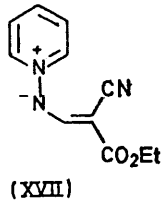
The thermal behaviour of compounds (VIa, b, and d) was analogous to that of the related compounds (XII) [7] and (XIII),[8] which have already been shown to undergo 1,5-cyclisation to give the corresponding pyrazolo[1,5-*a*]pyridine derivatives. Thus, when heated in refluxing xylene for 1—1·5 h, compounds (VIa, b, and d) were transformed into the corresponding ethyl pyrazolo[1,5-*a*]pyridine-3-carboxylates (Xa, b and d) in 13—23% yields. This reaction was successfully applied to the syntheses of the pyrazolo[1,5-*a*]pyridines (Xe and f) with substituents other than methyl on the six-membered ring, which have not been described previously. The pyrazolo[1,5-*a*]pyridines were characterised by analyses and the spectral comparisons with the known compound (Xa). The reaction of (VI) to form (X) can be envisaged as occurring by initial formation of a dihydropyrazolo[1,5-*a*]pyridine intermediate (XI), followed by formal elimination of ethyl formate.

In sharp contrast, the diacetylvinylaminides (IVa—c) and the acetyl(ethoxycarbonyl)vinylaminides (Va—c), on heating in refluxing benzene until the yellow colour of the solution faded (10 min—2 h), underwent nitrogen–nitrogen bond fission to give the known 4-acetyl-5-methylisoxazole (XV) [9] and 4-ethoxycarbonyl-5-methylisoxazole (XVI) [4] respectively, in high yields.* The fact that the thermolysis of (IV) and (V) occurred smoothly at relatively low temperature suggests that a nitrene intermediate is not involved, but that pyridine elimination is concerted with cyclisation [see (XIV)]. There is an analogy for this type of reaction in the transformation of 2-azidovinyl ketones into isoxazoles.[11]

Thus the nature of the acyl groups has a significant effect on determining the course of the thermal reaction.



(XIV) (XV) R = Me (XVI) R = OEt



(XVII)

This may be attributed to differences in the degree of delocalisation of negative charge over the carbonyl groups ($\nu_{max.}$ 1570—1580 for the acetyl carbonyl group, and 1670—1690 cm^{-1} for the ester carbonyl group).

* The isoxazole (XV) was also formed by photoreaction of (IVb) in acetone or alcohol, but in low yield, presumably *via* a nitrene intermediate. The photoinduced nitrogen–nitrogen bond cleavage of pyridine *N*-imides to pyridines and nitrenes is well known.[10]

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TABLE 2

N.m.r. spectra for diacylvinylaminides (τ values; Me_4Si internal standard; $CDCl_3$)

Compound	Pyridine ring proton(s) α	β γ	Olefinic proton	Ac	$CO_2{\cdot}CH_2{\cdot}CH_3$	$CO_2{\cdot}CH_2{\cdot}CH_3$	Other signals
(IVa)	1·37br (2H, d)	1·90—2·35 (3H, m)	1·17 (1H, s)	7·54 (6H, s)			
(IVb)	1·45 (1H, dd)	1·90—2·50 (3H, m)	1·20 (1H, s)	7·51 (6H, s)			7·25 (3H, s, Me)
(IVc)		1·95—2·55 (3H, m)	1·57 (1H, s)	7·49 (6H, s)			7·34 (6H, s, 2 × Me)
(Va)	1·46 (2H, dd)	1·95—2·25 (3H, m)	1·34 (1H, s)	7·57 (3H, s)	5·75 (2H, q)	8·68 (3H, t)	
(Vb)	1·46 (1H, dd)	2·00—2·50 (3H, m)	1·41 (1H, s)	7·58 (3H, s)	5·76 (2H, q)	8·70 (3H, t)	7·26 (3H, s, Me)
(Vc)		2·08—2·60 (3H, m)	1·80 (1H, s)	7·57 (3H, s)	5·76 (2H, q)	8·71 (3H, t)	7·57 (6H, s, 2 × Me)
(VIa)	1·42 (2H, dd)	2·00—2·45 (3H, m)	1·46 (1H, s)		5·77 (4H, q)	8·68 (6H, t)	
(VIb)	1·61 (1H, dd)	2·00—2·45 (3H, m)	1·54 (1H, s)		5·78 (4H, q)	8·68 (6H, t)	7·25 (3H, s, Me)
(VId)	1·55 (2H, d)	2·49 (2H, d)	1·48 (1H, s)		5·81 (4H, q)	8·72 (6H, t)	7·47 (3H, s, Me)
(VIe)	1·48 (2H, d)	2·00 (2H, d)	1·58 (1H, s)		5·79 (4H, q)	8·62 (6H, t)	7·38 (3H, s, Ac)
(VIf)	1·50 (2H, d)	1·92 (2H, d)	1·53 (1H, s)		5·77 (4H, q)	8·70 (6H, t)	5·56 (2H, q, $CO_2{\cdot}CH_2{\cdot}CH_3$) 8·58 (3H, t, $CO_2{\cdot}CH_2{\cdot}CH_3$)
(XVII)	1·07 (2H, dd)	1·75—2·20 (3H, m)	1·55 (1H, s)		5·95 (2H, q)	8·84 (3H, t)	

For comparison, 2-cyano-2-ethoxycarbonyl-*N*-(1-pyridinio)vinylaminide (XVII) was also prepared from pyridine *N*-imide (IIIa) and 2-cyano-3-ethoxyacrylate.[12] However, compound (XVII) was stable in refluxing xylene.

EXPERIMENTAL

N.m.r. spectra were determined with a Hitachi R-20A spectrometer (tetramethylsilane as internal standard). I.r. spectra were recorded with a Hitachi EPI-G2 spectrophotometer, and u.v. spectra with a Hitachi 124 spectrophotometer. Mass spectra were obtained with a Hitachi RMU-6D instrument with a direct inlet system operating at 70 eV. Preparative layer chromatography (p.l.c.) was carried out on Merck Alumina PF_{254}.

General Procedure for N-*Aminopyridinium Mesitylenesulphonates* (IIa—f).—A solution of *O*-mesitylsulphonylhydroxylamine (2 mmol) in methylene chloride (2 ml) was added to a solution of pyridine (2 mmol) in methylene chloride (2 ml), cooled in ice. The mixture was kept at room temperature for 30 min, ether was added, and the precipitated crystals (II) were recrystallised from methanol–ethyl acetate. N-*Aminopyridinium mesitylenesulphonate* (IIa) (80%) formed white plates, m.p. 125—126° (Found: C, 57·3; H, 6·2; N, 9·7. $C_{14}H_{18}N_2O_3S$ requires C, 57·1; H, 6·2; N, 9·5%); N-*amino*-2-*methylpyridinium mesitylenesulphonate* (IIb) (94%) formed white scales, m.p. 120—121° (Found: C, 58·5; H, 6·4; N, 9·1. $C_{15}H_{20}N_2O_3S$ requires C, 58·4; H, 6·5; N, 9·1%); N-*amino*-2,6-*dimethylpyridinium mesitylenesulphonate* (IIc) (89%) formed white cubes, m.p. 180—181° (Found: C, 59·7; H, 7·0; N, 8·8. $C_{16}H_{22}N_2O_3S$ requires C, 59·6; H, 6·9; N, 8·7%); N-*amino*-4-*methylpyridinium mesitylenesulphonate* (IId) (95%) formed white needles, m.p. 99—100° (Found: C, 58·2; H, 6·55; N, 9·0. $C_{15}H_{20}N_2O_3S$ requires C, 58·4; H, 6·5; N, 9·1%); 4-*acetyl*-N-*aminopyridinium mesitylenesulphonate* (IIe) (91%) formed pale yellow plates, m.p. 125—126° (Found: C, 57·3; H, 6·1; N, 8·2. $C_{16}H_{20}N_2O_4S$ requires C, 57·1; H, 6·0; N, 8·3%); and N-*amino*-4-*ethoxycarbonylpyridinium mesitylenesulphonate* (IIf) (87%), formed pale yellow scales, m.p. 57—58° (Found: C, 55·6; H, 6·2; N, 7·5. $C_{17}H_{22}N_2O_5S$ requires C, 55·7; H, 6·05; N, 7·65%).

General Procedure for 2,2-*Diacetyl*-N-(1-*pyridinio*)*vinylaminides* (IVa—c).—An ethanolic solution of the pyridine *N*-imide (III) was prepared by passing an ethanolic solution of the *N*-aminopyridinium mesitylenesulphonate (II) (2 mmol) through a column of Amberlite IRA-410 resin. 3-Ethoxymethylenepentane-2,4-dione (VII) [2] (2 mmol) was then added with stirring and the mixture was stirred at room temperature for a further 3 h. The solution was evaporated to dryness *in vacuo* below 35°, and the residue was purified by chromatography (alumina–chloroform) and recrystallisation from methylene chloride–ether. 2,2-*Diacetyl*-N-(1-*pyridinio*)*vinylaminide* (IVa) was obtained from (IIa) and (VII) in 86% yield as yellow needles, m.p. 151—153° (decomp.) (Found: C, 64·9; H, 6·1; N, 13·8. $C_{11}H_{12}N_2O_2$ requires C, 64·7; H, 5·9; N, 13·7%); 2,2-*diacetyl*-N-(2-*methyl*-1-*pyridinio*)*vinylaminide* (IVb) was obtained from (IIb) and (VII) in 76% yield as yellow needles, m.p. 151—153° (decomp.) (Found: C, 65·8; H, 6·5; N, 13·0. $C_{12}H_{14}N_2O_2$ requires C, 66·0; H, 6·5; N, 12·8%); 2,2-*diacetyl*-N-(2,6-*dimethyl*-1-*pyridinio*)*vinylaminide* (IVc) was obtained from (IIc) and (VII) in 37% yield as a pale yellow powder, m.p. 154—156° (decomp.) (Found: C, 67·5; H, 7·0; N, 12·3. $C_{13}H_{16}N_2O_2$ requires C, 67·3; H, 6·9; N, 12·1%).

General Procedure for 2-*Acetyl*-2-*ethoxycarbonyl*-N-(1-*pyridinio*)*vinylaminides* (Va—c).—The procedure described for (IV) was used; the *N*-imide (IIIa) was treated with ethyl ethoxymethyleneacetoacetate (VIII).[4] The solution was evaporated *in vacuo* below 15°, and the residue was chromatographed on alumina. Elution with chloroform gave chromatographically homogeneous but very hygroscopic

yellow crystals of (Va) in 80% yield, which were used for spectral determination and further reaction. Similarly, compounds (Vb and c) were obtained from the corresponding *N*-imides (IIIb and c) and (VIII) as very hygroscopic crystals in 89 and 47% yields, respectively.

General Procedure for 2,2-*Bisethoxycarbonyl*-N-(1-*pyridinio*)*vinylaminides* (VIa—f).—An ethanolic solution of the pyridine *N*-imide (IIIa, b, and d—f) prepared from the sulphonate (IIa, b, and d—f) (3 mmol) was added to a vigorously stirred solution of diethyl ethoxymethylenemalonate (IX) [5] (3 mmol) in ethanol (20 ml). The mixture was stirred at room temperature for 20—25 h, then evaporated, and the residue recrystallised. 2,2-*Bisethoxycarbonyl*-N-(1-*pyridinio*)*vinylaminide* (VIa) (56%) formed tan needles, m.p. 127—128° (from benzene) (Found: C, 59·4; H, 6·2; N, 10·5. $C_{13}H_{16}N_2O_4$ requires C, 59·1; H, 6·1; N, 10·6%); 2,2-*bisethoxycarbonyl*-N-(2-*methyl*-1-*pyridinio*)-*vinylaminide* (VIb) (78%) gave yellow plates, m.p. 86—88° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 60·7; H, 6·65; N, 9·9. $C_{14}H_{18}N_2O_4$ requires C, 60·4; H, 6·5; N, 10·1%); 2,2-*bisethoxycarbonyl*-N-(4-*methyl*-1-*pyridinio*)*vinylaminide* (VId) (74%) formed yellow needles, m.p. 132—134° [from ethanol–light petroleum (b.p. 30—60°)] (Found: C, 60·5; H, 6·7; N, 10·2%); 2,2-*bisethoxycarbonyl*-N-(4-*acetyl*-1-*pyridinio*)*vinylaminide* (VIe) (71%) was a dark red powder, m.p. 155—157° (from ethanol–light petroleum) (Found: C, 58·75; H, 6·0; N, 9·25. $C_{15}H_{18}N_2O_5$ requires C, 58·8; H, 5·9; N, 9·1%); 2,2-*bisethoxycarbonyl*-N-(4-*ethoxycarbonyl*-1-*pyridinio*)*vinylaminide* (VIf) (70%) gave red scales, m.p. 153—155° (from ethanol–light petroleum) (Found: C, 57·3; H, 6·1; N, 8·3. $C_{16}H_{20}N_2O_6$ requires C, 57·1; H, 6·0; N, 8·3%).

Thermal Reaction of the Bisethoxycarbonylvinylaminides (VIa, b, *and* d—f).—A suspension of compound (VIa) (389 mg) in xylene (80 ml) was heated under reflux for 1·5 h until the solution was colourless. The solvent was evaporated off *in vacuo*, and the residual oil was purified by p.l.c. with benzene to give, as an oil (65 mg, 23%), ethyl pyrazolo[1,5-*a*]pyridine-3-carboxylate (Xa), whose spectral data were identical with reported values.[13] By the same procedure, the following were synthesised; ethyl 7-methylpyrazolo[1,5-*a*]pyridine-3-carboxylate (Xb), from (VIb) in 13% yield as white cubes, m.p. 64·5—65° [from light petroleum (b.p. 30—60°)] (lit.,[13] 71—72°) (Found: C, 64·65; H, 5·9; N, 13·6. Calc. for $C_{11}H_{12}N_2O_2$: C, 64·7; H, 5·9; N, 13·7%); *ethyl* 5-*methylpyrazolo*[1,5-a]*pyridine*-3-*carboxylate* (Xd), from (VId) in 14% yield as white needles, m.p. 74—75° (from light petroleum) (Found: C, 64·8; H, 5·9; N, 13·5%); $\nu_{max.}$ (KCl) 1690 cm^{-1}; $\lambda_{max.}$ (EtOH) 219·5, 223·5, 241·5, 248sh, 292, and 308sh nm (log ε 4·59, 4·67, 4·03, 4·01, 4·08, and 3·98); τ ($CDCl_3$) 1·62 (1H, d, *J* 7 Hz, H-7), 1·69 (1H, s, H-2), 2·01 (1H, d, *J* 2 Hz, H-4), 3·26 (1H, dd, *J* 2 and 7 Hz, H-6), 5·64 (2H, q, *J* 7 Hz, O·CH_2·CH_3), 7·58 (3H, s, CH_3), and 8·61 (3H, t, *J* 7 Hz, O·CH_2·CH_3); *ethyl* 5-*acetylpyrazolo*[1,5-a]*pyridine*-3-*carboxylate* (Xe), from (VIe) in 25% yield as pale yellow cubes, m.p. 152—153° (from benzene) (Found: C, 62·2; H, 5·15; N, 11·6. $C_{12}H_{12}N_2O_3$ requires C, 62·1; H, 5·2; N, 12·1%), $\nu_{max.}$ (KCl) 1700 and 1670 cm^{-1}; $\lambda_{max.}$ (EtOH) 220sh, 226sh, 233, 243·5, 251, 286·5sh, and 339 nm (log ε 4·32, 4·39, 4·46, 4·34, 4·32, 3·55, and 3·97); τ ($CDCl_3$) 1·27 (1H, dd, *J* 1 and 2 Hz, H-4), 1·45 (1H, dd, *J* 1 and 7 Hz, H-7), 1·54 (1H, s, H-2), 2·51 (1H, dd, *J* 2 and 7 Hz, H-6), 5·59 (2H, q, *J* 7 Hz, O·CH_2·CH_3), 7·33 (3H, s, Ac), and 8·58 (3H, t, *J* 7 Hz, O·CH_2·CH_3); *diethyl pyrazolo*[1,5-a]*pyridine*-3,5-*dicarboxylate* (Xf), from (VIf) in 20% yield as pale yellow cubes, m.p. 78—79·5° (from light petroleum) (Found: C, 60·0; H, 5·5; N, 10·6. $C_{13}H_{14}N_2O_4$ requires C, 59·5; H, 5·4; N, 10·7%), $\nu_{max.}$ (KCl) 1715 and 1695 cm^{-1}; $\lambda_{max.}$ (EtOH) 223·5sh, 229·5, 241·5, 248·5, 286sh, and 332·5 nm (log ε 4·21, 4·28, 4·07, 4·02, 3·37, and 3·71); τ ($CDCl_3$) 1·17 (1H, dd, *J* 1 and 2 Hz, H-4), 1·47 (1H, dd, *J* 1 and 7 Hz, H-7), 1·56 (1H, s, H-2), 2·50 (1H, dd, *J* 2 and 7 Hz, H-6), 5·57 and 5·59 (each 2H, q, *J* 7 Hz, O·CH_2·CH_3), and 8·58 (6H, t, *J* 7 Hz, 2 × O·CH_2·CH_3).

Thermal Reaction of the Diacetylvinylanimides (IVa—c).—A solution of (IVa) (112 mg) in benzene (15 ml) was heated under reflux for 1 h until it was almost colourless. The solvent was evaporated off and the residue was purified by p.l.c. with benzene to give white crystals (57 mg, 83%) of 4-acetyl-5-methylisoxazole (XV), m.p. below 30°; $\nu_{max.}$ ($CHCl_3$) 1680 cm^{-1}; τ ($CDCl_3$) 1·52 (1H, s, H-3), 7·34 (3H, s, CH_3), and 7·61 (3H, s, Ac); semicarbazone, m.p. 196·5—197·5° (lit.,[9] 196—197°).

Similar treatment of (IVb) and (IVc) gave the same isoxazole (XV) in 54 and 58% yield, respectively.

Thermal Reaction of the Acetyl(*ethoxycarbonyl*)*vinylaminides* (Va—c).—A solution of (Va) (126 mg) in benzene (20 ml) was heated under reflux for 20 min until colourless. Work-up as described for (XV) gave an oil (54 mg, 65%), identified as ethyl 5-methylisoxazole-4-carboxylate (XVI) [4] by spectral comparisons with an authentic sample; $\nu_{max.}$ ($CHCl_3$) 1720 and 1610 cm^{-1}; τ ($CDCl_3$) 1·50 (1H, s, H-3), 5·67 (2H, q, *J* 8 Hz, CH_2·CH_3), 7·32 (3H, s, CH_3), and 8·66 (3H, t, *J* 7 Hz, CH_2·CH_3).

Similar treatment of (Vb) and (Vc) gave the same isoxazole (XVI) in 63 and 75% yield, respectively.

Photoreaction of 2,2-*Diacetyl*-N-(2-*methyl*-1-*pyridinio*)-*vinylaminide* (IVb).—A solution of (IVb) (115 mg) in acetone (70 ml) was irradiated (300 W high-pressure mercury lamp) for 3 h in a Pyrex vessel. T.l.c. indicated the presence of 2-picoline, the isoxazole (XV), and resinous products. The mixture was separated by p.l.c. with benzene to give white crystals (8 mg, 12%) of 4-acetyl-5-methylisoxazole (XV).

2-*Cyano*-2-*ethoxycarbonyl*-N-(1-*pyridinio*)*vinylaminide* (XVII).—By the procedure described for (Va), compound (XVII) (290 mg, 67%) was obtained from *N*-aminopyridinium mesitylenesulphonate (IIa) (598 mg) and ethyl 2-cyano-3-ethoxyacrylate [12] (338 mg) as yellow plates, m.p. 188—190° (from ethanol) (Found: C, 60·7; H, 5·2; N, 19·1. $C_{11}H_{11}N_3O_2$ requires C, 60·8; H, 5·1; N, 19·35%); for spectral data see Tables 1 and 2.

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