# Heterocyclic Rearrangements. Part XIV.[1] Attempts to Activate Ring-opening–Ring-closure Rearrangements with Carbon as the Central Atom

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Various 3-substituted quaternised pyridines and 4-substituted oxazoles have been prepared and studied, with a view to discovering substituents appropriate for reactions involving opening of the pyridine or oxazole ring with closure onto the substituent to form a new ring at the 2-(pyridine) or 5-(oxazole) position. None of these potential rearrangements succeeded; the reasons for this are discussed together with the evidence that this provides for the mechanism of previously reported rearrangements.

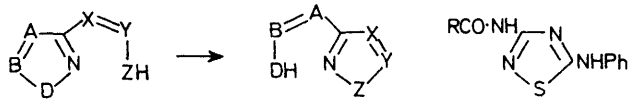
In an earlier paper,[2] a number of heterocyclic transformations were recognised as belonging to a general class of monocyclic rearrangement of the type (1) ⟶ (2). The occurrence of other rearrangements of this general type was predicted and several new examples were reported.[2] Recently, further examples of these general reactions have been described,[3,4] a notable example being the formation of 3-acylamino-5-anilino-1,2,4-thiadiazoles (3) by spontaneous thermal rearrangement of *N*-(5-substituted 1,2,4-oxadiazol-3-yl)-*N'*-phenylthioureas (4).[4] However, in spite of the large number of possible rearrangements of this type (1) ⟶ (2), as far as we are aware, the known rearrangements are restricted to heterocycles containing an N–O bond (1; D = O),

[1] Part XIII, A. J. Boulton, I. J. Fletcher, and A. R. Katritzky, *J. Chem. Soc.* (*C*), 1971, 1193.
[2] Part X, A. J. Boulton, A. R. Katritzky, and A. Majid Hamid, *J. Chem. Soc.* (*C*), 1967, 2005.
[3] M. Ruccia, N. Vivona, and G. Cusmano, *Tetrahedron Letters*, 1972, 4959.
[4] M. Ruccia, N. Vivona, and G. Cusmano, *J.C.S. Chem. Comm.*, 1974, 358.

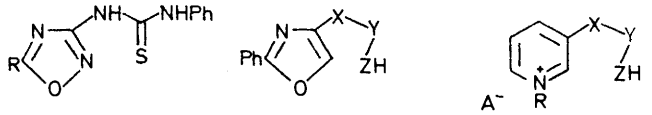
*i.e.* isoxazoles (1; A = B = CR, D = O),[5,6] 1,2,4-oxadiazoles (1; A = N, B = CR, D = O),[3,4,7] and 1,2,5-oxadiazoles (1; A = CR, B = N, D = O).[2,8] This is probably due to the ease of cleavage of the weak N–O bond and the low aromatic energy of the oxygen heterocycles (1; D = O) compared to that of the rearranged products (1; D = S or NR).

We now report some investigations into the occurrence of other monocyclic rearrangements, similar in type to the transformations (1) ⟶ (2). Our attention has been focused on two heterocyclic systems, each associated with a variety of side chains, namely 4-substituted 2-phenyloxazoles (5) and 3-substituted pyridinium salts (6).

*3-Substituted Pyridinium Salts* (6).—Since pyridinium salts are susceptible to nucleophilic attack in the 2-position, we were attracted by the possibility that certain 3-substituted pyridinium salts might undergo base-catalysed rearrangements of the general type



( 1 ) ( 2 ) ( 3 )



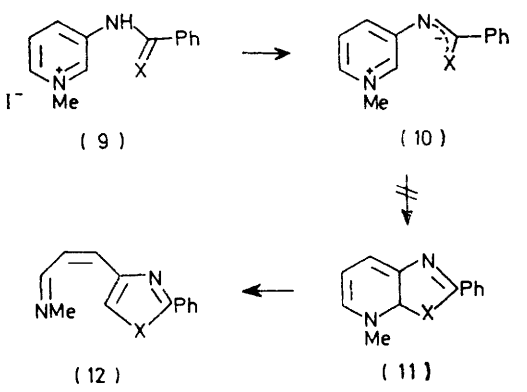
( 4 ) ( 5 ) ( 6 )

(6) ⟶ (7). We now report the preparation of a number of 3-substituted 1-methylpyridinium salts (6; R = Me) and their behaviour towards various bases.

( 7 ) ( 8 )

Our attempts to prepare 3-substituted *N*-(2,4-dinitrophenyl)pyridinium chlorides [6; R = $C_6H_3(NO_2)_2$, A = Cl] using 1-chloro-2,4-dinitrobenzene as quaternising agent were not successful. A similar failure to bring about reactions of this reagent with 3-halogeno-, 3-nitro-, and 3-ethoxycarbonyl-pyridines has been reported.[9]

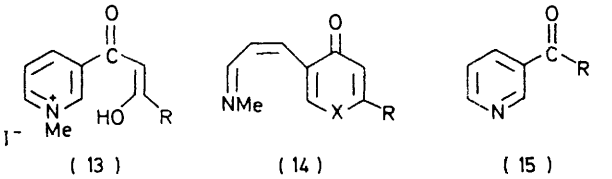
In principle 3-thiobenzamido-1-methylpyridinium iodide (9; X = S) in the presence of base could rearrange to the 1,3-thiazole (12; X = S) (Scheme 1). We have prepared the iodide (9; X = S) by treatment of 3-benzamidopyridine (8; R = COPh) [10] with phosphorus pentasulphide in pyridine followed by treatment of the yellow crystalline 3-thiobenzamidopyridine (8; R = CSPh) with methyl iodide. A reaction between this



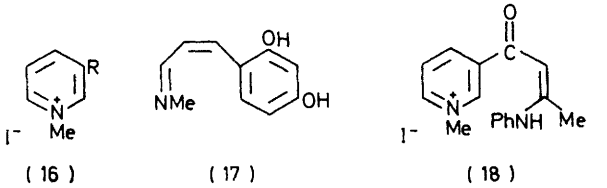
( 9 ) ( 10 ) ( 12 ) ( 11 )

SCHEME 1

iodide (9; X = S) and triethylamine in hot ethanol was not observed but treatment with sodium methoxide in hot methanol gave in low yield a yellow crystalline compound which did not contain iodine. The spectroscopic properties and elemental analysis of this compound suggest that it is the aromatic betaine, *N*-(1-methyl-3-pyridinio)thiobenzamidate (10; X = S). Thus the n.m.r. spectrum shows an *N*-methyl signal at τ 5.97 and signals for nine aromatic protons, and evidence for an NH group was not observed. No evidence for the formation of the 1,3-thiazole (12; X = S) was obtained and the isolation of the aromatic betaine (10; X = S) suggests that the formation of (12; X = S) is not favoured. Similar treatment of 3-benzamido-1-methylpyridinium iodide (9; X = O) with sodium methoxide



( 13 ) ( 14 ) ( 15 )



( 16 ) ( 17 ) ( 18 )

gave 3-amino-1-methylpyridinium iodide (16; R = $NH_2$), together with a very low yield of a compound whose spectroscopic properties are similar to those of the mesomeric betaine (10; X = S) and to which we have assigned the betaine structure (10; X = O).

[5] T. Ajello, *Gazzetta*, 1937, **67**, 779; T. Ajello and S. Cusmano, *ibid.*, 1938, **68**, 792; T. Ajello and S. Cusmano, *ibid.*, 1939, **69**, 391; T. Ajello and S. Cusmano, *ibid.*, 1940, **70**, 770; T. Ajello and B. Tornetta, *ibid.*, 1947, **77**, 332.

[6] H. Kano and E. Yamazaki, *Tetrahedron*, 1964, **20**, 159, 461.

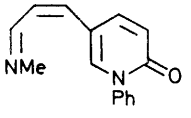
[7] G. Ponzio and L. Avogadro, *Gazzetta*, 1923, **53**, 318; G. Ponzio, *ibid.*, 1931, **61**, 138; P. Gramantieri, *ibid.*, 1935, **65**, 102.

[8] G. Ponzio and F. Biglietti, *Gazzetta*, 1933, **63**, 159; S. Cusmano and S. Giambrone, *ibid.*, 1951, **81**, 499.

[9] A. F. Vompe and N. F. Turitsyna, *Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, 341 (*Chem. Abs.*, 1949, **43**, 4671*a*).

[10] A. Binz and C. Räth, *Annalen*, 1931, **486**, 95.

We have examined several other systems in an attempt to effect intramolecular rearrangement of the general type (6) ⟶ (7). The possibility that rearrangement of the iodides (13) to γ-pyrone derivatives (14; X = O) may occur led us to prepare 3-acetoacetyl-1-methylpyridinium iodide (13; R = Me) from 3-acetoacetylpyridine (15; R = CH:CMe·OH) [11] and 3-benzoylacetyl-1-methylpyridinium iodide (13; R = Ph) from 3-benzoylacetylpyridine (15; R = CH:CPh·OH).[11] Neither of these iodides (13; R = Me nor Ph) reacted with triethylamine. When compound (13; R = Ph) was treated with methanolic sodium methoxide, ready cleavage of the side chain occurred, even at room temperature, giving sodium nicotinate methiodide (16; R = $CO_2^-$ $Na^+$). The alternative possibility that 3-acetoacetyl-1-methylpyridinium iodide (13; R = Me) and sodamide in liquid ammonia might give the resorcinol derivative (17) was also investigated, but only a complex mixture of products resulted. Two different



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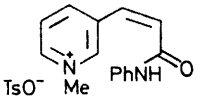

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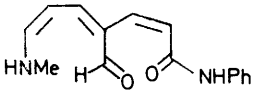

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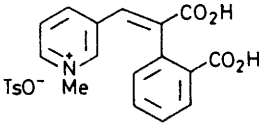

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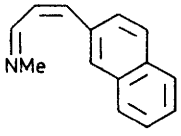
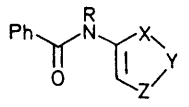


( 23 )

reactions of the iodides (13; R = Me or Ph) with primary amines were observed. Reaction of (13; R = Ph) with methylamine in ethanol resulted in cleavage of the side chain giving 1-methyl-3-methylcarbamoylpyridinium iodide (16; R = CO·NHMe); reaction of (13; R = Me) with aniline in ethanol resulted in substitution of the side chain giving 3-(3-anilinobut-2-enoyl)-1-methylpyridinium iodide (18). Attempts to rearrange compound (18) to the γ-pyridone (14; X = NPh) were unrewarding.

We have also attempted to form the α-pyridone (19), by treatment of 3-(3-anilino-3-oxoprop-1-enyl)-1-methylpyridinium tosylate (20) with base. The salt was recovered unchanged when heated under reflux with pyridine or triethylamine–ethanol. With sodium hydroxide a deep red crystalline compound ($C_{15}H_{16}N_2O_2$) was obtained, which may have the acyclic structure (21). Attempts to characterise this product fully or to prepare derivatives were unsuccessful.

Finally, the possibility that pyrolysis of the tosylate (22) in the presence of soda-lime would result in decarboxylation and rearrangement to the naphthalene derivative (23) has been investigated. No distillate



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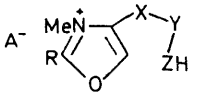

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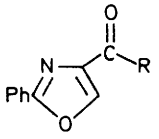

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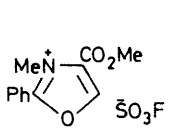


( 27 )

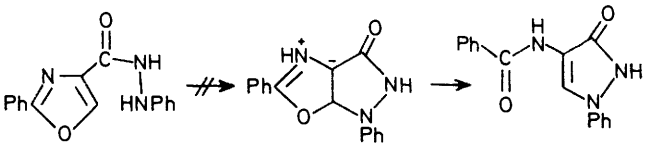
In (26) a; R = OH b; R = OMe c; R = Cl d; R = 2,4-$(NO_2)_2C_6H_3$·NH·NH e; R = PhCO·NH·NH f; R = 2-$C_5NH_4$·NH g; R = *o*-$NH_2$·$C_6H_4$·NH h; R = PhCH:N·NH

was obtained when compound (22) was heated under diminished pressure and the residual dark mass was shown to be a complex mixture of products.

*4-Substituted 2-Phenyloxazoles* (5).—The structural similarity between oxazoles (5) and the general structure (1) has led us to investigate the possible occurrence of intramolecular rearrangements of some oxazole derivatives [(5) ⟶ (24; R = H)]. We have also investigated the preparation of *N*-methyloxazolium salts (25) in the initial belief that the transformation (25) ⟶ (24; R = Me) would be particularly favoured.

Cornforth and Cookson [12] have prepared 2 phenyloxazole-4-carboxylic acid (26a), its methyl ester (26b), and the acid chloride (26c). The methyl ester (26b) did not form a quaternary salt with methyl iodide or methyl tosylate but treatment with methyl fluorosulphonate ($MeSO_3F$) gave 4-methoxycarbonyl-3-methyl-2-phenyloxazolium fluorosulphonate (27). Attempts to prepare derivatives of this salt (27) by treatment with various nucleophilic reagents (*e.g.* phenylhydrazine) resulted in demethylation of the ring. The possible rearrangements of 1,3-oxazolium salts (25) were not investigated further.

In principle, base-catalysed rearrangement of 2-phenyl-4-phenylcarbazoyl oxazole (28) could give 4-benzamido-1-phenylpyrazol-3-one (30) (Scheme 2).



( 28 ) ( 29 ) ( 30 )

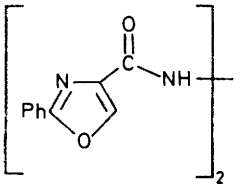
SCHEME 2

Compound (28) was prepared by condensation of the acid chloride (26c) with phenylhydrazine. In a similar

[11] L. F. Kuick and H. Adkins, *J. Amer. Chem. Soc.*, 1935, **57**, 143.

[12] J. W. Cornforth and E. Cookson, *J. Chem. Soc.*, 1952, 1085.

manner, by using 2,4-dinitrophenylhydrazine, benzoylhydrazine, 2-aminopyridine, and *o*-phenylenediamine, the derivatives (26d—g) were prepared. The reaction of (26c) with hydrazine hydrate gave *NN'*-bis-(2-phenyloxazol-4-ylcarbonyl)hydrazine (31), but hydrazine hydrate in the presence of benzaldehyde gave 4-benzylidenecarbazoyl-2-phenyloxazole (26h).



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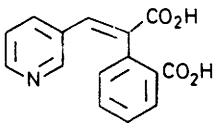
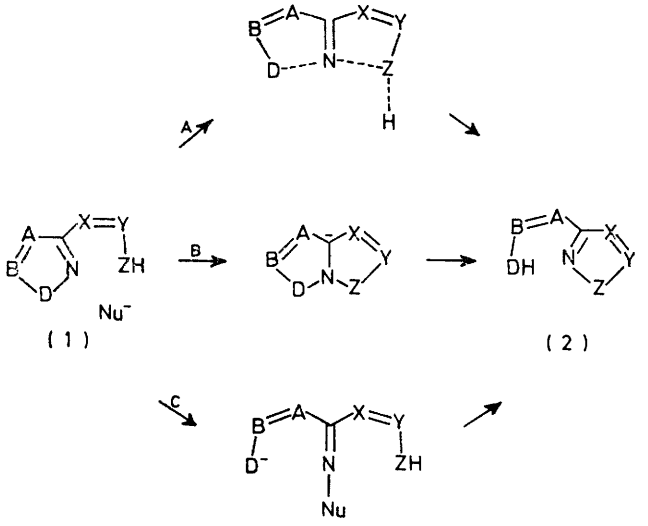


( 32 )

When the hydrazide (28) was treated with (*a*) sodium hydroxide in dimethyl sulphoxide under reflux, (*b*) sodium acetate at 300 °C, or (*c*) hot dilute hydrochloric acid, or fused with sodium hydride, no compounds other than starting material were isolated. Similar treatment of the derivatives (26d—g) was equally unrewarding.

*Conclusion.*—In principle, transformations of the type (1) ⟶ (2) can take place *via* three distinct mechanistic pathways involving: (*a*) a cyclic concerted transition state (Scheme 3, route A), (*b*) a bicyclic intermediate (Scheme 3, route B), or (*c*) an acyclic intermediate (Scheme 3, route C). In the systems we have studied [(6) and (5)] rearrangement by a cyclic concerted



SCHEME 3

mechanism is prohibited owing to the presence of an unfavourable CH group at the reaction site. There is no steric reason why the pyridinium salts (6) or the 1,3-oxazoles (5) should not rearrange by mechanisms similar to route B or C (Scheme 3). The absence of any observed rearrangement products suggests that this type of mechanism is not favourable in the systems we have studied. van der Plas and Vollering [13] have recently described two novel rearrangements of 5-substituted pyrimidines. These authors [13] have expressed the view that these transformations proceed *via* a concerted ring closure–ring fission mechanism. We are of the opinion that the CH group in the 4-position of the pyrimidine ring does not favour a concerted process. These reactions may well take place through a bicyclic intermediate, pyrimidines being particularly susceptible to nucleophilic attack at the 4-position.

There is some evidence to suggest that transformations of the type (1) ⟶ (2) proceed *via* cyclic concerted mechanisms [2] or acyclic intermediates,[5] depending upon the reaction conditions. Our results suggest that rearrangement *via* a bicyclic intermediate (Scheme 3, route B) is not favoured and support the view that the examples of particularly ready transformations (1) ⟶ (2) which occur in the absence of base do take place *via* a cyclic concerted transition state.

## EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for Nujol mulls, u.v. spectra for solutions in ethanol, and n.m.r. spectra (60 MHz) for solutions in deuteriochloroform (tetramethylsilane as internal reference). Only significant i.r. bands are quoted.

Evaporation refers to the removal of volatile materials under diminished pressure. When substances are stated to be identical, this refers to their m.p.s and i.r. spectra.

*3-Thiobenzamidopyridine* (8; R = CSPh).—3-Benzamidopyridine (19.8 g) [10] and phosphorus pentasulphide (22.2 g) in pyridine (50 ml) were heated under reflux (4 h). After cooling, 0.01N-sodium hydroxide (100 ml) was added. The solid which separated was recrystallised from aqueous ethanol (50%) and identified as *3-thiobenzamidopyridine* (8; R = CSPh) (10.7 g, 50%), yellow prisms, m.p. 128—130° (Found: C, 66.9; H. 4.9; N, 12.9. $C_{12}H_{10}N_2S$ requires C, 67.3; H, 4.7; N, 13.1%); $\lambda_{max.}$ 285 (ε 18 000) and 320 nm (13 000); $\nu_{max.}$ 3 300 (NH) and 1 200 cm$^{-1}$ (C=S); τ 0.3 (s, NH) and 1.3—2.9 (9 H, m, aromatic); *m/e* 214 ($M^{\cdot+}$) and 121 ($PhC{\equiv}S^+$).

*α-(2-Carboxyphenyl)-β-(3-pyridyl)acrylic Acid* (32).—Pyridine-3-carbaldehyde (15; R = H) (10.7 g) and homophthalic acid (18.0 g) in pyridine (25 ml) were heated at 110 °C (6 h). After cooling, chloroform (50 ml) and water (50 ml) were added. Evaporation of the chloroform layer left a residue which was recrystallised from ethanol and identified as *compound* (32) (20.2 g, 75%), prisms, m.p. 215—217° (Found: C, 66.8; H, 4.4; N, 5.1. $C_{15}H_{11}NO_4$ requires C, 66.9; H, 4.1; N, 5.2%); $\lambda_{max.}$ 287 nm (ε 15 000); $\nu_{max.}$ 1 740 cm$^{-1}$ (C=O); τ [$(CD_3)_2SO$] 1.5—3.0 (aromatic H); *m/e* 269 ($M^{\cdot+}$).

*Preparation of 1-Methylpyridinium Salts.*—(a) *By using methyl iodide. 3-Benzamido-1-methylpyridinium iodide* (9; X = O). 3-Benzamidopyridine (5.9 g) [10] and methyl iodide (4.3 g) in ethanol (30 ml) were heated at 60 °C (2 h). After cooling the solid product was collected, recrystallised from ethanol, and identified as *compound* (9; X = O) (7.2 g; 70%), prisms, m.p. 210° (Found: C, 45.6; H, 4.0; I, 37.1; N, 8.3. $C_{13}H_{13}IN_2O$ requires C, 45.9; H, 3.9; I, 37.3; N, 8.2%); $\lambda_{max.}$ (MeOH) 275 (ε 12 000) and 300 nm

[13] H. C. van der Plas and M. C. Vollering, *Rec. Trav. chim.*, 1974, **93**, 300.

(9 000); $\nu_{max.}$ 3 300 (NH) and 1 675 (C=O) $cm^{-1}$; τ [$(CD_3)_2$SO] 0.75 (s, NH), 1.3—2.8 (9 H, m, aromatic), and 5.8 (s, NMe); *m/e* 198 [$M^{\cdot+}$ — (MeI)].

The following compounds were similarly prepared from the appropriate pyridine derivatives: *1-methyl-3-thiobenzamidopyridinium iodide* (9; X = S) (2.48 g, 70%), yellow prisms (from ethanol), m.p. 172° (Found: C, 43.6; H, 3.9; I, 35.4; N, 7.7; S, 8.8. $C_{13}H_{13}IN_2S$ requires C, 43.8; H, 3.7; I, 35.7; N, 7.9; S, 9.0%); $\lambda_{max.}$ 278 nm (ε 12 500); $\nu_{max.}$ 3 300 (NH) $cm^{-1}$; τ ($CF_3{\cdot}CO_2H$) 0.2 (s, NH), 1.0—2.7 (9 H, m, aromatic), and 5.5 (s, NMe); *m/e* 214 [$M^{\cdot+}$ — (MeI)]; *3-acetoacetyl-1-methylpyridinium iodide* (13; R = Me) (1.86 g, 60%), yellow prisms (from ethanol), m.p. 170° (Found: C, 39.3; H, 4.3; I, 41.4; N, 4.7. $C_{10}H_{12}INO_2$ requires C, 39.4; H, 4.0; I, 41.6; N, 4.6%); $\lambda_{max.}$ 270 (ε 8 000) and 320 nm (15 500); $\nu_{max.}$ 1 600 $cm^{-1}$ (C=O); τ ($CF_3{\cdot}CO_2H$) 0.6—1.9 (4 H, m, aromatic), 3.30 (s, CH), 5.35 (NMe), and 7.50 (CMe); *m/e* 163 [$M^{\cdot+}$ — (MeI)]; *3-benzoylacetyl-1-methylpyridinium iodide* (13; R = Ph) (2.2 g, 60%), yellow prisms (from ethanol), m.p. 210° (Found: C, 48.9; H, 4.1; I, 34.6; N, 3.9. $C_{15}H_{14}INO_2$ requires C, 49.1; H, 3.8; I, 34.6; N, 3.8%); $\lambda_{max.}$ 275 (ε 8 500) and 350 nm (18 500); $\nu_{max.}$ 1 600 $cm^{-1}$ (C=O); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 0.50—2.65 (9 H, m, aromatic) and 2.85 (s, CH), and 5.43 (s, NMe); *m/e* 225 [$M^{\cdot+}$ — (MeI)].

(b) *By using methyl tosylate.* *3-(3-Anilino-3-oxoprop-1-enyl)-1-methylpyridinium tosylate* (20). 3-(3-Anilino-3-oxoprop-1-enyl) pyridine [14] (2.24 g) and methyl tosylate (1.86 g) in absolute ethanol were heated at 60 °C (2 h). The solid which separated on cooling was recrystallised from ethanol and identified as *compound* (20) (3.28 g, 80%), brown prisms, m.p. 225° (Found: C, 64.2; H, 5.4; N, 6.7; S, 7.6. $C_{22}H_{22}N_2O_4S$ requires C, 64.4; H, 5.4; N, 6.8; S, 7.8%); $\lambda_{max.}$ (MeOH) 280 (ε 17 000) and 310 nm (17 800); $\nu_{max.}$ 3 300 NH) and 1 680 $cm^{-1}$ (C=O); τ ($CF_3{\cdot}CO_2H$) 0.5—3.0, (m, aromatic H and two CH), 5.58 (s, NMe), and 7.67 (s CMe).

Prepared in a similar manner with ethanol–tetrahydrofuran (1 : 1) as solvent, *3-[2-carboxy-2-(2-carboxyphenyl)-ethenyl]-1-methylpyridinium tosylate* (22) (2.5 g, 70%) formed prisms (from tetrahydrofuran), m.p. 210—212° (Found: C, 60.3; H, 4.9; N, 3.0; S, 7.0. $C_{23}H_{21}NO_7S$ requires C, 60.7; H, 4.7; N, 3.1; S, 7.0%); $\lambda_{max.}$ 290 nm (ε 15 000); $\nu_{max.}$ 1 740 $cm^{-1}$ (C=O); τ ($CF_3{\cdot}CO_2H$) 1.5—2.9 (13 H, m, aromatic), 5.66 (s, NMe), and 7.58 (s, CMe); *m/e* 269 [$M^{\cdot+}$ — (MeOTs)].

*Reaction of 1-Methyl-3-thiobenzamidopyridinium Iodide* (9; X = S) *with Sodium Methoxide.*—Compound (9; X = S) (3.56 g) and sodium methoxide (0.54 g) in methanol (25 ml) were heated under reflux (12 h). Water (50 ml) was added and the solution extracted with chloroform. Evaporation of the extract left a residue which was recrystallised from ethanol and identified as *N-(1-methyl-3-pyridinio)-thiobenzamidate* (10; X = S) (0.46 g, 20%), yellow crystals, m.p. 170° (decomp.) (Found: C, 68.0; H, 5.5; N, 12.2; S, 13.8. $C_{13}H_{12}N_2S$ requires C, 68.4; H, 5.3; N, 12.3; S, 14.1%); $\lambda_{max.}$ 272 (ε 9 600) and 325 nm (10 800); $\nu_{max.}$ 1 200 $cm^{-1}$ (C=S); τ 1.2—2.8 (9 H, m, aromatic) and 5.97 (s, NMe); *m/e* 228 (very weak, $M^{\cdot+}$).

*Reaction of 3-Benzamido-1-methylpyridinium Iodide* (9; X = O) *with Sodium Methoxide.*—Compound (9; X = O) (3.4 g) and sodium methoxide (1.08 g) in methanol (25 ml) were heated under reflux (6 h). The solvent was evaporated off and the residue was extracted with ethanol (2 × 20 ml). After concentration of the extract (20 ml), ether was added. The solid which precipitated was recrystallised from ethanol–ether and identified as 3-amino-1-methylpyridinium iodide (16; R = $NH_2$) (1.0 g, 42%), m.p. 112°, identical with an authentic sample prepared from 3-aminopyridine and methyl iodide (Found: C, 30.6; H, 4.0; I, 54.0; N, 11.7. Calc. for $C_6H_9IN_2$: C, 30.5; H, 3.8; I, 53.8; N, 11.9%); $\nu_{max.}$ 3 100—3 400 $cm^{-1}$ (NH); τ [$(CD_3)_2$SO] 1.7—2.7 (m, aromatic H).

In a second experiment, after heating under reflux (10 h) water (10 ml) was added and the solution extracted with chloroform (100 ml). Evaporation of the dry extract gave a residue which solidified in ether. Spectral data suggest that this product is *N-(1-methyl-3-pyridinio)benzamidate* (10; X = O) (0.1 g, 4%), m.p. 170—175° (decomp.), but attempts to purify the sample were unrewarding; $\lambda_{max.}$ 275 (ε 10 000) and 298 nm (9 600); $\nu_{max.}$ 1 680 (C=O) $cm^{-1}$; τ 1.2—1.7 (3 H, m, aromatic), 1.9—2.5 (6 H, m, aromatic), and 5.76 (s, NMe); *m/e* 212 ($M^{\cdot+}$).

*Reactions of 3-Benzoyl- and 3-Acetoacetyl-1-methylpyridinium Iodide* (13; R = Me *and* Ph).—(a) *With triethylamine.* When either compound (13; R = Me or Ph) was heated with triethylamine at reflux temperature (2 h) only starting material was recovered.

(b) *With sodium methoxide.* Compound (13; R = Ph) (3.67 g) and sodium methoxide (1.62 g) in methanol were kept at room temperature (48 h). Evaporation and recrystallisation from methanol gave sodium nicotinate methiodide (16; R = $CO_2^-$ $Na^+$) (0.5 g, 14.6%) as the monohydrate, buff crystals, m.p. 210° (decomp.) (Found: C, 27.3; H, 3.1; I, 41.5; N, 4.3. $C_7H_7INNaO_2,H_2O$ requires C, 27.6; H, 3.0; I, 41.5; N, 4.6%); $\lambda_{max.}$ 209 (ε 11 800) and 221 nm (12 300); $\nu_{max.}$ (KBr) 3 450br (OH) and 1 640 $cm^{-1}$ (C=O); τ ($D_2O$) 0.7—2.2 (4 H, m, pyridinium) and 5.63 (s, NMe).

(c) *With methylamine.* Compound (13; R = Ph) (3.67 g) and methylamine (0.93 g) in methanol (20 ml) were heated under reflux (5 h). Upon cooling, crystals separated which after recrystallisation from ethanol were identified as 1-methyl-3-methylcarbamoylpyridinium iodide (16; R = CO·NHMe) (1.0 g, 36%), brown crystals, m.p. 165—167° (lit.,[15] 169.6°) (Found: C, 34.9; H, 3.8; N, 9.8. Calc. for $C_8H_{11}IN_2O$: C, 34.5; H, 4.0; N, 10.1%); $\lambda_{max.}$ 280 nm (ε 18 200); $\nu_{max.}$ 3 250 (NH) and 1 675 $cm^{-1}$ (C=O); τ ($CF_3{\cdot}CO_2H$) 0.5—2.0 (4 H, m, pyridinium and NH), 5.36 (s, NMe), and 6.77 (d, *J* 4 Hz, NMe); *m/e* 136 [$M^{\cdot+}$ — (MeI)].

(d) *With aniline.* Compound (13; R = Me) (3.05 g) and aniline (0.93 g) in ethanol (25 ml) were heated at 60 °C (2 h). After cooling, the crystals which separated were recrystallised from ethanol and identified as *3-(3-anilinobut-2-enoyl)-1-methylpyridinium iodide* (18) (2.7 g, 70%), yellow crystals, m.p. 210° (Found: C, 50.2; H, 4.8; I, 33.4; N, 6.9. $C_{16}H_{17}IN_2O$ requires C, 50.5; H, 4.5; I, 33.4; N, 7.4%); $\lambda_{max.}$ 275 (ε 9 400) and 350 nm (17 400); $\nu_{max.}$ 1 620 $cm^{-1}$ (C=O); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 0.4—3.5 (9 H, aromatic and one CH), 5.47 (s, NMe), and 7.62 and 7.69 (two singlets, diastereotopic CMe); *m/e* 238 [$M^{\cdot+}$ — (MeI)]. Attempts to rearrange compound (18) (3.8 g) with sodium methoxide (0.54 g) in methanol (25 ml) at reflux temperature (2 h) were unrewarding. Only a complex mixture of products was obtained.

*Attempted Base-catalysed Rearrangements of 1-Methyl-*

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[15] M. R. Lamborg, R. M. Burton, and N. O. Kaplan, *J. Amer. Chem. Soc.*, 1957, **79**, 6173.

*pyridinium Tosylates*.—3-(3-*Anilino*-3-*oxoprop*-1-*enyl*)-1-*methylpyridinium tosylate* (20). Compound (20) (4.1 g) and sodium hydroxide (0.4 g) in ethanol (20 ml) were heated at 60 °C (2 h). After cooling, crystals of sodium tosylate were collected and the filtrate was evaporated. Extraction with chloroform and recrystallisation from aqueous ethanol gave a deep red crystalline *compound* (1.26 g, 50%), m.p. 190° (decomp.) to which we have assigned the acyclic structure (21) [5-anilino-2-(3-methylaminoprop-2-enylidene)-5-oxopent-3-enal] (Found: C, 70.3; H, 6.1; N, 10.8. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.3; N, 10.9%); $\lambda_{max.}$ 285 nm (ε 15 400); $\nu_{max.}$ 3 100—3 400 (NH), and 1 655 and 1 670 $cm^{-1}$ (C=O); τ ($CDCl_3$–$D_2O$) 0.5—3.5 (m, aromatic H and CH), 6.19 (s, NH), 6.72 (d, *J* 4 Hz, NMe), and 8.4 (m, NH); *m/e* 254 ($M^{\cdot+}$ − 2).

3-[2-*Carboxy*-2-(2-*carboxyphenyl*)*ethenyl*]-1-*methylpyridinium tosylate* (22). Compound (22) (4.55 g) and soda-lime (1.92 g) were heated under diminished pressure (0.06 mmHg) with a free flame. No distillate was obtained. Extraction with chloroform and evaporation gave a dark, complex mixture (t.l.c.) which was not further investigated.

4-*Methoxycarbonyl*-3-*methyl*-2-*phenyloxazolium Fluorosulphonate* (27).—Methyl 2-phenyloxazole-4-carboxylate (26b) (2.03 g) in dry ether (30 ml) was stirred with methyl fluorosulphonate (2.3 g) at room temperature (15 min). Crystals separated and were collected and identified as the *oxazolium fluorosulphonate* (27) (1.5 g, 60%), prisms, m.p. 158—160°; $\nu_{max.}$ 1 740 $cm^{-1}$ (C=O); τ ($CF_3{\cdot}CO_2H$) 1.66 (s, CH), 2.2—2.9 (5 H, m, aromatic), 6.00 (s, NMe), and 6.30 (s, OMe); *m/e* 218 [$M^{\cdot+}$ − ($SO_3F$)]. Compound (27) is unstable and was kept under dry ether or used without further purification.

*Reactions of* 2-*Phenyloxazole*-4-*carbonyl Chloride* (26c).—(a) *With hydrazine hydrate*. Compound (26c) [12] (2.1 g) in benzene (50 ml) was added slowly (15 min) to a cold (0 °C) solution of hydrazine hydrate (0.6 g) in benzene (10 ml). The solid which separated was recrystallised from aqueous ethanol and identified as NN′-*bis*-(2-*phenyloxazol*-4-*ylcarbonyl*)*hydrazine* (31) (1.2 g, 27%), m.p. 200° (Found: C, 64.3; H, 3.9; N, 14.5. $C_{20}H_{14}N_4O_4$ requires C, 64.2; H, 3.8; N, 15.0%), $\lambda_{max.}$ 285 nm (ε 18 600); $\nu_{max.}$ 3 000—3 500 (NH) and 1 655 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] — 0.60br (s, NH), 0.91 (s, CH), and 1.5—2.3 (m, $C_6H_5$).

(b) *With hydrazine hydrate and benzaldehyde*. Compound (26c) (2.1 g) in benzaldehyde (1.1 g) was added to hydrazine hydrate (0.5 g) and stirred at 0 °C (1 h). The mixture was then heated at 60 °C (2 h), and after cooling the solid residue was washed with ether (50 ml) to remove benzaldehyde azine. Recrystallisation from benzene gave 4-(3-*benzylidenecarbazoyl*)-2-*phenyloxazole* (26h) (1.2 g, 35%), m.p. 150—152° (Found: C, 70.0; H, 4.2; N, 14.5. $C_{17}H_{13}N_3O_2$ requires C, 70.1; H, 4.5; N, 14.4%); $\lambda_{max.}$ 287 (ε 18 500) and 300sh nm (11 000); $\nu_{max.}$ 3 150 (NH) and 1 650 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] 0.6—2.4 (m, aromatic H, NH, and CH); *m/e* 291 ($M^{\cdot+}$).

(c) *With phenylhydrazine*. Compound (26c) (2.1 g) and phenylhydrazine (2.2 g) were mixed at 0—10 °C. When the reaction was complete the mixture was heated at 80 °C (2 h). After cooling, water (50 ml) was added and the solid which separated was recrystallised from aqueous ethanol and identified as 2-*phenyl*-4-(3-*phenylcarbazoyl*)-*oxazole* (28) (1.95 g, 70%), m.p. 195° (Found: C, 68.7; H, 4.6; N, 14.9. $C_{16}H_{13}N_3O_2$ requires C, 68.8; H, 4.7; N, 15.1%); $\lambda_{max.}$ 285 nm (ε 18 000); $\nu_{max.}$ 3 000—3 300 (NH) and 1 670 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] −0.2 (s, NH), 0.84 (s, CH), and 1.4—3.1 (10 H, m, aromatic and NH); *m/e* 279 ($M^{\cdot+}$).

A similar sequence gave 4-[3-(2,4-*dinitrophenyl*)*carbazoyl*]-2-*phenyloxazole* (26d) (2.22 g, 60%), yellow crystals, m.p. 274—276° (Found: C, 52.0; H, 3.2; N, 18.8. $C_{16}H_{11}N_5O_6$ requires C, 52.0; H, 3.0; N, 19.0%); $\lambda_{max.}$ 275 (ε 13 800), 300sh (6 800), and 430 nm (9 000); $\nu_{max.}$ 3 100—3 400 (NH) and 1 690 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] −1.1br (s, NH), −0.33 (s, NH), 1.00 (2 H, m, aromatic), and 1.4—2.8 (7 H, m, aromatic).

(d) *With benzoylhydrazine*. Compound (26c) (2.1 g) in benzene (50 ml) was slowly added to benzoylhydrazine (2.7 g) in ether (50 ml) at 0 °C. After heating under reflux (1 h), evaporation and addition of water (50 ml) gave a solid which was recrystallised from aqueous ethanol and identified as 4-(3-*benzoylcarbazoyl*)-2-*phenyloxazole* (26e) (1.81 g, 60%), prisms, m.p. 172° (Found: C, 65.9; H, 4.5; N, 13.2. $C_{17}H_{13}N_3O_3$ requires C, 66.4; H, 4.3; N, 13.7%); $\lambda_{max.}$ 282 nm (ε 14 400); $\nu_{max.}$ 3 200 (NH), and 1 680 and 1 640 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] −0.8 to −0.4 (m, two NH), 1.0 (s, CH), and 1.5—2.5 (10 H, m, aromatic); *m/e* 307 ($M^{\cdot+}$).

(e) *With* 2-*aminopyridine*. 2-Aminopyridine (0.94 g) was added slowly to compound (26c) (2.1 g) in pyridine (20 ml), chilled to −10 °C, and the pyridine was removed by distillation under diminished pressure. Water (50 ml) was added to the residue and recrystallisation of the solid product gave 2-*phenyl*-N-(2-*pyridyl*)*oxazole*-4-*carboxamide* (26f) (1.86 g, 70%), m.p. 119° (Found: C, 67.8; H, 4.6; N, 15.6. $C_{15}H_{11}N_3O_2$ requires C, 67.9; H, 4.2; N, 15.8%); $\lambda_{max.}$ 285 nm (ε 13 200); $\nu_{max.}$ 3 300—3 500 (NH), and 1 675 and 1 690 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] 0.4 (s, NH), 1.25 (s, CH), and 1.7—3.2 (9 H, m, aromatic); *m/e* 265 ($M^{\cdot+}$). Treatment of (26f) with dilute hydrochloric acid and recrystallisation from ethanol gave its *hydrochloride*, m.p. 230° (Found: C, 59.7; H, 4.1; N, 13.9. $C_{15}H_{12}ClN_3O_2$ requires C, 59.7; H, 4.0; N, 13.9%); $\lambda_{max.}$ 283 nm (ε 13 000) $\nu_{max.}$ 3 000—3 100 (NH) and 1 685 $cm^{-1}$ (C=O); τ ($CF_3{\cdot}CO_2H$) 0.91 (s, CH) and 1.3—2.6 (m, aromatic H).

(f) *With* o-*phenylenediamine*. Compound (26c) (2.1 g) and *o*-phenylenediamine (1.5 g) were melted together (30 min) and then aqueous ethanol was added. The solid which separated was recrystallised several times from aqueous ethanol and identified as N-(2-*aminophenyl*)-2-*phenyloxazole*-4-*carboxamide* (26g) (1.82 g, 65%), m.p. 153—155°, prisms (Found: C, 68.4; N, 14.7; H, 4.6. $C_{16}H_{13}N_3O_2$ requires C, 68.8; N, 15.1; H, 4.7%), $\lambda_{max.}$ 280 nm (ε 14 600); $\nu_{max.}$ 3 300—3 400 (NH) and 1 670 $cm^{-1}$ (C=O); τ [$(CD_3)_2SO$] 0.2 (s, NH), 0.5 (s, CH), 1.0—3.0 (9 H, m, aromatic), and 4.4br (s, $NH_2$); *m/e* 279 ($M^{\cdot+}$).

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