Heterocyclic Compounds with Bridgehead Nitrogen Atoms. Part 9.[1,2] Synthesis in the Pyrrolo[2,1,5-*de*]quinolizine ([2.3.3]Cyclazine) Series starting from Indolizines

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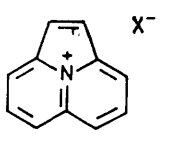
Pyrrolo[2,1,5-*de*]quinolizines may be obtained from various 3-substituted derivatives of 5-methyl-2-phenyl- and 2,5-dimethyl-indolizine by base-catalysed condensation of the 5-methyl group with a carbonyl group in the β-position of the 3-substituent. The 1,3-diethoxalyl derivatives of these indolizines were converted, by treatment with sodium ethoxide or methoxide, into mixtures of pyrrolo[2,1,5-*cd*]indolizines ([2.2.3]cyclazines) and 4-hydroxy-3*H*-pyrrolo[2,1,5-*de*]quinolizin-3-ones. Under similar conditions, 5-methyl-2-phenyl-3-pyruvoyl-indolizine gave a low yield of 4-methyl-2-phenyl-3*H*-pyrrolo[2,1,5-*de*]quinolizin-3-one. When the 3-substituent was a 2-oxopropano- or 2-oxo-2-phenylethano-hydroximoyl group, cyclisation was effected with potassium t-butoxide in dimethyl sulphoxide, and the resulting 3-hydroxyimino-3*H*-pyrrolo[2,1,5-*de*]quinolizines were cleanly converted into the corresponding pyrroloquinolizinones by treatment with silver(I) oxide. 4-Methyl-2-phenyl-3*H*-pyrrolo[2,1,5-*de*]quinolizin-3-one was converted into the corresponding thione and thence, by methylation, into a methylthiopyrrolo[2,1,5-*de*]quinolizinylium salt.

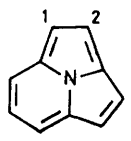
THE first recorded mention of the pyrido[2,1,5-*de*]-quinolizinylium ion occurs in a footnote to the original publication on cyclazines by Boekelheide and his co-workers [3] who gave the name ' cycl[3.3.2]azinium bromide '† to the salt (1; X = Br). It has been suggested [5] that this ion might be responsible for the base peak, $[M - 1]^+$, in the electron-impact mass spectrum of 1-methyl[2.2.3]cyclazine (2a) but no chemical synthesis has ever been reported. Indeed, the only known representative of the pyrrolo[2,1,5-*de*]quinolizine ring system, prior to our work,[2] was the so-called ' second stable adduct ' (3) [6] derived from 2-styrylpyridine and dimethyl butynedioate.

In principle, derivatives of [2.3.3]cyclazine might be synthesised either from indolizines or from quinolizines. We have investigated both of these routes and report here on the synthesis of 3*H*-[2.3.3]cyclazin-3-ones and related compounds from indolizines. Our work on the quinolizine route, which has led to the parent [2.3.3]-cyclazinylium salt (1; X = ClO_4), will be the subject of another publication in this series.

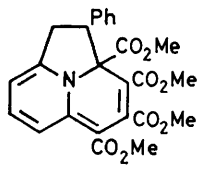
All the syntheses to be described here involve the construction of cyclazine precursors of the general type (4) and depend on the known [3] acidity of a 5-methyl group in indolizines for a base-induced condensation with the β-carbonyl group of the 3-substituent. Because of its ready availability from the acyl chloride, an ethoxalyl group (X = O; Y = OEt) was initially chosen as the 3-substituent, in the belief that the reactivity of the ketonic (α) carbonyl group would be sufficiently suppressed by



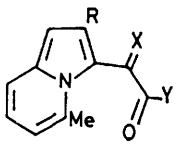
(1)



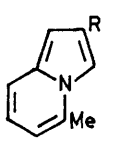
(2)
a; 1-Me
b; 2-Ph



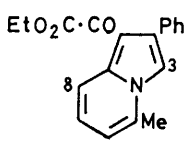
(3)
a; R = Ph
b; R = Me



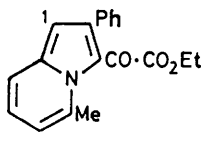
(4)



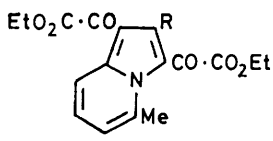
(5)
a; R = Ph
b; R = Me



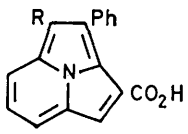
(6)



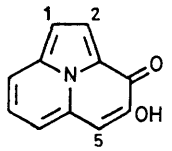
(7)



(8) a; R = Ph
b; R = Me



(9)
a; R = H
b; R = CO_2H



(10)
a; 1-CO·CO_2Et, 2-Ph
b; 1-CO·CO_2Me, 2-Me
c; 1-CO·CO_2H, 2-Ph
d; 1-CO_2H, 2-Ph
e; 2-Ph

† We have here used a modification of Boekelheide's cyclazine nomenclature, first outlined in a footnote to Part 7,[4] in which the bracketed numerals, in increasing order, are placed before the word ' cyclazine ' rather than in the middle of it. Since the periphery of [2.3.3]cyclazine contains an odd number of carbon atoms, the parent neutral molecule must always have one saturated carbon atom and the names of its tautomeric forms should include indicated hydrogen. The name ' cyclazinium ' for the fully unsaturated cation is therefore incorrect (since it implies protonation of the parent cyclazine) and should be replaced by ' cyclazinylium '.

conjugation with the electron-rich indolizine nucleus, to allow intramolecular condensation to occur at the ester (β) carbonyl group.

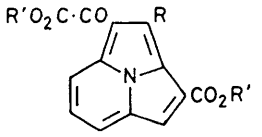
The reaction of 5-methyl-2-phenylindolizine (5a) with ethoxalyl chloride in dichloromethane gave two mono-ethoxalyl derivatives, separable by chromatography. The minor product (10%) was recognised as the 1-ethoxalyl derivative (6) by the presence, in its ^{1}H n.m.r. spectrum, of a high frequency doublet (δ 8.40) due to H-8 which is deshielded by the adjacent carbonyl group. The major product (60%) was then clearly the 3-ethoxalyl derivative (7) since its n.m.r. spectrum lacked the high frequency doublet and showed a singlet, due to the remaining pyrrole ring proton (H-1), at lower frequency (δ 6.57) than the corresponding singlet (δ 7.15; H-3) in the spectrum of the 1-ethoxalyl isomer. Reaction of the indolizine (5a) with ethoxalyl chloride in the absence of a solvent and for a longer time gave the 1,3-diethoxalyl derivative (8a).

Treatment of 3-ethoxalyl-5-methyl-2-phenylindolizine (7) with sodium ethoxide in refluxing ethanol yielded two major products, 5-methyl-2-phenylindolizine (52%) and ethyl 3-phenyl[2.2.3]cyclazine-2-carboxylate (17%). The cyclazine, a yellow oil, was identified by its mass spectrum and by hydrolysis to the known [7] carboxylic acid (9a).

This reaction did not support our original premise concerning relative carbonyl reactivities in the ethoxalyl group but the outcome of a similar reaction with the 1,3-diethoxalyl compound (8a) was more satisfactory. In this case, the ketonic and ester carbonyl groups appeared to be of comparable reactivity and two products were formed: 1-ethoxalyl-4-hydroxy-2-phenyl-3*H*-[2.3.3]-cyclazin-3-one (10a) was deposited from the reaction mixture as a sodium salt, and ethyl 4-ethoxalyl-3-phenyl[2.2.3]cyclazine-2-carboxylate (11a) was obtained from the ethanolic solution. The latter compound was identified by hydrolysis to the oxodicarboxylic acid (11c) and oxidation of this, with alkaline hydrogen peroxide, to the dicarboxylic acid (9b) which was decarboxylated to give the known [3] 2-phenyl[2.2.3]cyclazine (2b).

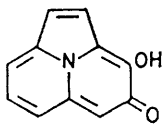
The cyclazinone (10a) showed a hydroxy-band at 3 220 cm^{-1} in its i.r. spectrum and was converted, by treatment with diazomethane, into a methyl ether. Hydrolysis of the ester function of (10a) and oxidation of the resulting oxo-acid (10c) with alkaline hydrogen peroxide gave an acid (10d) which was readily decarboxylated to yield the parent hydroxycyclazinone (10e). This compound, a bright yellow crystalline solid, showed i.r. absorptions (in $CHCl_3$) characteristic of an internally hydrogen-bonded hydroxy-group (3 280 cm^{-1}, sharp) and of a highly polarised carbonyl group (1 590 cm^{-1}). Its ^{1}H n.m.r. spectrum showed a complex multiplet in the region δ 7.2—8.2 (intensity 10) and a singlet near δ 8.6 (intensity 1) which was assigned to the OH proton since it disappeared when the solution was shaken with deuterium oxide.

Although the compounds (10a) and (10e) are formulated as 4-hydroxy-3*H*-[2.3.3]cyclazin-3-ones, there is no direct evidence to exclude the tautomeric structures based on 3-hydroxy-4*H*-[2.3.3]cyclazin-4-one (12). In order to obtain a hydroxycyclazinone that might yield more definitive n.m.r. data, 2,5-dimethylindolizine (5b) was used as starting material in place of the 5-methyl-2-phenyl compound (5a). Treatment with ethoxalyl chloride gave the 1,3-diethoxalyl derivative (8b) which,



(11)

a; R = Ph, R' = Et
b; R = R' = Me
c; R = Ph, R' = H



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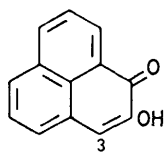
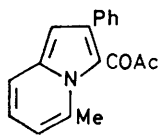
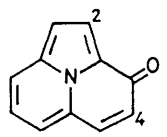


(13)

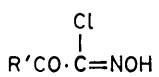


(14)



(15)

a; 2-Ph, 4-Me
b; 2-Me, 4-Ph
c; 2,4-Ph$_2$



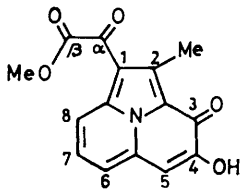
(16)

a; R' = Me
b; R' = Ph

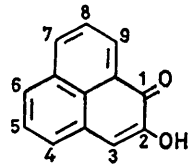
on treatment with sodium methoxide in dry methanol, was converted into the [2.2.3]cyclazine (11b) and a 2-methylhydroxy[2.3.3]cyclazinone. The ^{1}H n.m.r. absorptions of the latter, though well-resolved and easily assigned, were not diagnostic for either the 4-hydroxy-3-one or 3-hydroxy-4-one structures. The ^{13}C spectrum, on the other hand, yielded evidence in favour of the 4-hydroxycyclazin-3-one structure (10b), particularly when compared with the spectrum of 2-hydroxyphenalenone (13) [8] which contains a similar but tautomerically fixed structural unit in the carbonyl-containing ring. In both the cyclazinone and the phenalenone, long-range coupling to the methine proton in the carbonyl-containing ring (H-5 in the cyclazinone; H-3 in the phenalenone) was greater for the carbonyl carbon ($^3J_{CH}$ *ca.* 7 Hz) than for the hydroxy-bearing carbon ($^2J_{CH}$ *ca.* 5 Hz). This is to be expected for a 4-hydroxycyclazin-3-one and it is unlikely that the corresponding coupling constants for a 3-hydroxycyclazin-4-one would be similar in magnitude.

To improve this type of approach to the synthesis of [2.3.3]cyclazinones, it was clearly necessary to suppress the competitive formation of [2.2.3]cyclazines: (*a*) by

^{13}C N.m.r. data (90.6 MHz) of compounds (10b) and (13) (δ/p.p.m. from $SiMe_4$; J/Hz)



(10b)



(13)

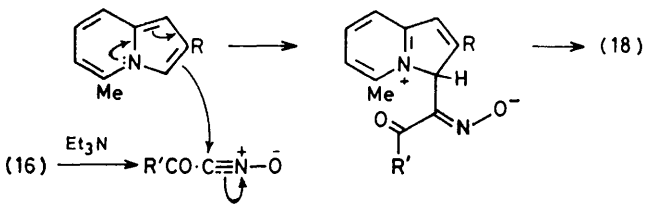
Carbon number	δ	Multiplicity[a]	$^2J_{CH}$[b]	$^3J_{CH}$[b]	Carbon number	δ	Multiplicity[a]	$^2J_{CH}$[b]	$^3J_{CH}$[b]
3	166.6	d		7 (H-5)	1	180.3	dd[c]		7.5 (H-3)
									4.5 (H-9)
4	156.2	d	5 (H-5)		2	149.5	d[c]	5 (H-3)	
5	103.2	Dd		4 (H-6)	3	113.6	Dd[c]		6.5 (H-4)
5a	130.6	dt	4 (H-5,6)	8 (H-7)	3a[d]	127.4	d		7 (H-5)
6	117.3	Ddd		8 (H-8)	4[e]	130.3	Ddd		8.5 (H-6)
				3 (H-5)					4.5 (H-3)
7	128.5	D			5[f]	126.7	D		
8	117.3	Dd		8 (H-6)	6[g]	129.6	Ddd		7.5 (H-4)
									5.5 (H-7)
8a	136.2	dd	4 (H-8)	8 (H-7)	6a	131.9	obscured		
1	115.3	q		4 (2-Me)	7[e]	136.4	Ddd		7.5 (H-9)
									4.5 (H-6)
2	123.2	q	4 (2-Me)		8	127.1	D		
2a	141.0	q		6.5 (2-Me)	9	130.9	Dd		8 (H-7)
α	182.4	S			9a[d]	128.3	d		7 (H-8)
β	165.1	q		4 (OMe)	9b	124.3	sextet		6.5 (H-3,4,6,7,9)

[a] In fully proton-coupled spectra. Upper case letters refer to one-bond coupling, lower case letters to longer-range coupling. [b] Protons believed to be responsible for splitting shown in parentheses. [c] Coupling to OH proton also present; multiplicities are those observed after exchange with D_2O. [d,e,f] Assignments are tentative within each of these sets of carbons.

making the β-carbonyl group of the precursor (4) more reactive and/or (*b*) by masking the α-carbonyl group. Both of these possibilities were investigated: (a) by using a precursor containing a ketonic β-carbonyl group (4; X = O, Y = Me) and (b) by using precursors of the type (4; X = NOH, Y = Me or Ph).

The precursor (14) was obtained in low yield (27%) by reaction of 5-methyl-2-phenylindolizine (5a) with pyruvic acid in the presence of phosphoryl chloride and triethylamine. It was identified as the 3-pyruvoyl compound, rather than the 1-isomer, by the presence of the H-1 resonance at δ 6.57 in its n.m.r. spectrum and by the absence of a high frequency signal due to a deshielded 8-proton. Acylation of the indolizine with pre-formed pyruvoyl chloride did not improve the yield of this product. Treatment of the 3-pyruvoylindolizine (14) with sodium methoxide in refluxing methanol gave 4-methyl-2-phenyl-3*H*-[2.3.3]cyclazin-3-one (15a) as an orange-yellow solid (15% yield) that showed a carbonyl absorption at 1 603 cm^{-1}, only a little higher in frequency than that of the internally hydrogen-bonded 4-hydroxy-compound (10e). In view of the low yields of the cyclazinone (15a) and of its precursor (14), it did not seem profitable to pursue this approach further.

Precursors of the type (4; X = NOH) were obtained by reaction of indolizines with α-oxohydroximoyl chlorides (16) in the presence of triethylamine. The reactions were carried out in chloroform at room temperature and, since no reaction was observed in the absence of triethylamine, it may be assumed that the hydroximoyl chloride is first converted into a nitrile oxide which is the effective reagent (Scheme). The reaction of 2,5-dimethylindolizine (5b) with 2-oxo-2-phenylethanohydroximoyl chloride (16b) gave a mixture of two isomers, one orange (major) and one yellow (minor), which were separated by chromatography. These were identified as

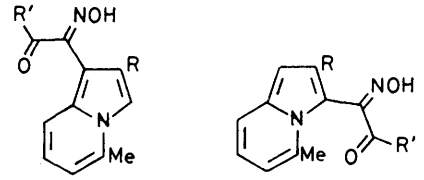


SCHEME

the 3- and 1-substituted indolizines (18b) and (17b), respectively, on the basis of their ^1H n.m.r. spectra which showed one clearly distinguishing feature, a prominent singlet, at lower frequency for the orange isomer (δ 6.38, H-1) than for the yellow isomer (δ 7.05, H-3). Other combinations of reactants, (5a) or (5b) with (16a) or (16b), gave similar products but no other chromatographic separation of the 1- and 3-substituted isomers was achieved. Pure specimens of the 3-hydroximoylindolizines (18a) and (18c) were obtained by repeated recrystallisation of the crude products, but compound (18d) could not be purified since its mixture with the 1-isomer (17d) was an oil.

Cyclisation of the 3-(2-oxohydroximoyl)indolizines,

to yield the 3-hydroxyimino-3*H*-[2.3.3]cyclazines (19), was brought about by treatment of the mixed isomers, (17) and (18), with potassium t-butoxide (1.2 mol equiv.). The first such reaction, which was carried out in refluxing t-butyl alcohol for 1.5 h, gave only a low yield (13%) of the diphenylcyclazine (19c) together with starting material, the two isomers of which, (17c) and (18c), were

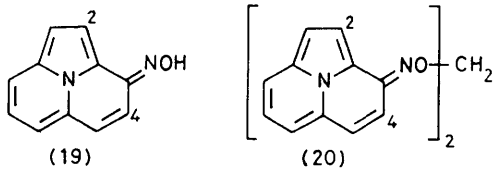


(17) (18)

a; R = Ph, R' = Me
b; R = Me, R' = Ph
c; R = R' = Ph
d; R = R' = Me

incidentally separated during work-up. A much better yield (74%) of the same cyclazine was obtained by conducting the reaction in refluxing dimethyl sulphoxide which is known to enhance the basic strength of the t-butoxide ion. Under these conditions, the reaction was complete in 5 min and neither isomer of the starting material was recovered. Moderate yields (*ca.* 50%) of the methylphenylcyclazines, (19a) and (19b), and a low yield (20%) of the dimethyl compound (19d) were obtained by the same procedure.

Some cyclisation experiments were carried out with a larger excess (2 mol equiv.) of potassium t-butoxide and under slightly different conditions. However, these



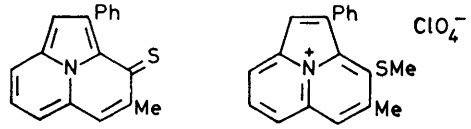
(19) (20)

a; 2-Ph, 4-Me
b; 2-Me, 4-Ph
c; 2,4-Ph_2
d; 2,4-Me_2

$(Ph_2C{=}NO\frac{}{}_2CH_2$
(21)

modifications were disadvantageous since they resulted in partial conversion of the hydroxyiminocyclazines into their *O,O'*-methylenebis-derivatives (20). The identification of these compounds rests on the following evidence: (*a*) their colours (bright orange) and u.v.–visible spectra were closely similar to those of the hydroxyiminocyclazines; (*b*) the ^1H n.m.r. spectrum of the 2-methyl-4-phenyl compound showed a sharp singlet at δ 5.6 (OCH_2O) but was otherwise very similar to that of the corresponding hydroxyimino-compound (19b); and (*c*) the proton-decoupled ^{13}C n.m.r. spectrum of the 2-methyl-4-phenyl compound (20b) could be matched, peak-for-peak, with that of the corresponding hydroxyiminocyclazine (19b) but showed one additional peak (triplet with off-resonance proton decoupling) at essentially the same frequency (δ 99) as that of the CH_2-carbon in the *O,O'*-methylenebis-derivative (21) [9] of benzophenone oxime. The formation of these methylenebis-derivatives is thought to involve formaldehyde (or a formaldehyde equivalent such as $CH_2{=}\overset{+}{S}Me$) formed by base-induced decomposition of dimethyl sulphoxide. Traynelis and Hergenrother [10] reported a related conversion of amides into their *N,N'*-methylenebis-derivatives by heating with dimethyl sulphoxide in the absence of a base.

Good yields of the orange-yellow 3*H*-[2.3.3]cyclazin-3-ones (15a—c) were obtained from the corresponding hydroxyiminocyclazines by treatment with silver(I) oxide in refluxing dichloromethane. These compounds are thus readily obtainable by a three-stage synthesis from indolizines However, in view of the low yield of the hydroxyimino-compound (19d), it seems likely that the method would not be satisfactory for cyclazinones lacking aryl substituents. The 4-methyl-2-phenylcyclazinone (15a) was converted, by treatment with



(22) (23)

phosphorus pentasulphide, into the corresponding thione (22) and thence, by methylation, into the [2.3.3]cyclazinylium salt (23).

EXPERIMENTAL

Unless otherwise stated, n.m.r. data were obtained at 100 (for ^1H) and 25.2 MHz (for ^{13}C) and refer to solutions in deuteriochloroform with $SiMe_4$ as internal standard; i.r. data refer to Nujol mulls; and u.v. data refer to ethanolic solutions. Alumina for chromatography (Laporte Type H) was deactivated by treatment with 10% aqueous acetic acid (0.05—0.1 cm^3 per g alumina). For drying, methanol and ethanol were refluxed with magnesium (5 g per dm^3 alcohol) and distilled from the resulting magnesium alkoxides; dimethyl sulphoxide was kept over Linde molecular sieve (Type 4A). Extracts were dried over magnesium sulphate and evaporated under reduced pressure.

1- *and* 3-*Ethoxalyl-5-methyl-2-phenylindolizines*.—Ethoxalyl chloride (1.7 g), in dichloromethane (5 cm^3), was added dropwise, during 15 min, to a stirred solution of 5-methyl-2-phenylindolizine (2.0 g) in dichloromethane (20 cm^3). After a further 4.5 h, the solution was diluted with ether (70 cm^3) and filtered to remove 5-methyl-2-phenylindolizinium chloride (0.86 g). The filtrate was washed (twice with water and once with aqueous sodium carbonate), dried, and evaporated. Chromatography of the residue on alumina in ether–hexane (1 : 1) gave (i) the 3-*ethoxalyl compound* (1.11 g) as yellow plates, m.p. 105—107 °C [from light petroleum (b.p. 60—80 °C)–ethanol] (Found: C, 74.4; H, 5.5; N, 4.5. $C_{19}H_{17}NO_3$ requires C, 74.3; H, 5.5; N, 4.6%) $\lambda_{max.}$ 238,

261 sh, and 385 nm (log ε 4.45, 4.16, and 4.08); δ 2.54 (3 H, s, Me), 6.57 (1 H, s, H-1), 6.78 (1 H, d, H-6), 7.20 (1 H, t, H-7), 7.3—7.5 (6 H, H-8 and Ph), and OEt signals; and (ii) the 1-*ethoxalyl compound* (0.19 g) as yellow needles, m.p. 142—143 °C [from light petroleum (b.p. 60—80 °C)–ethanol] (Found: C, 74.55; H, 5.7; N, 4.4%), $\lambda_{max.}$ 238, 360sh, and 374 nm (log ε 4.45, 4.24, and 4.27); δ 2.59 (3 H, s, Me), 6.75 (1 H, d, H-6), 7.15 (1 H, s, H-3), 7.25 (1 H, t, H-7), 7.3—7.5 (5 H, Ph), 8.40 (1 H, d, H-8), and OEt signals.

1,3-*Diethoxalyl*-5-*methyl*-2-*phenylindolizine*.—5-Methyl-2-phenylindolizine (10 g) was dissolved, by gentle heating, in ethoxalyl chloride (9.2 g) and the solution was kept overnight at room temperature. Repeated extraction of the mixture with boiling light petroleum (b.p. 60—80 °C) gave a viscous green residue and a golden yellow solution which, on cooling, deposited the *diethoxalyl compound* (4.8 g) as yellow needles, m.p. 144—145 °C (from ethanol) (Found: C, 67.1; H, 4.9; N, 3.9. $C_{23}H_{21}NO_6$ requires C, 67.6; H, 5.2; N, 3.4%), $\lambda_{max.}$ 230, 260, 285sh, 300sh, and 357 nm (log ε 4.31, 4.13, 3.97, 3.90, and 4.36); δ(60 MHz) 2.58 (3 H, s, Me), 7.14 (1 H, d, H-6), 7.42 (5 H, s, Ph), 7.67 (1 H, t, H-7), 8.65 (1 H, d, H-8), and OEt signals. The starting indolizine (5 g) was recovered from the green viscous residue (by partitioning between ether and aqueous alkali) and from the light petroleum mother liquor.

1,3-*Diethoxalyl*-2,5-*dimethylindolizine*.—Ethoxalyl chloride (41 g), in dichloromethane (50 cm³), was added dropwise, with ice-cooling, to a rapidly stirred solution of 2,5-dimethylindolizine (14.5 g) in dichloromethane (100 cm³). The solution was kept at 0 °C for 24 h, washed with water and aqueous sodium hydrogen carbonate, and dried. Evaporation of the solvent and trituration of the residual yellow oil with light petroleum gave the *diethoxalyl compound* (11.5 g) as yellow prisms, m.p. 73—74 °C (from ethanol) (Found: C, 62.4; H, 5.2; N, 4.0. $C_{18}H_{19}NO_6$ requires C, 62.6; H, 5.55; N, 4.1%), δ(60 MHz) 2.57 (6 H, s, 2 × Me), 7.05 (1 H, d, H-6), 7.59 (1 H, t, H-7), 8.45 (1 H, d, H-8), and OEt signals.

Cyclisation of 3-*Ethoxalyl*-5-*methyl*-2-*phenylindolizine*.—The indolizine (0.9 g) was heated under reflux with sodium ethoxide (from 0.07 g Na) in dry ethanol (12 cm³) for 1.5 h. Evaporation of the solution and ether extraction of an acidified aqueous solution of the residue gave an oil which was chromatographed on silica. Elution with ether–light petroleum (b.p. 40—60 °C) gave (i) 5-methyl-2-phenylindolizine (0.33 g), i.r. spectrum identical with that of an authentic sample, (ii) ethyl 3-phenylpyrrolo[2,1,5-*cd*]indolizine-2-carboxylate (0.15 g) as a yellow oil, M^+ 289, (iii) starting material (trace), and (iv) an unidentified yellow solid (trace). Fraction (ii) was heated under reflux with aqueous methanolic potassium hydroxide for 2 h, the solution was evaporated, and the residue was treated with aqueous hydrochloric acid to yield 3-phenylpyrrolo[2,1,5-*cd*]indolizine-2-carboxylic acid (0.11 g) as yellow needles, m.p. 185—186 °C (from aqueous ethanol) (lit.,[7] m.p. 184—185 °C).

Cyclisation of 1,3-*Diethoxalyl*-1-*methyl*-2-*phenylindolizine*.—The indolizine (4.2 g) was heated under reflux with sodium ethoxide (1 mol equiv.) in dry ethanol (30 cm³) for 10 min, during which time a red solid [sodium salt of (10a)] was precipitated from the solution. The solid was filtered off and dissolved in water and the aqueous solution was acidified. The resulting yellow precipitate was filtered off and recrystallised from ethanol to give 1-*ethoxalyl*-4-*hydroxy*-2-*phenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizin*-3-*one* (0.73 g, 21.5%) as yellow needles, m.p. 189—190 °C (Found: C, 69.5; H, 4.3; N, 4.0. $C_{21}H_{15}NO_5$ requires C, 69.8; H, 4.2; N, 3.9%), $\nu_{max.}$ 3 220 cm⁻¹ (OH); $\lambda_{max.}$ 249, 269sh, 328, 406sh, and 419 nm (log ε 4.64, 4.16, 4.32, 4.18, and 4.24). Treatment of the hydroxy-compound (0.3 g) with an excess of diazomethane in dichloromethane (15 cm³) gave an almost quantitative yield of the corresponding *methoxy-compound*, m.p. 238 °C (from aqueous acetic acid) (Found: C, 70.6; H, 4.6; N, 3.9. $C_{22}H_{17}NO_5$ requires C, 70.5; H, 4.5; N, 3.75%), $\lambda_{max.}$ 240, 295sh, 302, 356, 380sh, 400, and 420 nm (log ε 4.40, 4.29, 4.35, 3.84, 3.89, 4.17, and 4.34).

The filtrate from the sodium salt was evaporated and the residue was washed with water and recrystallised from ethanol to give *ethyl* 4-*ethoxalyl*-3-*phenylpyrrolo*[2,1,5-cd]-*indolizine*-2-*carboxylate* (1.0 g, 25%) as yellow needles, m.p. 139—141 °C (Found: C, 70.6; H, 5.1; N, 4.0. $C_{23}H_{19}NO_5$ requires C, 70.9; H, 4.9; N, 3.6%), $\lambda_{max.}$ 220, 297, 328, 417sh, and 435 nm (log ε 4.38, 4.03, 4.04, 3.92, and 4.17).

2-*Phenyl*-4-*hydroxy*-3H-*pyrrolo*[2,1,5-de]*quinolizin*-3-*one*.—The ethoxalyl compound (10a) (0.52 g) was heated under reflux with an excess of potassium hydroxide in methanol (25 cm³)–water (5 cm³) for 1 h. The solution was evaporated and the residual red potassium salt was redissolved in water and treated with hydrochloric acid to give the corresponding α-oxo-acid (0.45 g), m.p. 268 °C. A solution of the oxo-acid in 2M aqueous sodium hydroxide (6 cm³) was cooled to 0 °C, treated with 10% aqueous hydrogen peroxide (1.5 cm³), and kept at 0 °C for 40 h. Manganese(IV) oxide was added to destroy excess of peroxide and, after a further 1 h at 0 °C, the solution was filtered and acidified. The resulting acid (10d) (0.41 g) was filtered off, dried, and heated at 250 °C and 0.03 mmHg in a sublimation apparatus. The sublimate was recrystallised from acetic acid to yield the *pyrroloquinolizinone* (0.2 g) as yellow prisms, m.p. 149—150 °C (Found: C, 78.4; H, 4.2; N, 5.3. $C_{17}H_{11}NO_2$ requires C, 78.2; H, 4.2; N, 5.4%), $\nu_{max.}$ ($CHCl_3$) 1 590 (C=O) and 3 280 cm⁻¹ (OH); $\lambda_{max.}$ 228, 263, 294, 310sh, 340, 395sh, and 411 nm (log ε 4.41, 4.65, 4.34, 4.09, 4.05, 4.01, and 4.24); δ(60 MHz) 7.2—8.2 (10 H, complex m) and 8.6 (1 H, s, OH; absent after shaking solution with D_2O).

2-*Phenylpyrrolo*[2,1,5-cd]*indolizine*.—Alkaline hydrolysis of the diester (11a) and oxidation of the resulting oxodicarboxylic acid with hydrogen peroxide, as in the preceding experiment, gave 2-phenylpyrrolo[2,1,5-*cd*]indolizine-1,3-dicarboxylic acid (9b) (60%). This diacid (0.2 g) was heated with copper chromite catalyst [11] (0.35 g) in quinoline (50 cm³) for 5 h at 230—240 °C. The cooled solution was filtered, added to an excess of 2M aqueous hydrochloric acid, and extracted with ether. The extract was washed several times with 2M HCl, dried, and evaporated. Recrystallisation of the residue from aqueous acetic acid gave 2-phenylpyrrolo[2,1,5-*cd*]indolizine (0.1 g, 70%), m.p. 93—94 °C (lit.,[3] m.p. 93.5—94.5 °C), i.r. spectrum identical with that of an authentic specimen synthesised by the method of Boekelheide.[3]

Cyclisation of 1,3-*Diethoxalyl*-2,5-*dimethylindolizine*.—The indolizine (6.9 g) was heated under reflux with sodium methoxide (1 mol equiv.) in dry methanol (50 cm³) for 1.5 h. A precipitate, which appeared when the solution was allowed to cool, was filtered off and extracted with boiling water. The insoluble portion was filtered off and recrystallised from methanol to give *methyl* 4-*methoxalyl*-3-*methylpyrrolo*[2,1,5-cd]-*indolizine*-2-*carboxylate* (1.8 g, 28%) as yellow needles, m.p. 146 °C (Found: C, 64.4; H, 4.2; N, 4.8. $C_{16}H_{13}NO_5$ requires C, 64.2; H, 4.4; N, 4.7%), $\lambda_{max.}$ 216, 246sh, 274, 294sh, 322sh, 331, 410sh, and 430 nm (log ε 4.49, 4.17, 4.30,

4.17, 4.14, 4.17, 4.05, and 4.31); δ 3.02 (3 H, s, 3-Me), 3.99 (3 H, s, OMe), 4.04 (3 H, s, OMe), 7.69 (1 H, s, H-1), 7.74—7.90 (2 H, m, H-6 and -7), and 8.10 (1 H, dd, H-5).

The aqueous filtrate was acidified and the resulting precipitate was filtered off and recrystallised from ethanol to give *4-hydroxy-1-methoxalyl-2-methyl-3H-pyrrolo*[2,1,5-de]*quinolizin-3-one* (1.2 g, 20%) as yellow plates, m.p. 197 °C (Found: C, 62.9; H, 3.8; N, 4.8. $C_{15}H_{11}NO_5$ requires C, 63.2; H, 3.9; N, 4.9%), $\nu_{max.}$ 1 600, 1 655, 1 740 (3 × CO), and 3 210 cm^{-1} (OH); $\lambda_{max.}$ 225sh, 244, 304, 395, and 415 nm (log ε 4.27, 4.51, 4.27, 4.15, and 4.34); δ 3.05 (3 H, s, 2-Me), 4.03 (3 H, s, OMe), 7.37 (1 H, s, H-5), 7.70 (1 H, d, H-6), 7.90 (1 H, t, H-7), and 8.60 (1 H, d, H-8); ^{13}C n.m.r. data in Table.

5-Methyl-2-phenyl-3-pyruvoylindolizine.—Phosphoryl chloride (4.6 g), in dichloromethane (20 cm^3), was added dropwise, with stirring, to a cooled (ice–sodium chloride) solution of 5-methyl-2-phenylindolizine (6.2 g), pyruvic acid (2.65 g), and triethylamine (6.1 g) in dichloromethane (100 cm^3). The solution was kept overnight at room temperature, washed with water, dried, and evaporated, and the residue was chromatographed on alumina. Elution with benzene gave a quantity of the original indolizine, and elution with benzene–ether (1 : 1) gave the *pyruvoyl compound* (1.2 g, 27%), as orange-yellow prisms, m.p. 102 °C (from benzene) (Found: C, 77.75; H, 5.6; N, 5.3. $C_{18}H_{15}NO_2$ requires C, 78.0; H, 5.45; N, 5.05%), δ(60 MHz) 1.95 (3 H, s, MeCO), 2.50 (3 H, s, 5-Me), 6.57 (1 H, s, H-1), 6.77 (1 H, d, H-6), and 3.05—3.60 (7 H, m, H-7,8, and Ph).

Cyclisation of 5-Methyl-2-phenyl-3-pyruvoylindolizine.—The indolizine (0.5 g) was heated under reflux with sodium methoxide (1 mol equiv.) in dry methanol (30 cm^3) for 1.5 h. Evaporation of the solvent and chromatography of the residue on alumina in benzene–ether (1 : 1) gave (i) starting material (0.3 g) and (ii) *4-methyl-2-phenyl-3H-pyrrolo*[2,1,5-de]*quinolizin-3-one* (0.07 g, 15%) as orange-yellow needles), m.p. 176 °C (from benzene) (Found: C, 83.65; H, 4.7; N, 5.4. $C_{18}H_{13}NO$ requires C, 83.4; H, 5.05; N, 5.4%), $\nu_{max.}$ 1 603 cm^{-1} (CO); $\lambda_{max.}$ 223 sh, 231, 263, 303sh, 345, 408, and 428 nm (log ε 4.31, 4.34, 4.52, 4.01, 3.60, 3.90, and 3.99); δ 2.40 (3 H, d, $^4J_{HH}$ 1 Hz, 4-Me), 7.19 (1 H, s, H-1), 7.4—8.2 (9 H, m, H-5, -6, -7, -8, and Ph). Longer periods of reflux caused more decomposition but did not significantly improve the yield.

Reactions of 2,5-Dimethylindolizine with α-Oxohydroximoyl Chlorides.—(*a*) Triethylamine (3.5 g, 0.034 mol) was added dropwise, during 3 h, to a stirred solution of the indolizine (5 g, 0.034 mol) and 2-oxo-2-phenylethanohydroximoyl chloride [12] (6.3 g, 0.034 mol) in chloroform (180 cm^3). After a further 24 h, the solution was washed with water, dried, and evaporated, and the residue was chromatographed on alumina. Elution with benzene–ether (1 : 1) gave (i) *2,5-dimethyl-3-(2-oxo-2-phenylethanohydroximoyl)indolizine* (7.6 g, 75%) as orange needles, m.p. 142—144 °C (from benzene) (Found: C, 73.9; H, 5.3; N, 9.5. $C_{18}H_{16}N_2O_2$ requires C, 74.0; H, 5.5; N, 9.6%), δ 2.13 (3 H, s, Me), 2.29 (3 H, s, Me), 6.27 (1 H, d, H-6), 6.38 (1 H, s, H-1), 6.69 (1 H, t, H-7), 7.22 (1 H, d, H-8), 7.3—7.6 (3 H, m, *m*- and *p*-Ph protons), and 8.0 (2 H, dd, *o*-Ph protons); and (ii) *2,5-dimethyl-1-(2-oxo-2-phenylethanohydroximoyl)indolizine* (0.15 g) as yellow needles, m.p. 182—183 °C (from methanol–benzene) (Found: C, 74.2; H, 5.3; N, 9.7%), δ 2.20 (3 H, s, Me), 2.43 (3 H, s, Me), 6.40 (1 H, d, H-6), 6.78 (1 H, t, H-7), 7.05 (1 H, s, H-3), 7.16 (1 H, d, H-8), 7.3—7.7 (3 H, m, *m*- and *p*-Ph protons), and 8.0 (2 H, dd, *o*-Ph protons).

(*b*) A similar reaction of 2,5-dimethylindolizine (2.0 g) with 2-oxopropanohydroximoyl chloride [13] (1.68 g) gave a mixture of the 1- and 3-(2-oxopropanohydroximoyl)indolizines (2.2 g, 72%) as a red oil, δ (60 MHz) 2.05, 2.20, 2.49 (major Me peaks), 2.13, 2.39, 2.52 (minor Me peaks), and 6.0—7.2 [m, indolizine protons (including a prominent H-1 singlet at δ 6.38)].

Reactions of 5-Methyl-2-phenylindolizine with α-Oxohydroximoyl Chlorides.—(*a*) Triethylamine (2 g, 0.02 mol) was added dropwise, during 2 h, to a stirred solution of the indolizine (4.1 g, 0.02 mol) and 2-oxo-2-phenylethanohydroximoyl chloride (3.7 g, 0.02 mol) in chloroform (175 cm^3). After 24 h, the solution was washed with water, dried, and evaporated, and the residue was chromatographed on alumina. Elution with benzene–ether (1 : 1) gave a mixture of the 1- and 3-(2-oxo-2-phenylethanohydroximoyl)-indolizines (5.1 g, 72%) as a red solid. A portion of the mixture was repeatedly recrystallised from benzene to give *5-methyl-3-(2-oxo-2-phenylethanohydroximoyl)-2-phenylindolizine* as orange prisms, m.p. 161 °C (Found: C, 77.7; H, 5.2; N, 7.8. $C_{23}H_{18}N_2O_2$ requires C, 77.9; H, 5.1; N, 7.9%), δ 2.34 (3 H, s, Me), 6.33 (1 H, d, H-6), 6.63 (1 H, s, H-1), 6.72 (1 H, t, H-7), 7.1—7.5 (9 H, m, H-8, 2-Ph, and *m*- and *p*-PhCO protons), and 7.7 (2 H, dd, *o*-PhCO protons).

(*b*) A similar reaction of 5-methyl-2-phenylindolizine (5 g, 0.024 mol) with 2-oxopropanohydroximoyl chloride (5.2 g, 0.043 mol) and triethylamine (0.043 mol) in chloroform (120 cm^3) gave a mixture of the 1- and 3-(2-oxopropanohydroximoyl)indolizines (4.6 g, 66%) as a red-orange solid. A portion of the mixture was repeatedly recrystallised from benzene to give *5-methyl-3-(2-oxopropanohydroximoyl)-2-phenylindolizine* as orange-red prisms, m.p. 184 °C (Found: C, 73.7; H, 5.3; N, 9.7. $C_{18}H_{16}N_2O_2$ requires C, 74.0; H, 5.5; N, 9.6%), δ 2.30 (3 H, s, 5-Me), 2.38 (3 H, s, MeCO), 6.34 (1 H, d, H-6); 6.67 (1 H, s, H-1), 6.74 (1 H, t, H-7), and 7.1—7.4 (6 H, m, H-8 and Ph).

3-Hydroxyimino-3H-[2.3.3]cyclazines.—(*a*) *In t-butyl alcohol*. A mixture of the isomeric 5-methyl-(2-oxo-2-phenylethanohydroximoyl)-2-phenylindolizines (7.3 g) was heated under reflux with potassium t-butoxide (1.2 mol equiv.) in t-butyl alcohol for 1.5 h. The solvent was distilled off under reduced pressure and the residual solid was extracted with boiling water. Acidification of the aqueous extract and recrystallisation of the resulting precipitate from benzene gave 5-methyl-3-(2-oxo-1-phenylethanohydroximoyl)-2-phenylindolizine (5.3 g), i.r. spectrum identical with that of an authentic specimen.

The water-insoluble fraction was dried and dissolved in boiling chloroform which, on cooling, deposited *5-methyl-1-(2-oxo-2-phenylethanohydroximoyl)-2-phenylindolizine* (0.7 g) as yellow needles, m.p. 200 °C (Found: C, 78.3; H, 4.7; N, 8.0%; M^+ 354. $C_{23}H_{18}N_2O_2$ requires C, 77.9; H, 5.1; N, 7.9%; *M* 354), δ 2.55 (3 H, s, Me), 6.51 (1 H, d, H-6), 6.85 (1 H, t, H-7), 7.1—7.5 (10 H, m, H-3, -8 and 2-Ph and *m*- and *p*-PhCO protons), and 7.84 (2 H, dd, *o*-PhCO protons).

Evaporation of the chloroform mother-liquor and recrystallisation of the residue from benzene gave *3-hydroxyimino-2,4-diphenyl-3H-pyrrolo*[2,1,5-de]*quinolizine* (0.9 g, 13%) as orange plates, m.p. 198 °C (decomp.) (Found: C, 82.3; H, 4.7; N, 8.7. $C_{23}H_{16}N_2O$ requires C, 82.1; H, 4.8; N, 8.3%), $\nu_{max.}$ (Nujol) 3 300br, ($CHCl_3$) 3 560 cm^{-1} (OH); $\lambda_{max.}$ 245sh, 274, 362, 382, and 458 nm (log ε 4.42, 4.52, 3.62, 3.65, and 3.67); δ 6.85 (1 H, d, H-6), 6.91 (1 H, s, H-1 or 5), 6.95 (1 H, s, H-5 or 1), 7.07 (1 H, t, H-7), and 7.2—7.6 (11 H, m, H-8 and Ph).

(*b*) *In dimethyl sulphoxide.* The following procedure is typical. A mixture of the isomeric 5-methyl-(2-oxo-2-phenylethanohydroximoyl)-2-phenylindolizines (1 g) was heated under reflux with potassium t-butoxide (1.2 mol equiv.) in dry dimethyl sulphoxide (10 cm^3) for 5 min. The solution was cooled, treated with acetic acid (1.2 mol equiv.), and evaporated to dryness (rotary evaporator and oil pump). The residue was extracted with dichloromethane and the extract was chromatographed on alumina, in dichloromethane, to give 3-hydroxyimino-2,4-diphenyl-3*H*-pyrrolo-[2,1,5-*de*]quinolizine (0.7 g, 74%), m.p. 198 °C, identical with the product obtained by method (*a*).

The following compounds were obtained from the appropriate (2-oxohydroximoyl)indolizines by the same method: (i) 3-*hydroxyimino*-2-*methyl*-4-*phenyl*-3H-*pyrrolo*[2,1,5-de]-*quinolizine* (52%), orange needles, m.p. 204 °C (decomp.) (from benzene) (Found: C, 78.4; H, 5.1; N, 10.1. $C_{18}H_{14}N_2O$ requires C, 78.8; H, 5.1; N, 10.2%), $\nu_{max.}$ (Nujol) 3 250br, ($CHCl_3$) 3 560sharp, and 3 200br (OH); $\lambda_{max.}$ 250sh, 277, 360, 378, and 462 nm (log ε 4.35, 4.54, 3.70, 3.76, and 3.64); δ 2.56 (3 H, s, Me) 6.61br (1 H, s, H-1), 6.74 (1 H, d, H-6), 6.80 (1 H, s, H-5), 6.99 (1 H, t, H-7), and 7.2—7.6 (6 H, m, H-8 and Ph); δ_C (quaternary) 115.9, 129.4, 131.6, 132.4, 139.1, 141.1, and 144.4; (non-quaternary) 18.2 (Me), 107.5, 112.0, 117.2, 120.9 (2 C), 127.8 (1 C, Ph), 127.9 (2 C, Ph), and 128.7 (2 C, Ph); (ii) 3-*hydroxyimino*-4-*methyl*-2-*phenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizine* (53%), orange prisms, m.p. 202 °C (decomp.) (from benzene) (Found: C, 79.15; H, 5.15; N, 10.15%), $\nu_{max.}$ (Nujol) 3 250br, ($CHCl_3$) 3 560-sharp, and 3 250br cm^{-1} (OH); $\lambda_{max.}$ 232, 268, 357, 375, and 440 nm (log ε 4.43, 4.58, 3.76, 3.82, and 3.72); δ 2.10 (3 H, s, Me), 6.82—6.90 (3 H, m, H-1, 5 and 6), 7.10 (1 H, t, H-7), and 7.2–7.6 (6 H, m, H-8 and Ph); and (iii) 3-*hydroxyimino*-2,4-*dimethyl*-3H-*pyrrolo*[2,1,5-de]*quinolizine* (20%), orange plates, m.p. 110 °C (decomp.) (from benzene) (Found: C, 73.9; H, 5.9; N, 12.7. $C_{13}H_{12}N_2O$ requires C, 73.6; H, 5.7; N, 13.2%), $\lambda_{max.}$ 261sh, 273, 407sh, and 421 nm (log ε 4.35, 4.43, 3.88, and 3.91).

O,O′-*Methylenebis*-(3-*oxyimino*-3H-[2.3.3]*cyclazines*).—(*a*) A mixture of the isomeric 5-methyl-(2-oxo-2-phenylethanohydroximoyl)-2-phenylindolizines (1 g) was heated at 100 °C with potassium t-butoxide (2 mol equiv.) in dry dimethyl sulphoxide (10 cm^3) for 5 min. The solution was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. Chromatography of the extracted material on alumina in benzene–ether (1 : 1) gave (i) O,O′-*methylenebis*-(3-*oxyimino*-2,4-*diphenyl*-3H-*pyrrolo*-[2,1,5-de]*quinolizine*) (12%) as orange-red prisms, m.p. 225—226 °C (decomp.) (from 2-methoxyethanol) (Found: C, 82.3; H, 4.8; N, 8.5. $C_{47}H_{32}N_4O_2$ requires C, 82.4; H, 4.8; N, 8.2%), $\lambda_{max.}$ 245sh, 265, 365, 380, and 450 nm; δ 4.0 (s, OCH_2O) and 6.6—7.7 (m); and (ii) 3-hydroxyimino-2,4-diphenyl-3*H*-pyrrolo[2,1,5-*de*]quinolizine (36%). Repetition of this experiment with the same quantities of reactants and the same experimental conditions, but with neutralisation (acetic acid) of the solution before evaporation to dryness, gave starting material (38%) and the hydroxyimino-compound (27%).

(*b*) A mixture of the isomeric 2,5-dimethyl-(2-oxo-2-phenylethanohydroximoyl)indolizines (1 g) was treated as in (*a*), (no neutralisation) and yielded O,O′-*methylenebis*-(2-*methyl*-3-*oxyimino*-4-*phenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizine*) (30%) as red-orange microcrystals, m.p. 192—193 °C (from 2-methoxyethanol) (Found: C, 79.2; H, 5.0; N, 9.9. $C_{37}H_{28}N_4O_2$ requires C, 79.2; H, 5.0; N, 10.0%), $\lambda_{max.}$ 256sh, 279, 361, 380, and 460 nm (log ε 4.83, 4.88, 4.22, 4.22, and 4.17); δ 2.62 (6 H, s, 2 × Me), 5.58 (2 H, s, OCH_2O), 6.60 (2 H, s, H-1 and 1′), 6.71 (2 H, dd, H-6 and 6′), 6.83 (2 H, s, H-5 and 5′), 6.92 (2 H, t, H-7 and 7′), and 7.2—7.7 (12 H, m, H-8, 8′, and 2 × Ph); δ_C (quaternary) 116.2, 131.3, 132.3, 132.9, 138.6, 141.0, and 146.2; (non-quaternary) 18.7 (Me), 98.9 (CH_2), 108.3, 112.0, 116.9, 120.4, 121.9, 127.7 (4 C, Ph), 127.8 (2 C, Ph), and 128.9 (4 C, Ph). For comparison, *O,O′*-methylenebis(oxyiminodiphenylmethane) showed δ_C (CH_2) 99.3.

(*c*) A mixture of the isomeric 5-methyl-(2-oxopropanohydroximoyl)-2-phenylindolizines (5 g) was treated with potassium t-butoxide (2 mol equiv.) in dry dimethyl sulphoxide (30 cm^3) as in (*a*). After evaporation to dryness, the residue was neutralised with HCl before being extracted with dichloromethane. Chromatography of the extracted material yielded *O,O′-methylenebis*(4-*methyl*-3-*oxyimino*-2-*phenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizine*) (15%) as red-orange microcrystals, m.p. 171—172 °C (from 2-methoxyethanol) (Found: C, 79.0; H, 5.0; N, 10.0%), $\lambda_{max.}$ 230, 268, 355, 372, and 435 nm (log ε 4.83, 4.90, 4.24, 4.24, and 4.21).

3H-[2.3.3]*Cyclazin*-3-*ones*.—The 3-hydroxyiminocyclazines were heated under reflux with an equal weight of silver(I) oxide in dichloromethane for 2 h. The solutions were filtered and evaporated, and the residues were recrystallised from benzene to give the cyclazinones (75—80%) which were somewhat hygroscopic. Analytically pure specimens were best obtained by sublimation at 180—200 °C and 0.1 mmHg. The following cyclazinones were obtained in this way: (i) 4-methyl-2-phenyl-3*H*-pyrrolo-[2,1,5-*de*]quinolizin-3-one, m.p. 176 °C, i.r. spectrum identical with that of the specimen obtained from 5-methyl-2-phenyl-3-pyruvoylindolizine; (ii) 2-*methyl*-4-*phenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizin*-3-one, orange-yellow prisms, m.p. 153 °C (Found: C, 83.5; H, 5.0; N, 5.5. $C_{18}H_{13}NO$ requires C, 83.4; H, 5.05; N, 5.4%), $\nu_{max.}$ 1 603 cm^{-1} (CO), $\lambda_{max.}$ 241sh, 271, 290sh, 335sh, 346, 425sh, and 440 nm (log ε 4.30, 4.66, 4.41, 3.81, 3.84, 4.01, and 4.04); and (iii) 2,4-*diphenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizin*-3-*one*, orange-yellow prisms, m.p. 198—199 °C (Found: C, 85.7; H, 4.8; N, 4.6. $C_{23}H_{15}NO$ requires C, 86.0; H, 4.7; N, 4.4%), $\nu_{max.}$ 1 603 cm^{-1} (CO); $\lambda_{max.}$ 238, 273, 299sh, 348sh, 426sh, and 433 nm (log ε 4.44, 4.45, 4.27, 3.83, 3.96, and 4.03).

4-*Methyl*-2-*phenyl*-3H-*pyrrolo*[2,1,5-de]*quinolizine*-3-*thione*.—The reaction vessel and chromatography column were wrapped with aluminium foil to prevent light-induced decomposition of the thione. 4-Methyl-2-phenyl-3*H*-pyrrolo[2,1,5-*de*]quinolizin-3-one (0.5 g) was heated under reflux with phosphorus pentasulphide (1.0 g) in benzene (70 cm^3) for 1.5 h. The solution was decanted and the viscous residue was stirred with an excess of aqueous sodium sulphide at 50 °C for 30 min. The aqueous digest was extracted with benzene and the extract was combined with the original benzene solution. After being dried and evaporated to 20 cm^3, the solution was chromatographed on alumina, in benzene, to give (i) the *thione* (0.35 g, 66%) as red-brown prisms, m.p. 176—178 °C (from ethanol) (Found: C, 78.4; H, 4.6; N, 5.3. $C_{18}H_{13}NS$ requires C, 78.5; H, 4.7; N, 5.1%), and (ii) starting material (30%).

4-*Methyl*-3-*methylthio*-2-*phenylpyrrolo*[2,1,5-de]*quinolizinylium Perchlorate*.—The foregoing thione (0.05 g) was heated under reflux with an excess of iodomethane in dry ether (20 cm^3) for 30 min. The resulting methiodide (0.07 g) was filtered off, dissolved in the minimum volume of warm methanol, and treated with 70% perchloric acid (1 mol

equiv.). Addition of ether gave the *pyrroloquinolizinylium perchlorate* as yellow needles, m.p. 199—200 °C (from ethanol containing a trace of $HClO_4$) (Found: C, 58.6; H, 3.8; N, 3.9. $C_{19}H_{16}ClNO_4S$ requires C, 58.5; H, 4.1; N, 3.6%), δ (CF_3CO_2H), 2.18 (3 H, s, SMe), 3.11 (3 H, s, 4-Me), 7.5—7.9 (5 H, m, Ph), 8.14 (1 H, s, H-1), and 8.73—8.80 (4 H, s with 2 small satellites, H-5, -6, -7, and -8).

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