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PHOTOCYCLISATION OF 2-AROYLQUINOXALINES; FORMATION OF COLOURED INDOLO[1,2-a]QUINOXALINES

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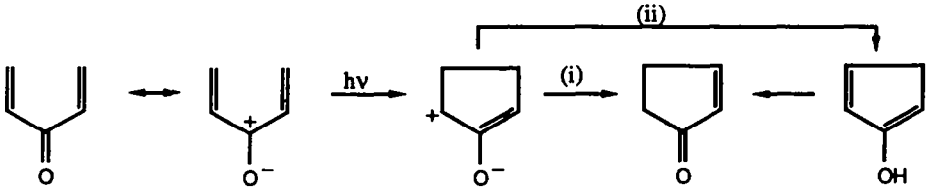
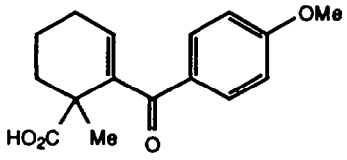
Abstract: Irradiation of 2-benzoylquinoxaline (**10**) and 2-benzoyl-3-methylquinoxaline (**11**) in the presence of trifluoroacetic acid resulted in cyclisation to the orange-red 7-hydroxyindolo-[1,2-a]quinoxalin-5-ium trifluoroacetate (**16**) and the 6-methyl homologue **17** respectively. Similarly, irradiation of quinoxaline **11**, 2-benzoyl-3-benzylquinoxaline (**12**), 2-(2,4-dimethylbenzoyl)-3-methylquinoxaline (**23**), and 2-benzoyl-3,6,7-trimethylquinoxaline (**24**) in methanol, or in ether, containing *p*-toluenesulphonic acid gave orange-red salts; 6-methyl- (**18**), 6-benzyl- (**19**), 6,8,10-trimethyl- (**26**), and 2,3,6-trimethyl-7-hydroxyindolo[1,2-a]-quinoxalin-5-ium *p*-toluenesulphonate (**27**) respectively. The purple photoproduct, 6-methyl-indolo[1,2-a]quinoxalin-7(5*H*)-one (**15**) was formed on irradiation of quinoxaline **11** in methanol. The 7-hydroxyindolo[1,2-a]quinoxalinium salts **16**, **18**, **19** and **27** formed yellow 7-acetoxyindolo[1,2-a]quinoxalines **20**, **21**, **22**, and **29** respectively, and quinoxalinium salt **26** was converted into 6,8,10-trimethyl-7-propionoxyindolo[1,2-a]quinoxaline (**28**). In aerated methanolic sodium methoxide, the purple photoproduct **15** was converted into 1-(2-carboxyphenyl)-3-methylquinoxalin-2(1*H*)-one (**34**).

Photocyclisation of a dienone system **1** to a cyclopentenone **3** may formally be considered as a 4π electrocyclisation to intermediate **2** followed either by a hydride shift [path (i)] or by protonation-deprotonation to give enol **4** and subsequent ketonisation [path (ii)] (Scheme 1). Cyclisation of **1** to **2** is related to the photocyclisation of a pentadienyl cation[1] and was proposed as the first step in the photorearrangement of cyclohexadienones,[2] which is generally followed by skeletal rearrangement rather than by a shift of hydrogen. When one of the C=C bonds in **1** is part of an aromatic ring, dimerisation (2 + 2 cycloaddition at the other C=C bond) is a typical photoreaction[3] and with both C=C bonds part of aromatic rings, photoreduction generally occurs.[4] In either case, photocyclisation is uncommon. The few reported examples include photocyclisation of the hindered aryl enone **5** to the indanones **6** and **7**,[5] and cyclisation of pyridyl ketones **8** (which formally contain an aza-dienone system) to heterocycles **9**.[6] We report the ready photocyclisation of 2-quinoxalinyl aryl ketones **10**, **11**, **12**, **23**, and **24** to indolo[1,2-a]quinoxalines (e.g. **16**, **18**, **19**, **26**, and **27** respectively). This reaction is related to the photocylisation of **8** to **9** but the reaction conditions and



1 2 3 4

Scheme 1



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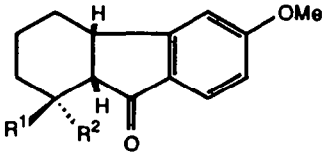
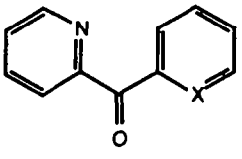


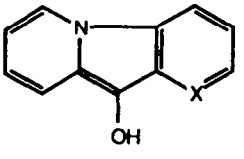
6 R^1 = Me, R^2 = CO_2H

7 R^1 = CO_2H, R^2 = Me



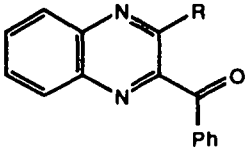
8a X = N

8b X = CH



9a X = N

9b X = CH



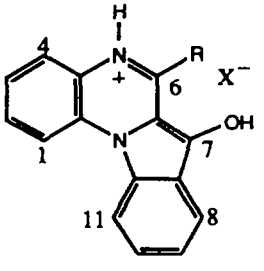
10 R = H

11 R = Me

12 R = CH_2Ph

13 R = Ph

14 R = CO_2Et



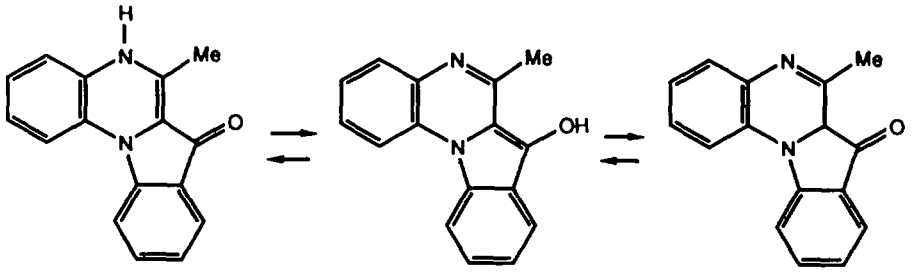
16 R = H, X = $CF_3CO_2^-$

17 R = Me, X = $CF_3CO_2^-$

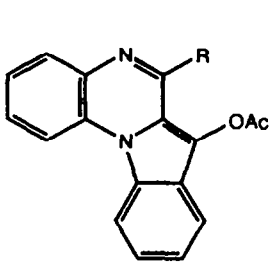
18 R = Me, X = 4-$MeC_6H_4SO_3^-$

19 R = CH_2Ph, X = 4-$MeC_6H_4SO_3^-$

properties of the photoproducts are significantly different.



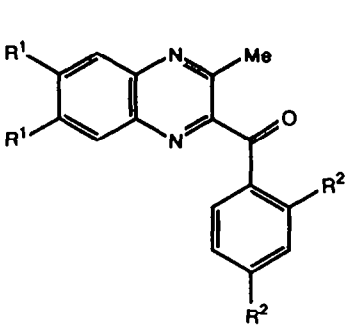
15a **15b** **15c**



20 R = H

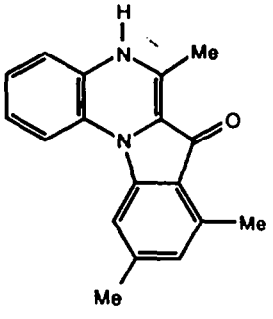
21 R = Me

22 R = CH_2Ph



23 R^1 = H, R^2 = Me

24 R^1 = Me, R^2 = H



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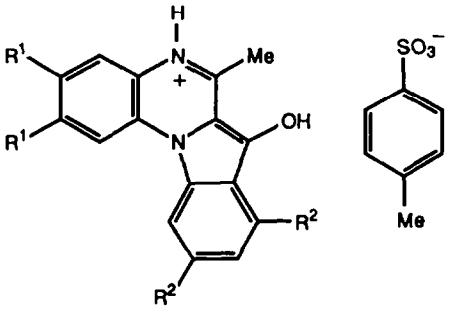
Results

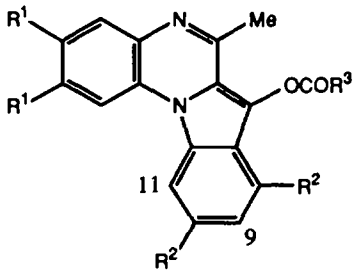
2-Benzoyl-3-methylquinoxaline (**11**) in methanol, ethanol, 2-propanol, aqueous tetrahydrofuran, or aqueous dimethylformamide, or adsorbed onto silica gel, was converted into a purple photoproduct **15** on exposure to daylight or to ultraviolet radiation. The colour becomes visible within a few seconds.* In contrast, irradiation of quinoxaline **11** in ether, dichloromethane, tetrahydrofuran, or dry dimethylformamide caused only slight decomposition with no change in colour. Unreacted quinoxaline **11** and small amounts of minor products may be separated from the sparingly-soluble purple indolo[1,2-a]quinoxaline **15** by extraction into ether or by chromatography over silica gel. However, as photoproduct **15** reacts slowly with oxygen in

*The formation of a 'wine-red' colour on exposure of an ethanolic solution of quinoxaline **11** to daylight was noted by Schellenberg and Steinmetz.[7]



26 $R^1 = H, R^2 = Me$

27 $R^1 = Me, R^2 = H$



28 $R^1 = H, R^2 = Me, R^3 = Et$

29 $R^1 = Me, R^2 = H, R^3 = Me$

solution,* it was found more convenient to irradiate quinoxaline **11** in the presence of an acid and to isolate the photoproduct as a salt which is stable in air. Hence, irradiation of **11**, in the presence of trifluoroacetic acid (TFA) or *p*-toluenesulphonic acid (PTSA), in methanol or in ether (from which the photoproduct precipitates in a pure state) yielded orange-red indolo[1,2-a]quinoxalinium salts **17** and **18** respectively (see Table). The purple indoloquinoxaline **15** was also obtained (78% yield) when a solution of tosylate **18** was eluted with methanol through a column of neutral alumina.

Irradiation of quinoxaline **11** was carried out under a variety of conditions and the yield of indoloquinoxalinium salt (**17** or **18**) was calculated from its absorption at 477 nm. U.v./visible spectra were determined for 0.25 M methanolic sulphuric acid solutions in which the indoloquinoxalinium salt was stable and for which the optical density was at a maximum. The photocyclisation was accelerated by acid in low concentration. Irradiation of 0.1% solutions of quinoxaline **11** containing PTSA showed that the yield of salt **18** had reached a maximum after 1 hour (yield of **18**: 71, 76, 78 and 72% in the presence of 1, 2, 5, and 50 equivalents of PTSA respectively). Prolonged irradiation led to a decrease in yield (47% after 7 hours with 1 equivalent of PTSA) except for the higher concentration of acid (50 equivalents), when little change occurred. Irradiation of a 0.5% solution of quinoxaline **11** in dry THF for 20 minutes in the presence of TFA (0.01, 0.1, 1.0, 2.0 and 10 equivalents) gave indoloquinoxalinium salt **17** in ca. 0.4, ca. 0.4, 1.0, 1.3, and 8.5% yield respectively. Quinoxaline **11** was irradiated with PTSA (1.2 equivalents) for 15 minutes in methanol. The yield of salt **18** was 22% when the solution was degassed and not agitated; 39% and 41% when a stream of nitrogen or oxygen respectively was bubbled through the solution.

Quinoxalines **12**, **23**, and **24** also underwent photocyclisation to indoloquinoxalinium salts (**19**, **26**, and **27** respectively) in the presence of PTSA (see Table). Addition of water to a dilute methanolic solution of salt **26** yielded the indoloquinoxalinone **25** which was stable enough to be characterised fully. In contrast to the

*The mass spectrum of photoproduct **15** shows a peak at *m/z* 280 which is probably due to contamination by a hydroperoxide of **15** and/or by another oxidation product (e.g. **34**).

Table: Irradiation of 2-Aroylquinoxalines

Aroyl-quinoxaline	Light source [a]	Reaction medium	Time (h)	% Yield (Indolo[1,2-a]quinoxaline)
10	A	TFA	2.3	54 (**16**)
11	B	Ar/MeOH	0.75	18 (**15**)
11	A	Et_2O + TFA[b]	2.0	56 (**17**)
11	B	MeOH + PTSA[c]	3.0	65 (**18**)
11	A	Et_2O:MeOH (20:1) + PTSA[c]	2.0	45 (**18**)
11	B	degassed MeOH + PTSA[d]	0.25	22 (**18**)
11	B	O_2/MeOH + PTSA[e]	0.25	41 (**18**)
11	B	N_2/MeOH + PTSA[e]	0.25	39 (**18**)
12	B	MeOH + PTSA[c]	4.0	50 (**19**)
23	B	MeOH + PTSA[c]	4.0	75 (**26**)
24	B	MeOH + PTSA[c]	4.0	50 (**27**)

[a] A: High-pressure mercury vapour lamp obtained by removing the outer glass envelope from a 125-W Thorn Electric Kolorlux MBF lamp; B: Rayonet RPR-100 photoreactor fitted with 3000 Å lamps.

[b] 2.0 Equivalents of trifluoroacetic acid.

[c] 1.25 Equivalents of *p*-toluenesulphonic acid monohydrate (PTSA).

[d] 1.25 Equivalents of PTSA, no agitation; yield of **18** calculated from the u.v. spectrum.

[e] 1.25 Equivalents of PTSA with a stream of gas (oxygen or nitrogen) bubbled through the solution; yield of **18** calculated from the u.v. spectrum.

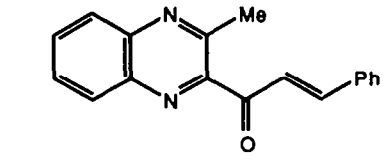
above photoreactions, irradiation of 2-benzoylquinoxaline (**10**) in methanol or in ether, with TFA or PTSA, gave a red solution, containing mainly quinoxaline **10**, from which no product could be isolated. Irradiation in aqueous methanol gave a purple solution whose colour faded on keeping several hours in the dark. No colour change resulted from irradiating in methanol alone. The rose-red indoloquinoxalinium salt **16** was successfully obtained (54%) by irradiating a shallow layer of quinoxaline **10** in neat TFA.

Indoloquinoxalinium salts **16**, **18**, **19**, and **27** were converted into stable yellow acetates **20**, **21**, **22**, and **29** on treatment with acetic anhydride. Similarly, salt **26** reacted with propionic anhydride to give the propionate **28**.

No coloured products were formed when quinoxalines **13** and **14** were irradiated in methanol or in methanol containing TFA, and quinoxaline **13** underwent little change on irradiation with PTSA in ether. The 2-cinnamoylquinoxaline **30** was irradiated for 5 hours in methanol, chloroform, acetonitrile, benzene, and

with PTSA in methanol. In all cases the reaction mixture consisted largely of **30** together with a complex mixture of minor products. Irradiation of benzil mono-anil (**31**) in methanol caused little change and in the presence of PTSA or TFA, a complex mixture of products resulted. Attempts to prepare salts of pyrido-indole **9b** by irradiating 2-benzoylpyridine **8b** with PTSA in ether, chloroform, or methanol, or in neat or methanolic TFA gave complex mixtures with little change in colour.

A solution of indoloquinoxaline **15** in methanol reacted slowly with dissolved oxygen in the dark as shown by a reduction in optical density at 535 nm of 26% after 3 days. Addition of sodium methoxide to a fresh solution of **15** gave an orange solution ($\lambda_{max.}$ 482 nm), presumably of anion **32**, whose colour faded rapidly (half-life approximately 90 minutes). After 21 hours the solution was colourless and its u.v. spectrum was similar to that of acid **34**, which was obtained in 61% yield when tosylate **18** was allowed to react with oxygen in methanolic sodium methoxide.



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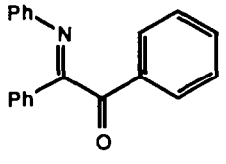

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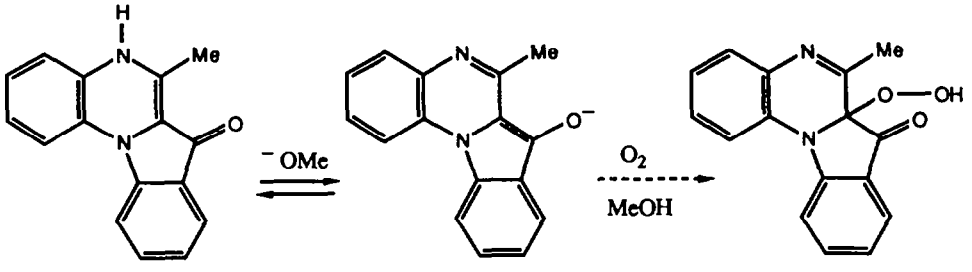
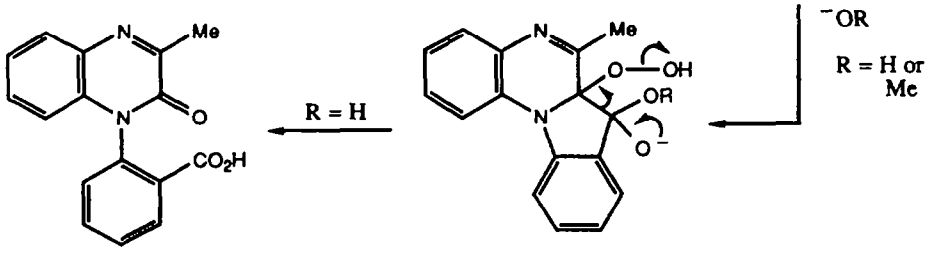


15a **32** **33**



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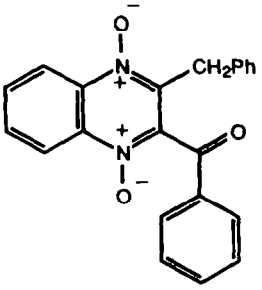
Scheme 2



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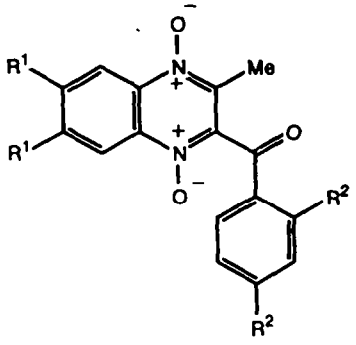
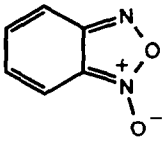


36 R^1 = H, R^2 = Me

37 R^1 = Me, R^2 = H



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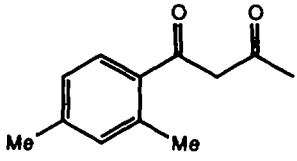

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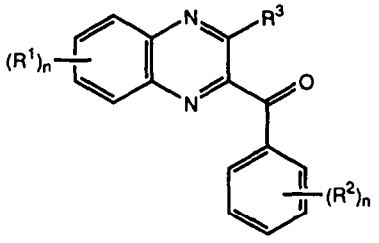
Preparation of 2-Aroylquinoxalines - Quinoxalines **12**, **23**, and **24** were obtained on reduction of 1,4-dioxides **35**, **36**, and **37** respectively using sodium dithionite. 1,4-Dioxide **36** was prepared by the base-catalysed reaction of benzofurazan 1-oxide (**38**) with 1-(2,4-dimethylphenyl)butane-1,3-dione (**39**). Other quinoxalines (**10**, **11**, **13**, **14**, and **30**) and benzil mono-anil (**31**) were synthesised according to literature procedures (see Experimental).

Discussion

The photocyclisation of 2-aroylquinoxalines to indolo[1,2-a]quinoxalines, as represented by the conversion of **11** into **15** (or its salts **17** and **18**), appears analogous to the photocylisation of aroylpyridines **8** to pyrido-indoles **9**.[6] However, irradiation of dipyridyl ketone **8a** in isopropanol causes reduction to the corresponding alcohol and the conversion of **8** into **9** requires the absence of oxygen. In contrast, quinoxaline **11** cyclises to indoloquinoxaline **15** in neutral alcoholic solution (methanol, ethanol, or isopropanol) in the presence of air.* In acidic solution, oxygen does not interfere with the photoreaction (see Table) and the photoproduct salts (**17** and **18**) are stable in air.

*In methanol, reaction of **15** with oxygen is slow (see Results section) and little decomposition occurs during the short time of the photoreaction.



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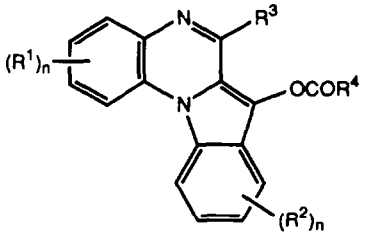

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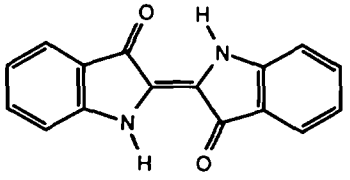

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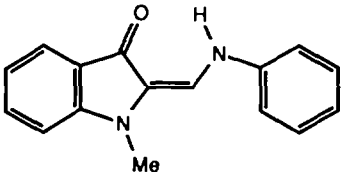

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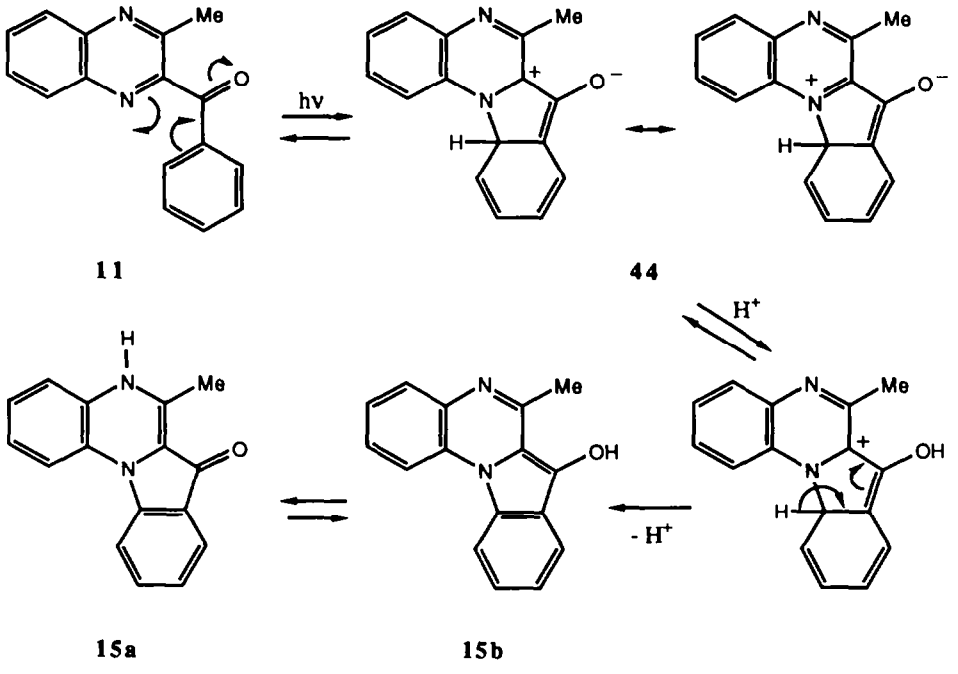
The indolo[1,2-a]quinoxaline structure assigned to the photoproducts is consistent with their spectroscopic properties. As the first photoproduct of the series to be prepared, indoloquinoxaline **15**, was somewhat unstable in air, did not readily crystallise, and whose solution (in deuteriomethanol) did not yield an n.m.r. spectrum, all the photoproducts were characterised as trifluoroacetate or tosylate salts. N.m.r. spectra for the photoproduct esters **20** - **22**, **28** and **29** were generally more informative than those of the salts, which were less well resolved in most cases. The most noticeable difference between the n.m.r. spectra of the quinoxalinyl ketones (general structure **40**) and the photoproduct esters (general strucutre **41**) was in the number of signals for aromatic protons, one less in **41**. This difference is best observed for quinoxaline **23** and the corresponding photoproduct ester **28**; the proton at C-5 in the xylyl group of **23**, seen as a doublet at δ 6.99, becomes the proton at C-11 in **28**, seen as a singlet at δ 7.99. Apart from slight line-broadening, *meta*-coupling was not observed between the protons at C-3 and C-5 in the xylyl ring of **23** and between the protons at C-9 and C-11 in **28**.

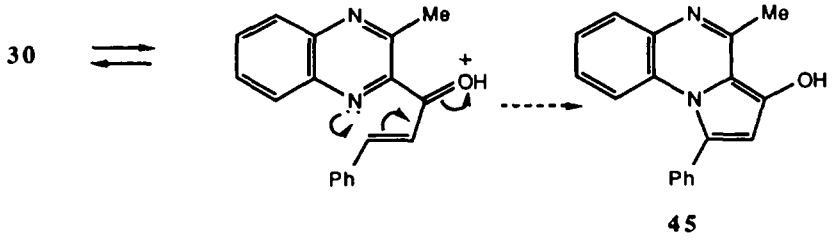
Tautomeric structures **15a**, **15b**, and **15c** are possible for the neutral photoproduct **15**. Structure **15c**, which is less conjugated, can probably be discounted. Of the remaining tautomers, **15a** appears to be predominant as shown by a carbonyl absorption in the infrared spectrum at 1650 cm^{-1} and by its purple colour (visible absorption at 570 nm). Structure **15a** has some similarity to that of the blue dye indigo (**42**) [$\lambda_{max.}$ (EtOH) 606 nm][8] and to that of the indolone derivative **43** [$\lambda_{max.}$ (2-propanol) 520 nm][9] although in **15a** the nitrogen atoms are held in a *cis*-configuration. In contrast, the structure of tautomer **15b** is similar to that of the acetate **21** which is yellow ($\lambda_{max.}$ 394 nm). However, this structure is believed to be present in a protonated form in the orange salts **17** and **18** ($\lambda_{max.}$ 477 nm in methanolic sulphuric acid). Allowing for the

hypsochromic shift caused by the acetyl group, the acetate **21** shows a similar absorption, at 441 nm, in acidic methanol.

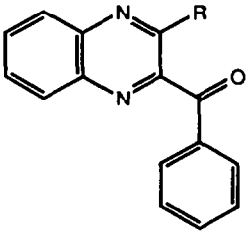


Scheme 3

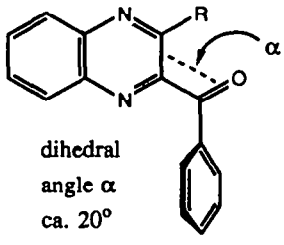
The proposed mechanism for the photocyclisation is shown in Scheme 3, using quinoxaline **11** as an example. Protonation of the initial product **44** of photocyclisation may aid the forward reaction leading to product **15** at the expense of reversal to the starting material. This is consistent with (i) the requirement of the photocyclisation for a protic solvent or the presence of acid, and (ii) the small increase in the rate of the



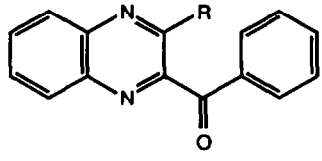
reaction in methanol on increasing the concentration of PTSA (1-5 equivalents). In the polar but aprotic solvent dimethylformamide, no photocyclisation occurred. Alternatively, the cyclisation of **11** to **44** could be seen as nucleophilic attack by nitrogen at the *ortho*-position of the benzoyl group. This is less likely as the reaction rate in methanol is lower in the presence of a high concentration of acid (50 equivalents of PTSA) whereas cyclisation of the cinnamoylquinoxaline **30** to pyrroloquinoxaline **45** occurs on heating in ethanol with concentrated hydrochloric acid.[10] This reaction presumably involves nucleophilic attack by the quinoxaline nitrogen at the protonated enone side-chain. Quinoxaline **11** does not cyclise under these conditions and irradiation of quinoxaline **30** does not cause cyclisation to **45** either in the absence or in the presence of acid.



46A



46B



46C

A conformation approaching that of **46A**, in which the quinoxaline ring system and the benzene ring are approximately coplanar, is required for the photocyclisation. If the size of the substituent R is increased, the energy of conformation **46A** will be higher and it will be more difficult for the molecule to achieve the conformation necessary for cyclisation. This may explain the lack of photoreaction with quinoxalines **13** and **14** (R = Ph and CO_2Et respectively). In these two cases, a further factor hindering cyclisation may be conjugation of the 3-substituent with the quinoxaline ring resulting in a reduction in electron density at the N_1-C_2 bond. With quinoxaline **10**, 'unreactive' conformations such as **46C** (R = H) may be significant and this may partly account for the greater difficulty in achieving photocyclisation with this compound.

2-Benzoyl-3-methylquinoxaline **11** did not fluoresce in hexane but, in a methylcyclohexane glass at 77°K, phosphorescence was observed ($\lambda_{max.}$ 484 and 512 nm). These observations are consistent with excited singlet ketone **11** undergoing efficient intersystem crossing to excited triplet ketone, with subsequent rearrangement occurring from the latter state. As oxygen is a well known quencher of triplets,[11a] the absence of any effect by oxygen on the photorearrangement of ketone **11** into indoloquinoxaline **18** (see Table) suggests that the excited triplet ketone undergoes rearrangement at a rate which is significantly higher than that of interaction with oxygen.* An alternative explanation for the lack of fluorescence by ketone **11** is that, as well as crossing over to the triplet state, the excited singlet ketone cyclises rapidly to the unstable intermediate

*A rate constant of 1.8×10^9 l mol^{-1} sec^{-1}, reported for the interaction of oxygen with triplet benzophenone in acetonitrile,[12] is typical for quenching of triplets by oxygen.

44 which, in a non-protic solvent (i.e. hexane), then reverts back to the starting ketone. This seems less likely as no significant fluorescence could be detected in a methylcyclohexane glass at 77°K, when the rate of the photorearrangement **11** → **44** should be lower since the conformation required for cyclisation has a higher strain energy than that of a low-energy conformation (such as **46B**) in which the quinoxaline and benzene rings are approximately at right angles.[13] A luminescence spectrum of ketone **11** in the protic solvent methanol could not be determined as conversion into photoproduct occurred during the measurement.

The emission by ketone **11** at 512 nm corresponds to a relatively low triplet energy of 55.8 kcal mol^{-1} which is typical for ketones (e.g. naphthyl ketones) whose first excited triplet states are $\pi\pi^*$ and which are generally fairly unreactive with respect to photoreduction.[11b] This may account for the absence of photoreduction on irradiation of ketone **11** in isopropanol.

The indoloquinoxalinium salts **16** - **19**, **26**, and **27**, and the corresponding acetyl or propionyl derivatives **20** - **22**, **28**, and **29** are stable solids. The salts are also stable in acidic solution in the dark in the presence of air. Salt **18** decomposed slowly on irradiation in methanol except when in the presence of a large excess of PTSA when little change occurred. In contrast, the indoloquinoxaline **15** was found to react slowly with dissolved oxygen in neutral methanol and rapidly in the presence of alkali. The reaction of **15** with oxygen in methanolic sodium methoxide was followed by observing the change in optical density of the initially formed anion **32** ($\lambda_{max.}$ 482 nm). After 21 hours this absorption had disappeared and the spectrum was qualitatively similar to that of the acid **34**. An isobestic point at 360 nm indicated a clean conversion of anion **32** into a single product. It is likely, however, that the product, acid **34**, is formed together with some of the corresponding methyl ester, but both compounds would be expected to have almost identical u.v. spectra. Ester formation may account for the relatively low yield of isolated acid **34** (61%) which was obtained when oxygen was bubbled through a solution of indoloquinoxaline **15** (formed *in situ* from the salt **18**) in methanolic sodium methoxide. The reaction pathway proposed for the conversion of indoloquinoxaline **15** into acid **34** is outlined in Scheme 2. Formation of the hydroperoxide **33** from **15a** is similar to the air oxidation of tetrahydrocarbazole to a hydroperoxide.[14] In the presence of alkali, when the reaction rate is much higher, the transformation is more likely to involve attack of oxygen at the enolate portion of anion **32** rather than attack at the enamine portion of **15a**. Cleavage of a hydroperoxide group to form a carbonyl group, the last step in the sequence leading to acid **34**, has precedence in the reported air oxidation of a dienamine to an enedione.[15]

The photocyclisation of aryl 2-quinoxalinyl ketones to indolo[1,2-a]quinoxalines is one of the few examples of intramolecular cyclisation at an aromatic ring which involves formation of an N-C bond (see also ref. 6).* As the yield of the cyclisation product may be readily determined from the visible absorption of the irradiation mixture, the reaction has potential for use in a simple u.v. actinometer system. This application may be limited by the competition for absorption of the incident u.v. radiation between the photoproduct and the starting ketone (see Results section). Absorption by the photoproduct decreases with increasing agitation

*Photochemical cyclodehydration of 3,4-diphenyl-3-buten-2-one oxime to 2-methyl-3-phenylquinoline presumably involves an initial 6π electrocyclisation with formation of an N-C bond, and so is a further example of this type of cyclisation.[16]

of the reaction mixture and so the yield and apparent quantum yield for the photoreaction will vary according to the precise experimental conditions, particularly for longer reaction times.

Experimental Section

I.r. spectra were recorded as Nujol mulls and n.m.r. spectra were recorded at 300 MHz in $CDCl_3$ unless otherwise stated. For u.v. spectra, $\log_{10} \varepsilon_{max.}$ is quoted in parentheses.

The following compounds were prepared according to literature procedures; 2-benzoylquinoxaline (**10**),[17] 2-benzoyl-3-methylquinoxaline (**11**),[18] 2-benzoyl-3-phenylquinoxaline (**13**),[19] ethyl 3-benzoylquinoxaline-2-carboxylate (**14**),[17] 2-cinnamoyl-3-methylquinoxaline (**30**),[10] 2-benzoyl-3-benzylquinoxaline 1,4-dioxide (**35**),[20] 2-benzoyl-3,6,7-trimethylquinoxaline 1,4-dioxide (**37**),[21] benzil mono-anil (**31**),[22] benzofurazan 1-oxide (**38**),[23] and 1-(2,4-dimethylphenyl)butane-1,3-dione (**39**).[24] 2-Benzoylpyridine (**8b**) was obtained from Aldrich Chemical Company Ltd. PTSA = *p*-toluenesulphonic acid monohydrate and TFA = trifluoroacetic acid.

General Method for the Reduction of Quinoxaline 1,4-*Dioxides* **35**, **36**, *and* **37** *to Quinoxalines* **12**, **23**, *and* **24** *Respectively*. - A hot solution of sodium dithionite (2 g) was added in portions to a solution of the quinoxaline 1,4-dioxide (2 mmol) in the minimum amount of dimethylformamide (7 - 15 ml) heated on a water-bath. Reduction is complete when the reaction mixture acquires a deep purple colour which persists for several minutes. The mixture was cooled and water was added to precipitate the product. After cooling for several hours at ca. 4°C, the product was collected and crystallised from aqueous methanol. Yield, m.p., and spectroscopic data are quoted for the following quinoxalines.

2-Benzoyl-3-benzylquinoxaline (**12**) (0.48 g, 74%), m.p. 97-98°C (Found: C, 81.6; H, 5.25; N, 8.6. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 5.0; N, 8.6%); $\nu_{max.}$ 1680 and 1600 cm^{-1}; δ (90 MHz) 4.5 (2H, s, CH_2), 6.9 - ca. 8.0 (12H, m, ArH), and 8.0-8.25 (2H, m, ArH); *m/z* 324 (M^+, 100%), 323 (39), 295 (15), 247 (33), 219 (*M*-PhCO, 17), 105 ($PhCO^+$, 47), 91 ($PhCH_2^+$, 33), and 77 (Ph^+, 46). *2-(2,4-Dimethylbenzoyl)-3-methylquinoxaline* (**23**) (0.45 g, 82%), m.p. 88-90°C (Found: C, 78.4; H, 6.1; N, 10.4. $C_{18}H_{16}N_2O$ requires C, 78.2; H, 5.8; N, 10.1%); $\nu_{max.}$ 1665 and 1610 cm^{-1}; δ 2.37 (3H, s, Me), 2.61 (3H, s, Me), 2.78 (3H, s, Me), 6.99 (1H, broad d *J* 8 Hz, benzoyl 5-H), 7.16 (1H, broad s, benzoyl 3-H), 7.28 (1H, d *J* 8 Hz, benzoyl 6-H), 7.68-7.82 (2H, m, 6- and 7-H), and 8.01-8.07 (2H, m, 5- and 8-H); *m/z* 276 (M^+, 25%), 248 (*M*-CO, 19), 247 (*M*-CHO, 26), 233 (33), 133 ($C_8H_9CO^+$, 100), 105 (55), 102 (21), 79 (22), and 77 (22). *2-Benzoyl-3,6,7-trimethylquinoxaline* (**24**) (0.45 g, 82%), m.p. 163-164°C (Found: C, 78.6; H, 6.1; N, 10.3. $C_{18}H_{16}N_2O$ requires C, 78.2; H, 5.8; N, 10.1%); $\nu_{max.}$ 1670 and 1600 cm^{-1}; δ (90 MHz) 2.47 (3H, s, Me), 2.50 (3H, s, Me), 2.76 (3H, s, Me), and 7.2-8.35 (7H, m, ArH); *m/z* 276 (M^+, 96%), 275 (57), 247 (73), 233 (25), 171 (15), 105 ($PhCO^+$, 100), 103 (20), and 77 (Ph^+, 66).

2-(2,4-Dimethylbenzoyl)-3-methylquinoxaline 1,4-*Dioxide* (**36**). - A warm solution of benzofurazan 1-oxide (3.4 g) in diethylamine (20 ml) was added to a warm solution of 1-(2,4-dimethylphenyl)butane-1,3-

dione (4.75 g) in diethylamine (15 ml). The mixture was left at room temperature for 18 h and then cooled. A little diethylamine was added to aid filtration and the product was collected, washed with a little cold methanol, and crystallised from chloroform/ethanol to give 2-(2,4-*dimethylbenzoyl*)-3-*methylquinoxaline* 1,4-*dioxide* (5.7 g, 74%), m.p. 185-187°C (Found: C, 70.2; H, 5.5; N, 9.2. $C_{18}H_{16}N_2O_3$ requires C, 70.1; H, 5.2; N, 9.1%); $\nu_{max.}$ 1650 (CO) and 1325 cm^{-1} (NO); δ 2.38 (3H, s, Me), 2.52 (3H, s, Me), 2.75 (3H, s, Me), 7.04 (1H, d *J* 8 Hz, benzoyl 5-H), 7.2 (1H, s, benzoyl 3-H), 7.37 (1H, d *J* 8 Hz, benzoyl 6-H), 7.78-8.0 (2H, m, 6- and 7-H), and 8.48-8.72 (2H, m, 5- and 8-H).

Irradiation of 2-*Aroylquinoxalines*. - Unless otherwise stated, one of the following methods (A or B) was used. *Method A*: A stirred solution of the aroylquinoxaline contained in a suitable vessel (open to the atmosphere) was irradiated using a high pressure mercury vapour lamp (obtained by removing the outer glass envelope from a 125-W Thorn Electric Kolorlux MBF lamp) enclosed in a water-cooled Pyrex cold-finger and which was situated *just above* the reaction solution. This procedure avoids the problem created by the precipitation of the photoproduct onto the cold-finger, resulting in reduced light transmission, when the lamp and cold-finger are immersed in the reaction mixture. *Method B*: A solution of the aroylquinoxaline contained in a Pyrex tube was irradiated in a Rayonet RPR-100 photoreactor fitted with 3000Å lamps.

Irradiation of 2-*Benzoylquinoxaline* (**10**). - A solution of quinoxaline **10** (0.2 g) in TFA (2 ml) was irradiated as a 'thin-film' in a 63 mm diameter Petri dish (Method A) for 2.33 h. The TFA was allowed to evaporate and the residue was triturated with dry ether and filtered to give 7-*hydroxyindolo*-[1,2-a]*quinoxalin*-5-*ium trifluoroacetate* (**16**) (0.16 g, 54%), m.p. ca. 215-220°C (decomp.) (from ethyl acetate containing a little methanol and TFA) (Found: C, 58.5; H, 3.2; N, 8.4. $C_{17}H_{11}F_3N_2O_3$ requires C, 58.6; H, 3.2; N, 8.0%); $\nu_{max.}$ ca. 3100-2200, 1655, and 1620 cm^{-1}; δ (CD_3OD + TFA) 7.39-7.48 (2H, m, ArH), 7.62-7.71 (2H, m, ArH), 7.8 (1H, apparent double t *J* 1.2 and 7.0 Hz, ArH), 8.13 (1H, d *J* 8.3 Hz, ArH), 8.38-8.42 (2H, m, ArH), and 9.1 (1H, s, 6-H); *m/z* 234 (*M*-CF_3CO_2H, 100%), 233 (70), 205 (11), 102 (13), 77 (19), and 76 (14).

Irradiation of 2-*Benzoyl*-3-*methylquinoxaline* (**11**). - (i) Quinoxaline **11** (210 mg) in methanol (20 ml) was irradiated (Method B) for 45 min. Argon was bubbled through the solution before and during the irradiation. The solvent was evaporated and the residue was extracted several times with ether. The insoluble deep purple residue was relatively pure (t.l.c.) 6-*methylindolo*[1,2-a]*quinoxalin*-7(5H)-*one* (**15**) (38 mg, 18%) (Found: M^+ 248.0960. $C_{16}H_{12}N_2O$ requires M^+ 248.0950); $\lambda_{max.}$ (MeOH) 237 (4.36); 269 (4.22), 298 (4.33), 318 (4.24), 359.5 (3.56), 377 (3.54), 535 (3.7), and 570 (3.64); $\lambda_{max.}$ (0.1 M potassium acetate in MeOH)* 359.5 (3.62), 377 (3.58), 535 (3.78), and 570 (3.7); $\nu_{max.}$ ca. 3250-2300, 1650, 1620, and 1600 cm^{-1}; *m/z* 280 (*M* + O_2, 16%), 248 (M^+, 98), 247 (58), 220 (47), 219 (20), 210

*The solution was prepared by adding methanolic potassium acetate to a solution of indoloquinoxalinium tosylate **18** in methanol and the spectrum was determined 1.5 min. after mixing.

(73), 207 (22), 105 (23), 85 (32), 83 (55), 79 (25), 78 (49), 77 (32), 76 (24), 73 (21), 63 (68), 50 (22), 45 (25), 44 (100), and 43 (63).

A sample of photoproduct **15** was also obtained when a solution of indoloquinoxalinium tosylate **18** (100 mg) in the minimum amount of methanol was eluted through a column of neutral alumina. The purple eluate was evaporated to give 6-methylindolo[1,2-a]quinoxalin-7(5*H*)-one (**15**) (46.2 mg).

(ii) Quinoxaline **11** (0.5 g) and TFA (0.3 ml) in dry ether (90 ml) were irradiated (Method A) for 2 h. The resulting red precipitate was collected and washed with ether to give *7-hydroxy-6-methylindolo-*[1,2-a]*quinoxalin-5-ium trifluoroacetate* (**17**) (0.41 g, 56%),[25] m.p. above 220°C (decomp.) (from ethanol containing TFA) (Found: C, 60.0; H, 3.6; N, 7.7. $C_{18}H_{13}F_3N_2O_3$ requires C, 59.7; H, 3.6; N, 7.7%); $\nu_{max.}$ ca. 3200-2200, 1665, 1635, and 1625 cm^{-1}; δ 2.28 (3H, s, Me), 7.2-7.9 (5H, m, ArH), and 7.95-8.25 (3H, m, ArH); *m/z* 248 (*M*-CF_3CO_2H, 100%), 247 (50), 219 (19), 124 (18), 109 (15), 102 (18), 77 (22), 76 (33), 75 (19), 51 (26), 50 (31), 45 (14), and 43 (16).

(iii) Quinoxaline **11** (1.0 g) and PTSA (0.96 g) in methanol (175 ml) was irradiated (Method B) for 3 h. Most of the methanol was evaporated and dry ether (100 ml) was added to the residual solution which was cooled. The resulting red solid was collected and washed with ether to give *7-hydroxy-6-methylindolo*[1,2-a]*quinoxalin-5-ium* p-*toluenesulphonate* **18** (1.1 g, 65%),[25] m.p. 252-257°C (decomp.) (from ethanol) (Found: C, 65.4; H, 4.8; N, 6.5. $C_{23}H_{20}N_2O_4S$ requires C, 65.7; H, 4.8; N, 6.7%); $\lambda_{max.}$ [0.25 M H_2SO_4 in methanol/water (ca. 9:1)] 355 (3.73), 373 (3.85), and 477 (3.89); $\nu_{max.}$ ca. 3200-2300 and 1622 cm^{-1}; δ (90 MHz, DMSO-d_6) 2.26 (3H, s, tosyl Me), 2.90 (3H, s, Me), 7.08-7.17 and 7.52-7.60 (4H, AA'BB' multiplet, tosyl ArH), 7.25-7.8 (5H, m, ArH), and 8.15-8.50 (3H, m, ArH); *m/z* 248 (*M*-$C_7H_7SO_3H$, 100%), 246 (55), 219 (20), 172 ($C_7H_7SO_3H$, 29), 124 (28), 107 (31), 102 (18), 91 (79), 90 (22), 89 (23), 77 (40), 76 (32), 65 (46), 63 (28), 51 (32), and 50 (39).

(iv) Quinoxaline **11** (1.0 g) and PTSA (0.95 g) in methanol (5 ml) and ether (100 ml) was irradiated (Method A) for 2 h to give indolo[1,2-a]quinoxalinium tosylate **18** (0.76 g, 45%) as a red solid which was filtered off and washed with dry ether.

Irradiation of 2-Benzoyl-3-methylquinoxaline (**11**) *and Determination of the Yield of Indolo*[1,2-a]*quinoxalinium Salt* **17** *or* **18** *from the U.V./Visible Spectrum.* - Solutions of quinoxaline **11** were irradiated in methanol or THF (Method B). Samples were taken and diluted with the appropriate amount of methanol and 2.5 M sulphuric acid in order to give a 0.25 M acid solution which was used to record the spectrum.

(i) A degassed solution of quinoxaline **11** (50 mg) and PTSA (48 mg) in methanol (10 ml) was irradiated for 15 min. without agitation. A sample (1 ml) was diluted to a volume of 50 ml by adding 2.5 M sulphuric acid (5 ml) and methanol. The yield of indoloquinoxalinium salt **18** was determined from the absorbance at 477 nm.

The irradiation was repeated as above except that a stream of gas (nitrogen or oxygen) was passed through the solution during the irradiation. Yields for all three irradiations are given in the Table.

(ii) A solution of quinoxaline **11** (100 mg) was irradiated in the presence of PTSA (1, 2, 5, and 50 equivalents) in methanol (10 ml).[25] Yields of indoloquinoxalinium salt **18**, determined from the spectrum as

in (i) above, were 71, 76, 78, and 72% respectively after 1 h and 68, 74, 77, and 72% respectively after 2 h. After irradiation for 7 h in the presence of 1 equivalent of PTSA, the yield was 47%.

(iii) A solution of quinoxaline **11** (50 mg) and TFA (0.01, 0.1, 1, 2, and 10 equivalents) in THF (10 ml) was irradiated for 20 min., with agitation of the solution every 5 min. Yields of indoloquinoxalinium salt **17**, determined from the spectrum as in (i) above, were ca. 0.4, ca. 0.4, 1.0, 1.3, and 8.5% respectively.

Irradiation of 2-*Aroylquinoxalines* **12**, **23**, *and* **24** *in the presence of PTSA*. - A solution of the quinoxaline (1 mmol) and PTSA (237 mg) in methanol (25 ml) was irradiated (Method B) for 4 h. The internal walls of the tube were scraped at intervals to remove deposited photoproduct. After evaporation of most of the solvent, the mixture was cooled, a little ether was added and the product was collected and washed with ether. Yield, m.p., and spectroscopic data for each photoproduct are given below.

6-*Benzyl*-7-*hydroxyindolo*[1,2-a]*quinoxalin*-5-*ium* p-*toluenesulphonate* (**19**) (228 mg, 46%), m.p. above 330°C (decomp.) (from dimethylformamide) (Found: C, 69.65; H, 4.7; N, 5.7. $C_{29}H_{24}N_2O_4S$ requires C, 70.1; H, 4.9; N, 5.6%); $\nu_{max.}$ ca. 3300-2000 and 1615 cm^{-1}; δ (80 MHz, DMSO-d_6) 2.28 (3H, s, Me), 4.71 (2H, s, CH_2), 7.0-7.9 (14H, m, ArH), and 8.2-8.65 (3H, m, ArH); *m/z* 324 (*M*-$C_7H_7SO_3H$, 62%), 323 (14), 246 (12), 153 (16), 146 (11), 91 (18), 83 (18), 77 (17), 76 (14), 71 (19), 70 (11), 69 (17), 57 (59), 56 (14), 55 (43), 51 (12), 45 (20), 44 (25), and 43 (100). 7-*Hydroxy*-6,8,10-*trimethylindolo*[1,2-a]*quinoxalin*-5-*ium* p-*toluenesulphonate* (**26**) (336 mg, 75%) 291-293°C (decomp.) (from methanol) (Found: C, 66.8; H, 5.45; N, 6.1. $C_{25}H_{24}N_2O_4S$ requires C, 66.9; H, 5.4; N, 6.25%); $\nu_{max.}$ ca. 3200-2300 and 1610 cm^{-1}; δ (DMSO-d_6 containing TFA and CD_3OD) 2.27 (3H, m, tosyl Me), 2.55 (3H, s, Me), 2.79 (3H, s, Me), 3.01 (3H, s, Me), 7.04 (1H, broad s, 9-H), 7.11-7.14 and 7.51-7.54 (4H, AA'BB' multiplet, tosyl ArH), 7.38-7.47 (1H, m, ArH), 7.6-7.72 (2H, m, ArH), 8.13 (1H, broad s, 11-H), and 8.51 (1H, broad d *J* 8 Hz, 1- or 4-H); *m/z* 276 (*M*-$C_7H_7SO_3H$, 100%), 275 (39), 172 ($C_7H_7SO_3H$, 6), 103 (9), 91 (18), 89 (11), 77 (16), 65 (12), and 51 (14). 7-*Hydroxy*-2,3,6-*trimethylindolo*[1,2-a]-*quinoxalin*-5-*ium* p-*toluenesulphonate* (**27**) (235 mg, 52%), m.p. 243°C (decomp.) (from ethanol) (Found: C, 64.4; H, 5.2; N, 5.9. $C_{25}H_{24}N_2O_4S.H_2O$ requires C, 64.4; H, 5.6; N, 6.0%); $\nu_{max.}$ ca. 3300-2200, 1675, and 1620 cm^{-1}; δ (80 MHz, DMSO-d_6) 2.3 (3H, s, tosyl Me), 2.44 (3H, s, Me), 2.49 (3H, s, Me), 2.97 (3H, s, Me), 7.07-7.15 and 7.47-7.55 (4H, AA'BB' multiplet, tosyl ArH), 7.34-7.63 (1H, m, ArH), 7.4 (1H, s, 1- or 4-H), 7.66-7.93 (1H, m, ArH), 8.20 (1H, s, 1- or 4-H), 8.32 (1H, apparent d *J* ca. 8 Hz, ArH), and 8.63 (1H, apparent d *J* ca. 8 Hz, ArH); *m/z* 276 (*M*-$C_7H_7SO_3H$, 100%), 138 (17), 91 (21), 77 (18), 65 (16) and 51 (11).

6,8,10-*Trimethylindolo*[1,2-a]*quinoxalin*-7(5H)-*one* (**25**). - Water (40 ml) was added to a solution of indoloquinoxalinium tosylate **26** (200 mg) in methanol (30 ml) and the solution was kept at ca. 4°C for 18 h. Filtration yielded 6,8,10-*trimethylindolo*[1,2-a]*quinoxalin*-7(5H)-*one* (**25**) (175 mg, 90%), m.p. 245°C (decomp.) (Found: C, 78.15; H, 5.8; N, 10.2. $C_{18}H_{16}N_2O$ requires C, 78.2; H, 5.8; N, 10.1%); $\nu_{max.}$ ca. 3000-2300, and 1650 cm^{-1}; δ (DMSO-d_6) 2.43 (3H, s, Me), 2.44 (3H, s, Me), 2.65 (3H, s, Me), 6.63 (1H, s, 9-H), 6.81-6.92 (2H, m, ArH), 6.96-7.03 (1H, m, ArH), 7.56 (1H, s, 11-H), 7.66 (1H, d *J* 7.9 Hz, 1- or 4-H), and 9.8 (1H, s, NH); *m/z* 276 (M^+, 100%), 275 (51), 247 (*M*-CHO, 7), 232 (12), 103 (15), 102

(12), 77 (24), 76 (16), 63 (11), and 51 (14).

Reaction of 6-*methylindolo*[1,2-a]*quinoxalin*-7(5H)-*one* (**15**) *with Oxygen.* - (i) A sample of indoloquinoxalinone **15**, on keeping after exposure to air, became contaminated with an impurity, presumably the hydroperoxide **33** and/or quinoxalinone **34** (or both) as shown by the presence in the mass spectrum of a peak at *m/z* 280 (Found: M^+ 280.0862. $C_{16}H_{12}N_2O_3$ requires M^+ 280.0848).

(ii) A solution (1 ml) of indoloquinoxalinone **15** [from **15** (46.2 mg) in methanol (50 ml)] was added to a methanolic solution of sodium methoxide [sodium (5.15 mg) in methanol (24 ml)]. The solution of the resulting anion **32** absorbed at ($\lambda_{max.}$) 365, 383, and 482 nm, and the absorbance at 482 nm was 0.735, 0.71, 0.68, 0.545, 0.305, and 0.02 measured 2, 5, 10, 30, 120 min. and 21.2 h respectively after mixing. The absorption of anion **32**, calculated by extrapolation to a time of 0.0 min. after mixing, was $\lambda_{max.}$ (log ε) 365 (3.47), 383 (3.53), and 482 nm (3.70). After 21.2 h, the absorption of the solution was $\lambda_{max.}$ 228.5, 280, and 338 nm.

(iii) Air was bubbled through a solution of the indoloquinoxalinium salt **18** (0.42 g) and sodium methoxide [from sodium (0.38 g)] in methanol (35 ml) for 5 h and the solution was left at room temperature for 16 h. The solution was filtered, the filtrate was evaporated, and the residue was dissolved in water. After acidification with glacial acetic acid, the solution was extracted into dichloromethane. Evaporation of the dried extract gave a crystalline residue which was crystallised from ethanol to give 1-(2-*carboxyphenyl*)-3-*methylquinoxalin*-2(1H)-*one* (**34**) (171 mg), m.p. 271-272°C (Found: C, 68.1; H, 4.4; N, 9.9. $C_{16}H_{12}N_2O_3$ requires C, 68.6; H, 4.3; N, 10.0%); $\lambda_{max.}$ 229 (ca. 4.4), 280 (3.82), and 338 (3.76); $\nu_{max.}$ ca. 3500-2300 and 1720 cm^{-1}; δ (DMSO-d_6) 2.47 (3H, s, Me), 6.45 (1H, dd *J* ca. 1.3 and 8 Hz, ArH), 7.27-7.39 (2H, m, ArH), 7.47 (1H, d, *J* 7.8 Hz, ArH), 7.71 (1H, apparent t *J* 7.6 Hz, ArH), 7.78-7.88 (2H, m, ArH), and 8.18 (1H, dd *J* ca. 1.4 and 7.8 Hz, ArH); *m/z* 280 (M^+, 98%), 236 (*M*-CO_2, 35), 235 (66), 234 (28), 208 (*M*-CO and CO_2, 50), 207 (100), 206 (47), 205 (20), 167 (22), 166 (22), 91 (20), 77 (29), and 65 (23).

O-*Acylation of Indoloquinoxalinium salts* **16**, **18**, **19**, **26**, and **27**. - Triethylamine (3 drops) was added to a suspension of the indoloquinoxalinium salt (**16**, **18**, **19** or **27**) (0.5 mmol) in acetic anhydride (2 ml) and the mixture was heated until a clear yellow solution was formed (2-3 min.). Cooling gave the *O*-acetate which was collected and crystallised from methanol containing a little acetic anhydride (unless otherwise stated). In a similar manner, using propionic anhydride, salt **26** was converted into an *O*-propionate. Yield, m.p., and spectroscopic data for each ester are as follows.

7-*Acetoxyindolo*[1,2-a]*quinoxaline* (**20**) (78%) m.p. 213-214°C (from acetic anhydride) (Found: C, 74.2; H, 4.4; N, 10.2. $C_{17}H_{12}N_2O_2$ requires C, 73.9; H, 4.4; N, 10.1%); $\nu_{max.}$ 1760 cm^{-1}; δ 2.5 (3H, s, Me), 7.33-7.42 (2H, m, 9- and 10-H), 7.46-7.56 (2H, m, 2- and 3-H), 7.71 (1H, d *J* 8.1, 1- or 4-H), 7.91 (1H, d *J* 7.9 Hz, 1- or 4-H), 8.29-8.33 (2H, m, 8- and 11-H), and 8.81 (1H, s, 6-H); *m/z* 276 (M^+, 10%), 234 (*M*-CH_2CO, 100), 233 (46), 102 (10), and 77 (11). 7-*Acetoxy*-6-*methylindolo*[1,2-a]-*quinoxaline* (**21**) (72%), m.p. 190°C (Found: C, 74.6; H, 4.7; N, 9.65. $C_{18}H_{14}N_2O_2$ requires C, 74.5;

H, 4.9; N, 9.7%); $\nu_{max.}$ 1760 and 1620 cm^{-1}; δ (^1H) 2.49 (3H, s, Me), 2.78 (3H, s, Me), 7.32-7.42 (2H, m, 9- and 10-H), 7.47-7.53 (2H, m, 2- and 3-H), 7.66 (1H, dd *J* ca. 1.0 and 8.0 Hz, 1- or 4-H), 7.85 (1H, dd *J* ca. 1.5 and 7.9 Hz, 1- or 4-H), and 8.32-8.37 (2H, m, 8- and 11-H); δ (^{13}C) 20.5 q (Me), 23.0 q (Me), 114.4 d, 118.9 d, 122.3 d, 123.8 d, 124.6 d (C-1, C-8, C-9, C-10, and C-11), 119.1 s (C-7), 121.7 s (C-6a), 125.4 s or d and 125.7 s or d (C-3 and C-11c), 127.8 d (C-2), 129.3 d (C-4), 129.3 s, 129.5 s (C-7a and C-11a), 135.3 s (C-4a), 153.1 s (C-6), and 169.1 s (CO) (suggested assignments based on literature data for 3-acetoxyindole[26] and pyrrolo[1,2-a]quinoxaline[27]); *m/z* 290 (M^+, 10%), 248 (*M*-CH_2CO, 100), 247 (44), 102 (14), 77 (33), 76 (60), and 75 (42). *7-Acetoxy-6-benzylindolo*[1,2-a]*quinoxaline* (**22**) (56%), m.p. 187-188°C (Found: C, 78.7; H, 5.0; N, 7.7. $C_{24}H_{18}N_2O_2$ requires C, 78.7; H, 5.0; N, 7.6%); $\nu_{max.}$ 1760 and 1615 cm^{-1}; δ (80 MHz) 2.26 (3H, s, Me), 4.53 (2H, s, CH_2), 7.2-7.7 (10H, m, ArH), 7.95 (1H, dd *J* ca. 1.9 and 7.6 Hz, ArH), and 8.37-8.49 (2H, m, ArH); *m/z* 366 (M^+, 6%), 325 (12), 324 (*M*-CH_2CO, 58), 322 (26), 246 (7), 146 (6), 91 (8),77 (9), 76 (10), 51 (6), and 43 (Ac^+, 100). *6,8,10-Trimethyl-7-propionoxyindolo*[1,2-a]*quinoxaline* (**28**) (73%), m.p. 182-183°C (Found: C, 75.8; H, 6.1; N, 8.5. $C_{21}H_{20}N_2O_2$ requires C, 75.9; H, 6.1; N, 8.4%); $\nu_{max.}$ 1750 cm^{-1}; δ 1.37 (3H, t *J* 7.5 Hz, propionyl Me), 2.55 (3H, s, Me), 2.59 (3H, s, Me), 2.70 (3H, s, Me), 2.76 (2H, q *J* 7.5 Hz, CH_2), 6.96 (1H, s, 9-H), 7.31-7.37 and 7.47-7.53 (2H, multiplets, 2- and 3-H), 7.83 (1H, dd, *J* 1.5 and 7.9 Hz, 1- or 4-H), 7.99 (1H, s, 11-H), and 8.34 (1H, dd *J* 1.0 and 8.3 Hz, 1- or 4-H); *m/z* 332 (M^+, 11%), 277 (25), 276 (*M*-CH_3CHCO, 100), and 275 (71). *7-Acetoxy-2,3,6-trimethylindolo*[1,2-a]*quinoxaline* (**29**) (90%), m.p. 250-251°C (Found: C, 75.2; H, 5.7; N, 8.8. $C_{20}H_{18}N_2O_2$ requires C, 75.4; H, 5.7; N, 8.8%); $\nu_{max.}$ 1760 cm^{-1}; δ 2.33 (3H, s, Me), 2.43 (3H, s, Me), 2.48 (3H, s, Me), 2.75 (3H, s, Me), 7.35-7.4 (1H, m, 10-H), 7.48-7.51 (1H, m, 9-H), 7.6 (1H, s, 1- or 4-H), 7.64 (1H, d *J* 8.0 Hz, 11-H), 8.09 (1H, s, 1- or 4-H), and 8.34 (1H, d *J* 8.6 Hz, 8-H); *m/z* 318 (M^+, 14%), 277 (12), 276 (*M*-CH_2CO, 68), 275 (56), 77 (9), 76 (7), 51 (5), and 43 (Ac^+, 100).

Luminescence of 2-*Benzoyl*-3-*methylquinoxaline* (**11**). - The phosphorescence spectrum, $\lambda_{max.}$ 484 and 512 nm (excitation at 340 nm; delay and gate times 0.01 and 5 msec respectively), was determined for a glass (formed from a 0.03% solution of ketone **11** in methylcyclohexane) at 77°K using a Perkin-Elmer LS-5B luminescence spectrometer.

Ketone **11** has a u.v. absorption at $\lambda_{max.}$ (EtOH) 246 (log ε 4.52) and 321 nm (3.81).[28]

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