

## Internuclear Cyclisation. Part XXX.<sup>1</sup> The Photolysis of 2-Iodo-2'-, -3'-, and -4'-methoxy-*N*-alkylbenzanilides in Benzene

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The title reactions give the expected variety of products derived from the radicals formed by loss of iodine. The initial reactions of these radicals are identified as cyclisation to  $\gamma$ - and  $\delta$ -lactam intermediates, together with a minor amount of 1,5-hydrogen transfer from the *N*-alkyl group. The  $\delta$ -lactam intermediates are oxidised to *N*-alkylphenanthridinones, and 1,5-hydrogen transfer results in dealkylation at the nitrogen atom. The  $\gamma$ -lactam intermediates react by several pathways. That from the 2'-methoxy-amide predominantly dimerises, whilst from the 3'-methoxy-amide a major product is a spirocyclohexenone  $\gamma$ -lactam, the result of demethylation at the oxygen atom (possibly catalysed by hydrogen iodide liberated during the reaction).

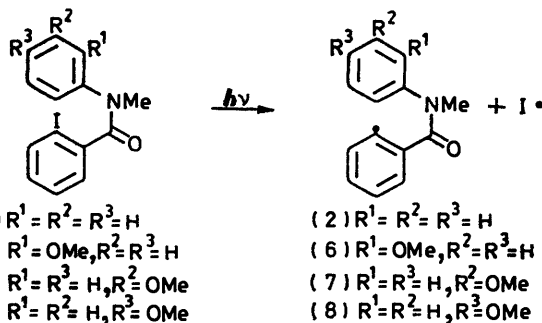
The  $\gamma$ -lactam intermediate from the 4'-methoxy-amide also suffers demethylation at the oxygen atom to give a spirocyclohexadienone  $\gamma$ -lactam; this is photoisomerised under the reaction conditions to the stereoisomeric cyclopentenones (23) and (24). Further products believed to be formed *via* this  $\gamma$ -lactam intermediate are 3-methoxy-*N*-methylphenanthridinone and 4'-methoxy-*N*-methylbiphenyl-2-carboxamide. The possibility is discussed that these two products may also arise by photoinduced rearrangement of a primary photoproduct.

IN Part XXVI<sup>2</sup> the products of photolysis of 2-iodo-*N*-methylbenzanilide (1) were reported. The results were discussed in terms of reactions of an initially formed aryl radical (2), and the products were, in general, similar to those produced from the same radical generated by alternative procedures. However minor differences were evident, and these were attributed to interception of intermediates by iodine or hydrogen iodide formed during the photochemical reaction.

When analogues of the radical (2) bearing a methoxy-substituent in the anilide ring had been generated by non-photochemical methods, several unexpected results had been found;<sup>3</sup> it was therefore of interest to extend the photochemical reaction to such analogues. The iodo-amides (3)–(5) were prepared<sup>†</sup> by conventional

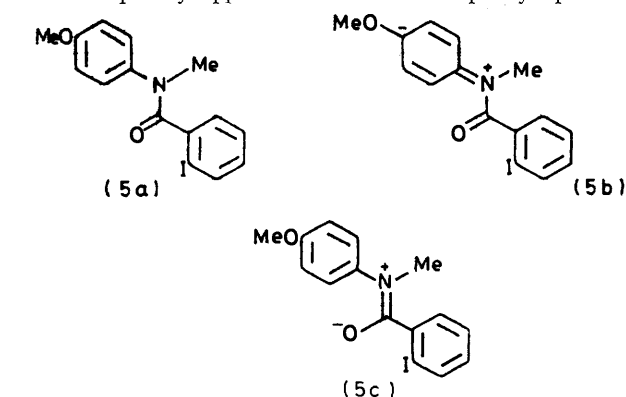
† In the course of these preparations, it was found that crystallisation of the 2-iodo-4'-methoxy-*N*-methylbenzanilide was particularly difficult. At first this was associated with an impurity (*ca.* 10%) exhibiting an *N*-methyl resonance 0.32 p.p.m. upfield from the main *N*-methyl singlet. However, it was subsequently appreciated that this 'impurity' peak was

procedures, and their photochemistry in benzene was investigated. The products obtained in these reactions fall into three distinct categories: (i) those which arise by simple radical reactions; (ii) those which require the



intervention of iodine or hydrogen iodide; and (iii) those which result from secondary photochemical reactions of primary products. Some of the simple radical products had not been detected in earlier work with the techniques then available, and this prompted a reinvestigation of the non-photochemical routes to radicals (6)–(8). A comparative survey of several such reactions is presented in the following paper.<sup>4</sup>

*Photolysis of 2-Iodo-2'-methoxy-*N*-methylbenzanilide (3) in Benzene.*—Photolysis of the 2'-methoxy-amide (3) by the general procedure previously described<sup>2</sup> gave small yields of the expected 4-methoxy-*N*-methylphenanthridinone (9) and 2'-methoxybenzanilide (10). The major product, obtained as a single chromatographic fraction, was identified spectroscopically as a mixture of the isomeric cyclohexadienyl dimers (11).<sup>5</sup> In earlier work, employing copper-catalysed diazonium salt decomposi-



due to the *trans*-conformer (5a) whereas the main *N*-methyl resonance corresponded to the *cis*-conformer. These peaks coalesced on heating to *ca.* 60°; the coalescence temperature for 2-iodo-*N*-methylbenzanilide itself was about 30°. Accurate measurements have not been made, but it seems reasonable to associate the higher coalescence temperature for the methoxy-derivative with an increased double-bond character in the amide C–N bond [structure (5c)]. This can in turn be associated with suppression of conjugation between the nitrogen lone pair and the aniline ring by the methoxy-substituent [unimportance of structure (5b)].

<sup>1</sup> Part XXIX, D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 118.

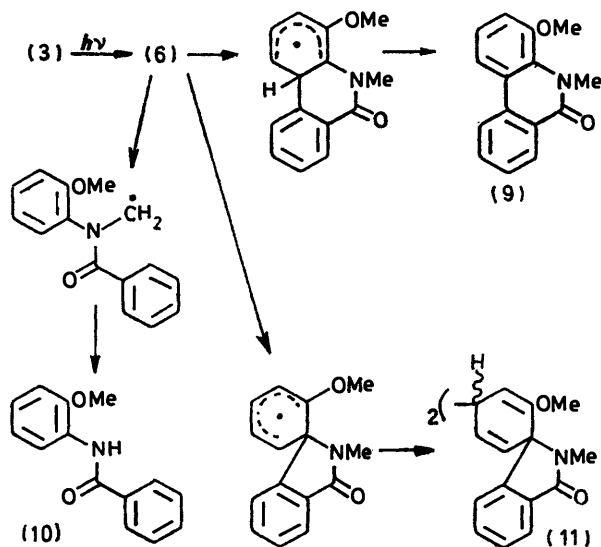
<sup>2</sup> D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc. (C)*, 1971, 116.

<sup>3</sup> D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc. (C)*, 1967, 1518, and earlier papers in this series.

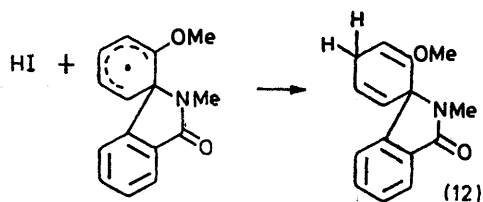
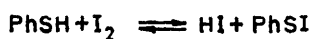
<sup>4</sup> D. H. Hey, G. H. Jones, and M. J. Perkins, following paper.

<sup>5</sup> D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 105.

tion as a means of generating the aryl radical (6), the spiro-dienyl dimers had not been identified.<sup>3</sup>

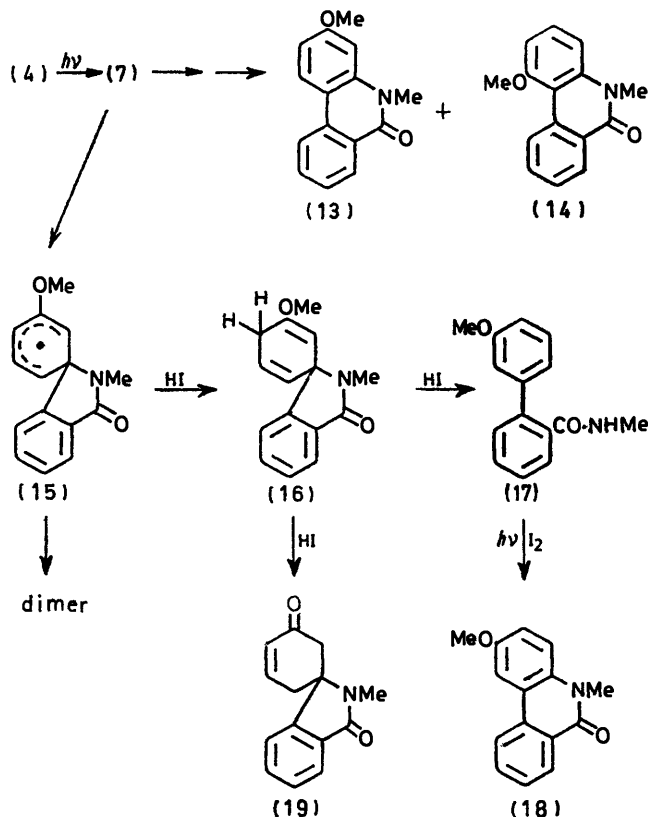


Because very little phenanthridinone is formed in this reaction, very little displacement of hydrogen from the anilide ring occurs, and consequently there is little opportunity for hydrogen iodide formation. Therefore the possible complications which may be caused by the presence of this reducing acid<sup>2</sup> are largely circumvented. However, when the photolysis was repeated in the presence of benzenethiol, the diene (12) was detected amongst the products. This probably results from the sequence of reactions shown. It is possible that benzenethiol itself is the hydrogen donor; however it has qualitatively been observed that addition of hydrogen iodide is more effective, and we tentatively prefer the mechanism indicated.



*Photolysis of 2-Iodo-3'-methoxy-N-methylbenzanilide (4) in Benzene.*—The expected products from photolysis of the 3'-methoxy-amide (4), namely 1- and 3-methoxy-N-methylphenanthridinones [(14) and (13)] (26 and 24%, respectively) and 3'-methoxybenzanilide were formed, but no more than a trace of spirocyclohexadienyl dimer was detected. Instead, additional products included the biphenyl derivative (17), the unexpected 2-methoxy-N-methylphenanthridinone (18), and the spirocyclohexenone (19). When the photolysis was repeated in the presence of pyridine, added to remove hydrogen iodide,<sup>2</sup>

none of the products (17)—(19) was formed. Under these conditions chromatographic examination of the products revealed a substantially increased proportion of dimers. One possible rationalisation for the formation of the three products (17)—(19) is that in the absence of pyridine, hydrogen iodide intercepts the



$\gamma$ -lactam cyclohexadienyl radical (15) to give the diene (16), which is rapidly isomerised by acid to give (17) or (19). Photolysis of (17) in the presence of iodine could then give (18). Support for this route to the enone (19) is presented in Part XXXI,<sup>4</sup> but the formation of the biphenyl derivative (17) in this way has not been established, and the high yield of an 'unexpected' phenanthridinone in the photolysis of the 4'-methoxy-amide (see later) suggests that some other mechanism may also be operative in the formation of the phenanthridinone (18).

*Photolysis of 2-Iodo-4'-methoxy-N-methylbenzanilide (5) in Benzene.*—Examination of the products of the photolysis of the 4'-methoxy-amide (5) by g.l.c. suggested the formation of the expected 2-methoxy-N-methylphenanthridinone (18), but in a yield which was surprisingly large (48%) and out of line with the results of other reactions involving the radical (8).<sup>4</sup> Careful chromatographic scrutiny of the products, however, revealed the presence of a second, more soluble, phenanthridinone, identified as the unexpected 3-methoxyphenanthridinone (13). Both these compounds had the same retention characteristics on available g.l.c. columns, thus explaining the initial overestimation of the yield of (18). This

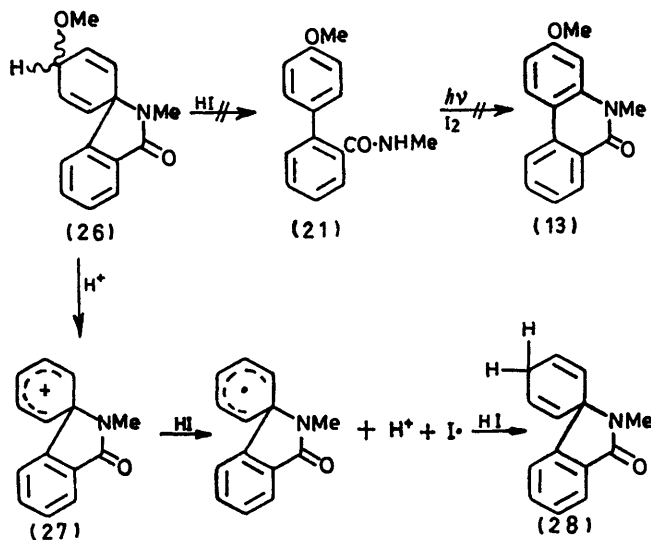
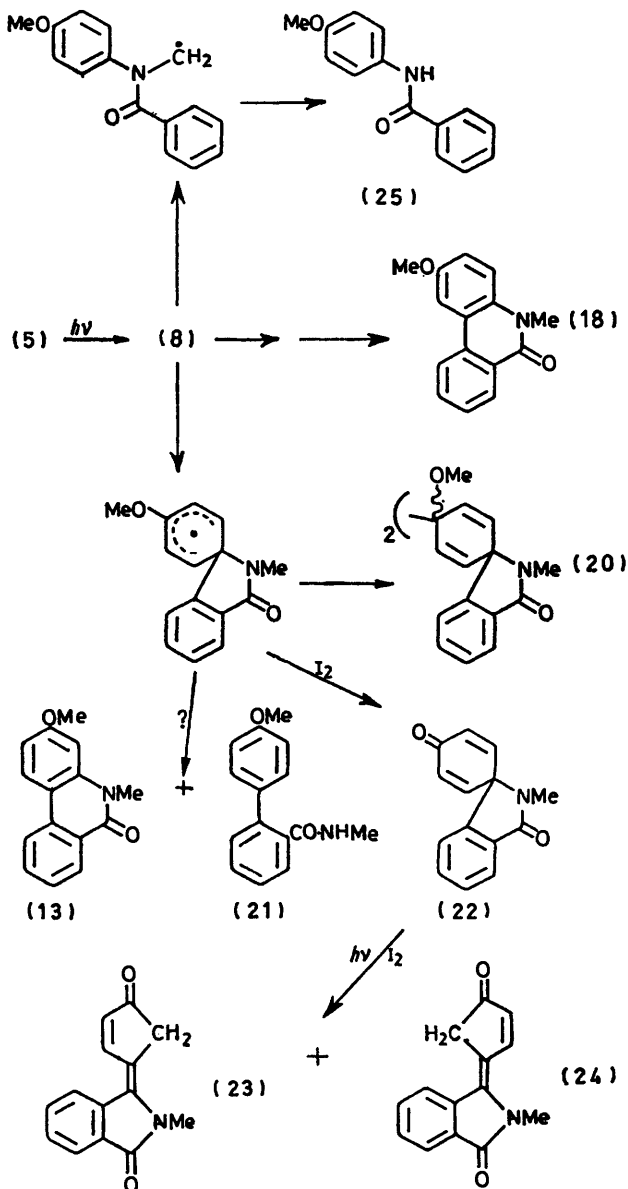
analytical difficulty was overcome by examining the photochemistry of *N*-ethyl-2-iodo-4'-methoxybenzanilide; g.l.c. separation of the 2- and 3-methoxy-*N*-ethylphenanthridinones presented no difficulty. These two isomers were formed in a ratio of 5:4; the combined yield was again *ca.* 50%.

In addition to the phenanthridinones, photolysis of (5) gave the stereoisomeric dimers (20) (in which coupling had taken place at the site of methoxy-substitution), the biphenyl derivative (21), the dienone (22), and isomeric

precedented in ground-state reactions,<sup>3</sup> and its photoisomerisation to (23) and (24) in the presence of iodine has already been noted.<sup>6</sup> Furthermore, the formation of the dimers (20) is mechanistically reasonable, although coupling of cyclohexadienyl radicals at a substituted carbon atom is unusual. Similar coupling of 'para' methoxy-substituted cyclohexadienyl radicals has been encountered elsewhere in the present work<sup>4,7</sup> but it could not be detected among the products from radical (8) generated by copper-catalysed decomposition of the corresponding fluoroborate.<sup>4</sup>

No wholly satisfactory rationalisation for the formation of compounds (13) and (21) in this reaction has been found. When the photolysis was repeated in the presence of pyridine, neither of these compounds was formed. Furthermore, compounds (23) and (24) were also absent from the products. Instead, a much increased yield of the dienone (22) was obtained, especially at low conversions of the iodo-amide (5), when it approached 50%. *N*-Ethyl-2-iodo-4'-methoxybenzanilide, on photolysis in the presence of pyridine, behaved similarly; examination of the product by g.l.c. confirmed the absence of *N*-ethyl-3-methoxyphenanthridinone.

One simple rationalisation for both the products (13) and (21), involving once again the formation of a diene (26), its acid-catalysed rearrangement to (21), and subsequent iodine-promoted cyclisation to give the phenanthridinone (13), does not stand up to experimental scrutiny. In the first place, dienes (26), synthesised by



another route,<sup>7,8</sup> are reduced by hydrogen iodide in benzene to give initially the parent spirodiene (28). This reaction probably involves one-electron reduction of the spirodienyl cation (27). The reverse of this, one-electron oxidation of a spirodienyl radical, was noted in Part

<sup>7</sup> D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 113.

<sup>8</sup> Part XXXII, D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 1162.

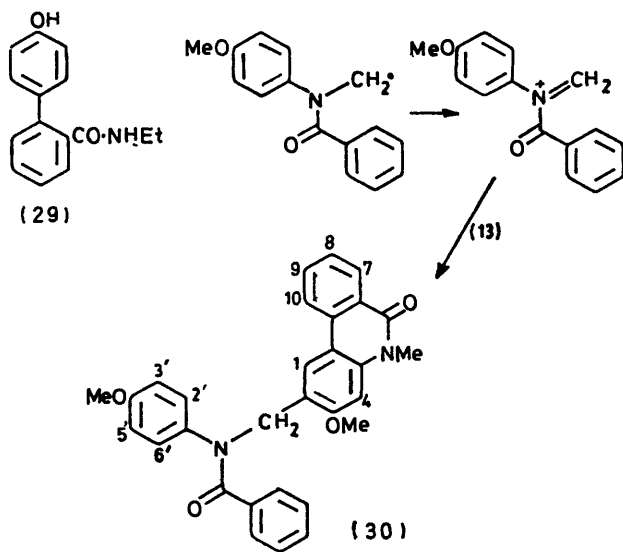
cyclopentenones (23) and (24), and a trace of 4'-methoxybenzanilide (25). The methoxybenzanilide is an expected product resulting from intramolecular hydrogen abstraction. Formation of the spirodienone (22) is also

<sup>6</sup> D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Comm.*, 1971, 47.

XXVII.<sup>5</sup> In that case, the oxidation reaction was favoured by the presence of an electron-donating methoxy-substituent. A second objection to this rationalisation for the formation of products (13) and (21) is that irradiation of (21) in the presence of iodine does not give the phenanthridinone (13), although irradiation of *N*-methylbiphenyl-2-carboxamide in the presence of iodine had given some *N*-methylphenanthridinone.<sup>2</sup>

It is tentatively suggested that both these products (13) and (21) are derived from the amide (5) by a two-quantum process, but the nature of the second photochemical step is as yet unidentified. In one control experiment, a benzene solution of the methoxy-dienes (26) was irradiated in the presence of iodine. The major products of this reaction were the cyclopentenones (23) and (24), presumably formed by way of the spiro-dienone (22), but these were accompanied by small quantities of both the carboxamide (21) and the methoxyphenanthridinone (13).

The last result is clearly only of qualitative significance. However, it must be remembered that the original photolysis system, containing as it does small quantities of hydrogen iodide and iodine formed *in situ*, cannot easily be reproduced, and that, although the product yields in several photolyses were reasonably constant, the concentrations of iodine and hydrogen iodide present during the reaction may be critically important. For instance it was found that if iodine was added to a photolysis of the *N*-ethyl analogue of (5), the yields of the two anomalous products analogous to (13) and (21) were drastically reduced. Under these conditions the yields of cyclopentenones were increased, and an additional product was the phenolic amide (29).



One further observation on the photolysis of (5) is of interest. In an isolated experiment, a trace of a dimeric product was isolated, spectroscopic data (n.m.r., mass) for which were consistent with its formulation as (30).

A reasonable rationalisation of the formation of this product involves the sequence of reactions shown, in which coupling of the two units occurs by electrophilic substitution into the 3-methoxyphenanthridinone.

#### EXPERIMENTAL

The photolysis procedure and general experimental and analytical details were as described in Part XXVI.<sup>3</sup>

**Preparations of Substituted *N*-Alkyl-2-iodobenzanilides.**—These followed the general procedure previously given for *N*-methyl-2-iodobenzanilide.<sup>3</sup> The intermediate 2-iodo-2'-methoxybenzanilide, m.p. 113–115° (Found: C, 47.6; H, 3.3; N, 4.2. C<sub>14</sub>H<sub>12</sub>INO<sub>2</sub> requires C, 47.7; H, 3.4; N, 4.0%), 2-iodo-3'-methoxybenzanilide, m.p. 153–155° (Found: C, 47.95; H, 3.4; N, 4.3%), and 2-iodo-4'-methoxybenzanilide, m.p. 167–169° (Found: C, 48.1; H, 3.3; N, 4.0%) all gave acceptable elemental analyses, as did the *N*-alkyl derivatives 2-iodo-2'-methoxy-*N*-methylbenzanilide, m.p. 122–123° (Found: C, 49.2; H, 4.1; N, 3.8%). C<sub>15</sub>H<sub>14</sub>INO<sub>2</sub> requires C, 49.0; H, 3.8; N, 3.8%), 2-iodo-3'-methoxy-*N*-methylbenzanilide, m.p. 58.5–61° (Found: C, 49.2; H, 3.8; N, 3.85%), 2-iodo-4'-methoxy-*N*-methylbenzanilide, m.p. 53–57.5° (Found: C, 49.45; H, 3.9; N, 3.9%), and *N*-ethyl-2-iodo-4'-methoxybenzanilide, m.p. 52–57° (Found: C, 50.6; H, 4.1; N, 3.7. C<sub>16</sub>H<sub>16</sub>INO<sub>2</sub> requires C, 50.4; H, 4.2; N, 3.7%). These *N*-alkyl derivatives exhibited a strong carbonyl absorption at 1650 cm<sup>-1</sup>. Despite the wide melting range of the last two, no impurities were detectable by n.m.r., g.l.c., or t.l.c. (see footnote in Discussion section).

**Photolysis Experiments.**—(i) 2-Iodo-2'-methoxy-*N*-methylbenzanilide (3).—The amide (1.5 g) in benzene (450 ml) was irradiated for 3 h; g.l.c. then indicated that consumption of starting material was ca. 95% complete. The benzene solution was washed thoroughly with aqueous 5% sodium thiosulphate, and with water, and then dried (MgSO<sub>4</sub>). Residual solids were washed from the photolysis apparatus with chloroform-ethanol (20 : 1); the resulting solution was separately washed with sodium thiosulphate solution and with water, and dried, and was then combined with the dried benzene solution. G.l.c. indicated the formation of 2'-methoxybenzanilide (2.5% based on starting material consumed) and 4-methoxy-*N*-methylphenanthridinone (9) (4%). Column chromatography of the reaction products gave a fraction which, after removal of solvent, left a yellow amorphous solid having spectroscopic (n.m.r.) characteristics and t.l.c. behaviour in accord with its formulation as the dimer (11) (ca. 45%). The material was evidently less pure than was the same dimer obtained by an alternative route described in Part XXVII;<sup>5</sup> it has not been further investigated.

When a similar photolysis of the amide (1 g) was conducted in the presence of benzenethiol (2 g), a major product in the early stages of the photolysis had g.l.c. retention characteristics (on FFAP and versamid) indistinguishable from those of authentic diene (12).<sup>7</sup>

(ii) 2-Iodo-3'-methoxy-*N*-methylbenzanilide (4).—The iodoamide (2 g) in benzene (450 ml) was irradiated for 12 h g.l.c. then revealed the consumption of starting material to be 89%. The mixture was worked up as described for the 2'-methoxy-isomer. G.l.c. analysis of the products then showed the formation of 1-methoxy-*N*-methylphenanthridinone (14) (26%, based on starting material consumed),

3-methoxy-*N*-methylphenanthridinone (13) (24%), 3'-methoxybenzanilide (1%), and 3'-methoxy-*N*-methylbiphenyl-2-carboxamide (17) (5%). Column chromatography on neutral alumina (benzene eluant) gave a major fraction containing the phenanthridinones, unchanged starting material, and methoxybenzanilide. This fraction was carefully rechromatographed by a combination of column and preparative layer techniques to isolate the two phenanthridinones. 1-Methoxy-*N*-methylphenanthridinone crystallised in needles (from ethanol), m.p. 151–152° (Found: C, 75.4; H, 5.5; N, 6.1. C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub> requires C, 75.3; H, 5.4; N, 5.9%),  $\tau$  0.87 (1H, d, H-10), 1.44 (1H, d, H-7); 2.2–2.6 (2H, m, H-8 and H-9), 2.64 (1H, t, H-3), 3.03 (1H, d, H-4), 3.2 (1H, d, H-2), 6.0 (3H, s, OMe), and 6.26 (3H, s, NMe). 3-Methoxy-*N*-methylphenanthridinone crystallised in needles (from ethanol–light petroleum), m.p. 92–94° (Found: *M*, 239. C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub> requires *M*, 239),  $\tau$  1.55 (1H, d, H-7), 1.95 (2H, d, H-1 and H-10), 2.36 and 2.57 (2H, m, H-8 and H-9), and 3.2 (2H, m, H-2 and H-4). The protons at C-2, C-3, and C-4 gave rise to a highly perturbed ABX pattern which was reproduced by computer simulation with typical *ortho* splittings (*J* ca. 8 Hz) for *J*<sub>2,3</sub> and *J*<sub>2,4</sub>. The compounds were indistinguishable from samples isolated from diazonium decompositions<sup>4</sup> and from pyrolysis of spirodienyl dimers.<sup>5</sup> In addition, a trace (9 mg) of 2-methoxy-*N*-methylphenanthridinone was isolated and similarly identified by comparison with authentic material. Elution with benzene–methylene chloride gave the 3'-methoxy-*N*-methylbiphenyl-2-carboxamide, the identity of which was again confirmed by comparison with authentic material.<sup>1</sup> Further elution gave a pale brown solid (230 mg) which crystallised from ethanol–light petroleum in plates, m.p. 139–141°. This product is considered to be 2-methyl-isoindoline-1-spiro-1'-cyclohex-4'-ene-3,3'-dione (19) on the basis of spectroscopic evidence (Found: *M*<sup>+</sup>, 227.0949. C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub> requires *M*, 227.0946),  $\nu_{\max}$  1700 ( $\gamma$ -lactam) and 1670 cm<sup>-1</sup> ( $\alpha\beta$ -unsaturated ketone),  $\tau$  2.1–2.6 (4H, m, aromatic), 2.88 (1H, dq, *J* 10 and 3.5 Hz, H-5'), 3.64 (1H, dt, *J* 10 and 2 Hz, H-4'), 6.95 (3H, s, NMe), and 7.26 (4H, m, H-2' and H-6'). Irradiation at  $\tau$  7.26 simplified the signals due to H-4' and H-5' to doublets (*J* 10 Hz). Further elution with methylene chloride and chloroform gave a trace of material which may have contained spirodienyl dimers. However, when a solution of the iodo-amide (1 g) in benzene (450 ml) was irradiated in the presence of pyridine (1 g) and the products were examined by g.l.c. and t.l.c., the 2-methoxy-*N*-methylphenanthridinone, the biphenyl-carboxamide, and the cyclohexenone (19) could not be detected. Instead, a product with the retention characteristics of spirodienyl dimers<sup>5</sup> was formed in substantial yield but not isolated.

(iii) 2-Iodo-4'-methoxy-*N*-methylbenzanilide (5).—The amide (2.1 g) in benzene (450 ml) was irradiated for 14 h; g.l.c. then showed that 84% of the starting material had disappeared. The following products were estimated by g.l.c.: 2-methoxy- (18) and 3-methoxy-*N*-methylphenanthridinone (13) (together 48% based on starting material consumed), 4'-methoxybenzanilide (1%), 4'-methoxy-*N*-methylbiphenyl-2-carboxamide (21) (13%), and the spirodienone (22) (6%).<sup>9</sup> When the progress of a similar photolysis had been monitored by g.l.c., it had been found that the yield of dienone remained low throughout the course of the reaction. Column chromatography of the products on

neutral alumina gave a major fraction (eluted with benzene) containing the phenanthridinones, from the n.m.r. spectrum of which it was determined that the yield of the 3-methoxy-derivative was ca. 20%. Further elution, with benzene–methylene chloride, yielded a fraction comprising the dienone and the isomeric cyclopentenones (23) and (24). These crystallised together from ethanol (yield 165 mg, 16%). In a separate experiment, in which they were isolated from irradiation of compound (22) in the presence of iodine, careful chromatography afforded the individual isomers, both of which were obtained as fine yellow needles. The less polar (t.l.c.) isomer had m.p. 231–233° (Found: C, 74.6; H, 4.8; N, 6.1. C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub> requires C, 74.7; H, 4.9; N, 6.2%); the more polar isomer had m.p. 220–221° (Found: C, 74.3; H, 4.9; N, 6.15%). Both had  $\nu_{\max}$  1705 ( $\gamma$ -lactam) and 1680 cm<sup>-1</sup> (five-membered ring  $\alpha\beta$ -unsaturated ketone), and  $\lambda_{\max}$  (EtOH) 375 ( $\epsilon$  ca. 20,000). The n.m.r. spectra of the two compounds were similar. Both showed signals for aromatic protons between  $\tau$  1.8 and 2.5; in addition the spectrum of the isomer of m.p. 233° had peaks at  $\tau$  1.3 and 3.46 (each 1H, d, *J* 6 Hz, protons on cyclopentenone double bond which is part of a vinylogous amide system), 6.35 (3H, s, NMe), and 6.5 (2H, s, CH<sub>2</sub>), and that of the isomer of m.p. 221° had peaks at  $\tau$  1.1 and 3.53 (each 1H, d, *J* 6 Hz) and 6.5 (5H, s, NMe and CH<sub>2</sub>). On the basis of the chemical shift data the higher-melting isomer is tentatively assigned structure (24). Hydrogenation of either compound (10% Pd–C) gave an oil,  $\nu_{\max}$  1685 ( $\gamma$ -lactam) and 1740 cm<sup>-1</sup> (cyclopentanone). Elution of the column with methylene chloride–chloroform finally gave a mixture of two compounds considered to be stereoisomers of bi-(2-methyl-4'-methoxy-3-oxoisoindoline-1-spiro-1'-cyclohexa-2',5'-dien-4'-yl) (20), which separated from ethanol as a white powder, m.p. 212–218° (76 mg, 7%) (Found: C, 74.6; H, 5.7; N, 5.7. C<sub>30</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> requires C, 75.0; H, 5.8; N, 5.8%),  $\nu_{\max}$  1695 cm<sup>-1</sup> ( $\gamma$ -lactam),  $\tau$  1.8–2.6 (8H, m), 3.9 (8H, ABq, *J* 10 Hz), 6.6 (6H, s), and 7.0 (6H, s).

In one experiment, an additional product, eluted between the cyclopentenones and the spiro-dimer, was isolated. It crystallised from ethanol in needles, m.p. 208–209° (ca. 3% yield). This product is considered to have structure (30) in view of the following spectral characteristics:  $\nu_{\max}$  1640 and 1620 cm<sup>-1</sup> (the latter is characteristic of a 3-substituted *N*-alkylphenanthridinone<sup>5</sup>),  $\tau$  1.45 (1H, d, H-7), 1.6 (1H, s, H-1), 1.8 (1H, d, H-10), 2.0–2.9 (7H, m), 3.19 (4H, ABq, *J* 9 Hz, H-2', H-3', H-5', and H-6'), 4.77 (2H, s, N-CH<sub>2</sub>), ca. 6.23 (6H, 2, s, 2-OMe), and 6.33 (3H, s, NMe), *m/e* 478 (*M*<sup>+</sup>), 252 [*m*\* 132.8 (478 → 252)], 222 [*m*\* 195.6 (252 → 222)], 105, and 77 [*m*\* 56.5 (105 → 77)] (primary fragmentation is across the N-CH<sub>2</sub> group, and is followed by loss of formaldehyde). The compound was not detected in subsequent experiments.

When the photolysis of the iodoamide (2 g) was repeated in the presence of pyridine, identified products included 2-methoxy-*N*-methylphenanthridinone (18) (28%), the spirodienone (22) (19%), and spiro-dimers (5%). The 3-methoxy-*N*-methylphenanthridinone, 4'-methoxy-*N*-methylbiphenyl-2-carboxamide and the cyclopentenones were not detected. The progress of this reaction was monitored by g.l.c., and in the early stages (ca. 10% conversion), the yield of spirodienone was ca. 45%.

(iv) *N*-Ethyl-2-iodo-4'-methoxybenzanilide.—The product distribution from photolysis of this compound in benzene essentially paralleled that found for the *N*-methyl analogue [see (iii)]. However, direct estimation of the isomeric

<sup>9</sup> D. H. Hey, J. A. Leonard, C. W. Rees, and A. R. Todd, *J. Chem. Soc. (C)*, 1967, 1513.

methoxyphenanthridinones by g.l.c. was possible in this case. The ratio of 2-methoxy-*N*-ethylphenanthridinone to 3-methoxy-*N*-ethylphenanthridinone was determined to be 5 : 4. Two yellow products were detected in the reaction mixture which, from their behaviour on t.l.c., were assumed to be the *N*-ethyl analogues of (23) and (24). These products have not, however, been isolated, but the n.m.r. spectrum of a chromatographic fraction containing both showed the characteristic resonances of the *N*-ethyl substituents and the AB patterns of the vinylogous amide groupings ( $J$  6 Hz).

Photolysis of the iodo-amide in the presence of pyridine gave no detectable 3-methoxy-*N*-ethylphenanthridinone (g.l.c.) or cyclopentenones (t.l.c.).

The photolysis of this iodo-amide (2 g) and iodine (200 mg) in benzene (450 ml) was also investigated. Disappearance of starting material occurred more slowly than in the absence of added iodine. The yield of the abnormal 3-methoxy-*N*-ethylphenanthridinone was drastically reduced (to ca. 3%) and that of the yellow cyclopentenones was qualitatively observed to be increased. Furthermore, an additional product, m.p. 183—185°, identified as 4'-hydroxy-*N*-ethylbiphenyl-2-carboxamide (29) (ca. 10%), was isolated from this reaction. This product was identified by comparison with a sample obtained by base-catalysed isomeris-

ation of 2-ethyl-4'-hydroxyisindoline-1-spiro-1'-cyclohexa-2',5'-diene-3-one.<sup>10</sup>

*Irradiation of the Dienes (26) in the Presence of Iodine.*—A mixture of the stereoisomeric dienes (26)<sup>7,8</sup> (200 mg) in benzene (450 ml) was irradiated in the presence of iodine. In experiments with 50 and 300 mg of iodine similar product distributions were found, although in the latter case the reaction was noticeably more rapid. The products included 3-methoxy-*N*-methylphenanthridinone (13) (ca. 10%; g.l.c.) and 4'-methoxy-*N*-methylbiphenyl-2-carboxamide (21) (ca. 5%; g.l.c.). The presence of these products was substantiated by t.l.c., which revealed that the major products were the isomeric cyclopentenones (23) and (24). The substitution pattern of the phenanthridinone was further substantiated by isolation and comparison with authentic material.

We thank the S.R.C. for a Studentship (to G. H. J.) and King's College, London, for financial assistance.

[1/2087 Received, 8th November, 1971]

<sup>10</sup> D. H. Hey, J. A. Leonard, T. M. Moynehan, and C. W. Rees, *J. Chem. Soc.*, 1961, 232.