Internuclear Cyclisation. Part XXXI.[1] Cyclisation of 2-(N-Alkyl-N-phenylcarbamoyl)phenyl Radicals: Formation of Cyclohexadienones and Cyclohexadienyl Iodides by scavenging of the Spiro-γ-lactam Intermediate

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A comparative survey has been made of the products of homolytic decomposition of 2-(N-alkyl-N-phenylcarbamoyl)benzenediazonium fluoroborates under a variety of conditions, and of those of photolysis of the corresponding N-alkyl-2-iodobenzanilides. Copper-catalysed decomposition of the diazonium salts in acetone purged with oxygen gives cyclohexadienones, the yields of which reflect the extent of radical cyclisation to γ-lactam intermediates. Decomposition of the diazonium salts induced by sodium iodide in methylene chloride containing a little added iodine gives cyclohexadienyl iodides. structures of which have been established by Ag⁺-catalysed methanolysis to cyclohexadienyl methyl ethers. and/or by photolysis, which gives cyclohexadienyl dimers.

INTRAMOLECULAR aromatic arylation[2] has found wide application in natural product synthesis, particularly in the alkaloid field. Recent examples have included closure of five-,[3] six-,[4] and seven-membered[5] rings and have involved a range of cyclisation procedures. In addition to cyclisations with simple displacement of a hydrogen atom, other examples involve spirocyclisation, usually to form cyclohexadienones. In such circumstances, the carbonyl oxygen atom of the dienone system may be derived from a phenolic hydroxy-group,[6] a phenoxide oxygen atom,[3] or a phenolic ether.[7] When the reaction leading to a dienone involves photochemical induction of the cyclisation step, a disadvantage is the photolability of the product. In one example this problem has been overcome by *in situ* reduction to the photostable dienol.[3]

Earlier papers in the present series have been concerned in particular with model systems in which intramolecular cationic or free radical arylation reactions have been employed to effect syntheses in the phenanthridinone series.[8] Our most recent work in this area has

[1] Part XXX, D. H. Hey, G. H. Jones, and M. J. Perkins, preceding paper.

[2] R. A. Abramovitch, *Adv. Free Radical Chem.*, 1967, **2**, 87; see also T. Kametani and K. Fukumoto, *J. Heterocyclic Chem.*, 1971, **8**, 341.

[3] *E.g.*, Z. Horii, Y. Nakashita, and C. Iwata, *Tetrahedron Letters*, 1971, 1167.

[4] B. Gregson-Allcott and J. M. Osbond, *Tetrahedron Letters*, 1969, 1771; B. Chauncy and E. Gellert, *Austral. J. Chem.*, 1970, **23**, 2503; G. Savona and F. Piozzi, *J. Heterocyclic Chem.*, 1971, **8**, 1627.

[5] P. W. Jeffs and J. F. Hansen, *J. Amer. Chem. Soc.*, 1967. **89**, 2798; O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *ibid.*, 1968, **90**, 776.

[6] T. Kametani, S. Shibuya, H. Sugi, O. Kusama, and K. Fukumoto, *J. Chem. Soc. (C)*, 1971, 2446.

[7] T. Kametani, M. Koizumi, and K. Fukumoto, *J. Chem. Soc. (C)*, 1971, 1792.

[8] D. H. Hey, *Quart. Rev.*, 1971, **25**, 483.

placed emphasis on free-radical cyclisations. In this paper a survey is presented of the results of the cyclisation of the 2-(N-alkyl-N-phenylcarbamoyl)phenyl radicals (1a—j) generated under a variety of conditions.

Whilst the range of structural types represented here is limited, condensed ring systems and, in particular, alkoxy-substitution, are common features in the naturally occurring molecules which have been the targets of this type of synthetic approach. Therefore, the structures investigated represent a useful range of model systems.
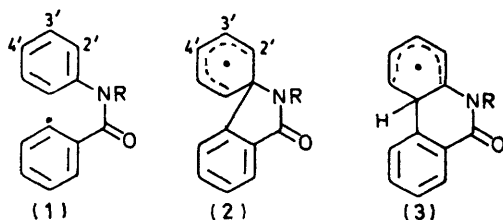
a; unsubst., R = Me
b; unsubst., R = Et
c; 2'-OMe, R = Me
d; 2'-OMe, R = Et
e; 3'-OMe, R = Me
f; 3'-OMe, R = Et
g; 4'-OMe, R = Me
h; 4'-OMe, R = Et
i; 2',3'-Benzo, R = Me
j; 3',4'-Benzo, R = Me

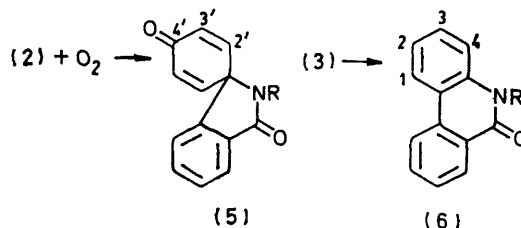Where relevant, suffixes a—j have also been used in conjunction with structures (2), (5), (7), (8), and (9)

In previous papers it has been indicated that the radical (1a) reacts by several competing pathways, in which cyclisation to a spiro-γ-lactam radical (2a) or a δ-lactam radical (3a), or intramolecular hydrogen abstraction from the N-methyl group, are the three principal alternatives. At room temperature the competition between these pathways appears to be almost independent of the reaction conditions, although the fates of the various secondary radicals are diverse. One important factor which influences the competition between cyclisation and intramolecular hydrogen transfer is believed to be the conformation of the aryl radical precursor,[9] for rotation about the C–N bond of the amide is almost certainly slow compared with intramolecular reaction. The hydrogen transfer process is invariably
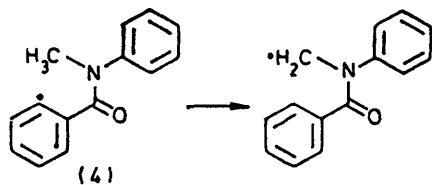
a minor pathway, and thus an amide conformation with the aryl groups *trans* (4) must be relatively unimportant.*

* This is in contrast with the data reported for several other tertiary anilides.[10] However, our assignment of the structure of major and minor conformers of the 2-iodo-N-methylbenzanilides, which is based on the chemical shift of the N-methyl group, finds support from the data on the shielding of the two N-methyl groups in 2,NN-trimethyl-3,5-dinitrobenzamide; the locations of these groups were determined by nuclear Overhauser effect measurements.[11]

Earlier papers in this series[12] (see also ref. 7) have shown that if the aromatic nucleus being attacked in the cyclisation step bears a *para*-methoxy-substituent, then cyclohexadienone formation may occur. However, it has also been noted that the spiro-γ-lactam intermediates may proceed to dienones when oxygen substitution is *absent*. This occurs in the presence of atmospheric oxygen, which can, for example, intercept the radical (2a) to give (5a).[13] To exploit this observation, we have examined the copper-catalysed decomposition of the appropriate diazonium salts in acetone continuously purged with oxygen. Under these conditions the dienone is the only detectable product from the spirodienyl intermediate (we were unable to detect cyclohexadienols[13]), and determination of the yields of phenanthrid-

inone (6) and dienone (by g.l.c.) appears to give a reliable indication of the competition between cyclisation to δ- and γ-lactam structures. In several instances, synthetically useful yields of otherwise inaccessible dienones have been obtained by this procedure.

Wherever possible, the proportions of δ- and γ-lactams have been compared with those resulting from alternative cyclisation procedures. These include diazonium salt decomposition induced by sodium iodide in acetone,[4,13] hydrogen iodide in methylene chloride,[14] and copper in acetone, each in the absence of oxygen, as well as by photolysis of the corresponding aryl iodide.[1] The differences between the reaction systems are found almost entirely in the products from the spirocyclohexadienyl-γ-lactam radicals (2). In the absence of oxygen these radicals may dimerise [to give (7)] or, in the presence of hydrogen iodide, give dienes, *e.g.* (8). In addition, when the cyclohexadienyl radical bears an alkoxy-substituent, oxidative dealkylation may occur. Finally, the cyclohexadienes formed in the experiments with hydrogen iodide, may undergo acid-catalysed rearrangement.

As the photochemical reactions liberate iodine, and thus hydrogen iodide also [by oxidation of (3) with

[9] D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc. (C)*, 1971, 116.
[10] M. E. Stewart and T. H. Siddall, *Chem. Rev.*, 1970, 70, 517.
[11] A. H. Lewin and H. Frucht, *Tetrahedron Letters*, 1970, 1083.
[12] D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc. (C)*, 1967, 1518.
[13] B. Chauncy and E. Gellert, *Austral. J. Chem.*, 1969, 22, 993.
[14] D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Comm.*, 1969, 1375.

iodine], these reactions are particularly complex.[1,9] It is possible that some simplification could be achieved if precautions were taken to remove iodine as it is formed.[15]

In addition to the reaction systems already mentioned, it has now been found that interception of the spirodienyl radicals by iodine can lead to spirodienyl iodides (9). This is best accomplished by conducting sodium composition of the diazonium salt (10), for which the principal fate of the intermediate aryl radical is cyclisation to a γ-lactam structure. The product (9i) was obtained as a mixture of stereoisomers. In other instances, examination of the total reaction products by n.m.r. indicated high conversion of the spirodienyl intermediates into iodides, but these were not isolated. Their

Products from the cyclisation of some 2-(N-alkyl-N-phenylcarbamoyl)phenyl radicals [a,b]

Products (%)

Procedure:	$ArN_2^+BF_4^-$–Cu, Me_2CO–O_2			$ArN_2^+BF_4^-$–Cu, Me_2CO–N_2			$ArN_2^+BF_4^-$–NaI, Me_2CO–N_2			$ArN_2^+BF_4^-$–HI, CH_2Cl_2–N_3			$ArN_2^+BF_4^-$–NaI, CH_2Cl_2–N_2–I_2			ArI–PhH–N_2, hν				
Aryl radical	Dienone	Phenanthridinone	Other	Dimer or dienone	Phenanthridinone	Other	Dimer	Phenanthridinone	Other	Dimer	Phenanthridinone	Other	Dienyl iodide	Phenanthridinone	Other	Dimer	Phenanthridinone	Other	Dealkylation	%γ/%δ
(1a)	(5a)(45)	(6k)(35)	(18)(4)	(7a)(36—40)	(6k)(35)	(18)(4)	(7a)(40)			(8a)(45)	(6k)(35)		(9a)[1·4]	(6k)[1]		(7a)(30—35)	(6k)(35)	(8a)(5)	(18)(4)	45/35
(1b)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(7b)(ca. 30)	(6)(ca. 55)		(18)(4)	
(1c)	(5c)(70)	(6s)(3)		(14; R = Me)(68)c	(6s)(1·5)		(7c)(74)			(8c)(ca. 10)			—	—	—	(7c)(45)	(6s)(4)		(19)(2·5)	70/3
(1d)	(5d)(68)	(6t)(3)		—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
(1e)	(5e)(ca. 30)	(6m), (6q)		—	—	—	—	—	—	(13; R = Me)(25)d			(9e)[1]	(6m) + (6q)[1·4]			(6m)(26), (6q)(24)	(13; R = Me)(22)	(20)(1)	35/48
(1f)	(5f)(33)	(6m)(25), (6r)	(23)	(7f)(ca. 30)	(6n)(26), (6r)	(23)	(7f)	(6n)+, (6r)(7)	(23)e											
(1g)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—				(21)(1)	60/26
(1h)	—	—	—	(5b)(60)	(6p)(26)		(7h)(9·5)		(5b)	—	—	—	n.d.	(6p)[1]	(5b)[2·4]	—	—	—	—	
(1i)	(5i)(67)	(6w)(1·5)	(22)(5)	(7i)(ca. 70)	(6w)(1·5)	(19)(5)	(7i)(71)		(17)				(9i)(61)g			—	—	—	—	70/1·5
(1j)	(15)[2]	(6u)[3], (6v)[1]		—	—	—	—	—	—	—	—	—	(16)[2]	(6u)[3], (6v)[1]		—	—	—	—	21/37 h

a Yields are given in parentheses after each product number. The figures in square brackets indicate *relative* yields of major products where quantitative examination of the reaction mixture was by n.m.r. spectroscopy only. The same system is used for the products from radical (1j), the diazonium precursor for which was not obtained free from solvent. A dash in the Table indicates that data are not available, a blank that investigation of the relevant product has not been made, and n.d. that the relevant product could not be detected. In a few instances products identified by isolation are entered without yield data. Several minor products which have been identified in earlier work [12] are omitted from this compilation. b The following key identifies the phenanthridinones and other products not given elsewhere:

(14)   (15)   (16)   (17)
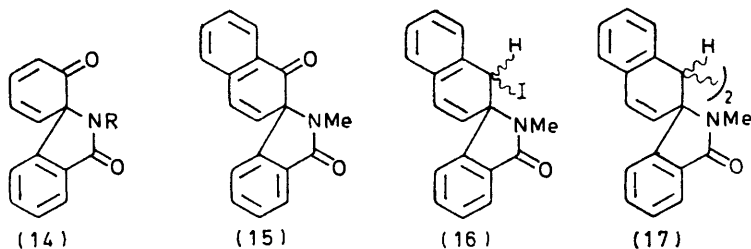
Phenanthridinones: (6)k; unsubst., R = Me
l; unsubst., R = Et
m; 1-OMe, R = Me
n; 1-OMe, R = Et
o; 2-OMe, R = Me
p; 2-OMe, R = Et
q; 3-OMe, R = Me
r; 3-OMe, R = Et
s; 4-OMe, R = Me
t; 4-OMe, R = Et
u; Benzo[a]-, R = Me
v; Benzo[b]-, R = Me
w; Benzo[c]-, R = Me

(18) Benzanilide
(19) 2'-Methoxybenzanilide
(20) 3'-Methoxybenzanilide
(21) 4'-Methoxybenzanilide
(22) N-1-Naphthylbenzamide
(23) N-Ethyl-3'-methoxybiphenyl-2-carboxamide

c These figures give the yields of products of a reaction in the presence of added copper(II) acetate. In the absence of this, some dimer (7c) was formed at the expense of linear dienone (13) (see text). d For experimental procedure see text. e The formation of this product has not been explained. f For details see ref. 1. g By isolation. h Based on free amine.

iodide-promoted diazonium decompositions in methylene chloride instead of acetone, where dimerisation is prevalent. The reaction is facilitated by addition of a little iodine to the solution. Probably solvation of the iodine is responsible for the difference found between the two solvent systems.

Only in one instance has any attempt been made to isolate a spirodienyl iodide. This was from the de- structures were established spectroscopically, and either by photolysis (which liberated iodine and gave spirodienyl dimers) or by silver-ion catalysed methanolysis to give spirodienyl methyl ethers [e.g. (11)].

The Table contains a comparative summary of the experimental results. As the principal interest has been

[15] E.g., J. M. Blair, D. Bryce-Smith, and B. W. Pengilly, J. Chem. Soc., 1959, 3174.

in the fate of the γ-lactam intermediate, quantitative information on products formed from other intermediate radicals is incomplete. However, where several routes

(2)+(2) ⟶ (7)

(2) + HI ⟶ (8) + I•

(2)+I₂ $\xrightarrow{CH_2Cl_2}$ (9) + I•
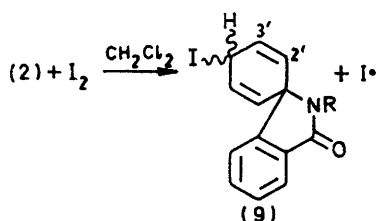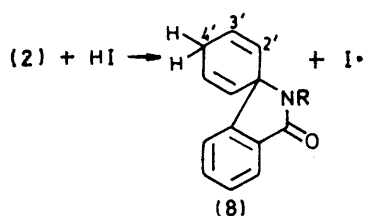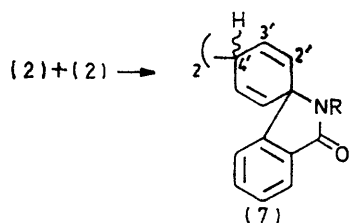
to any one of the aryl radicals (1a—j) have been investigated, it has qualitatively been observed that the yields of phenanthridinones (*i.e.* of δ-lactam cyclisation products), are independent of the mode of radical
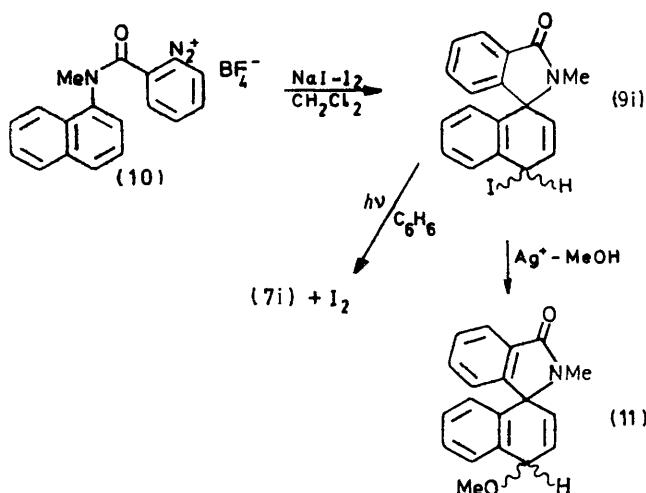
production. Probably the sodium iodide-promoted reaction in acetone is the most convenient experimental procedure for synthesis of these phenanthridinones, although electrochemical and other procedures documented recently for the Pschorr phenanthrene synthesis might

¹⁶ R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, 1971, **36**, 1769.

well prove to be equally suitable.[16] In the final column of the Table, estimates of the ratio of % γ-lactam cyclisation to % δ-lactam cyclisation are given for each of the aryl radicals investigated.

Dimer formation, which occurs in three of the reaction systems, is generally cleaner in the sodium iodide-catalysed diazonium decomposition than in the copper-promoted reaction.[17] It was at first thought that this might be associated with the high rate of the iodide-catalysed reaction, in which nitrogen evolution is usually complete within a few seconds of mixing; a relatively high radical concentration would result, favouring dimerisation. However, other factors are clearly of importance. For example, whilst the dimer (7g) is formed in the 4'-methoxy-series from the iodide- but not from the copper-promoted diazonium reaction, it is also formed in the corresponding iodide photolysis where the rate of radical production is very low. Probably copper(II) is, under the reaction conditions in question, a better oxidant for the intermediate methoxycyclohexadienyl radical (2g) than is iodine,
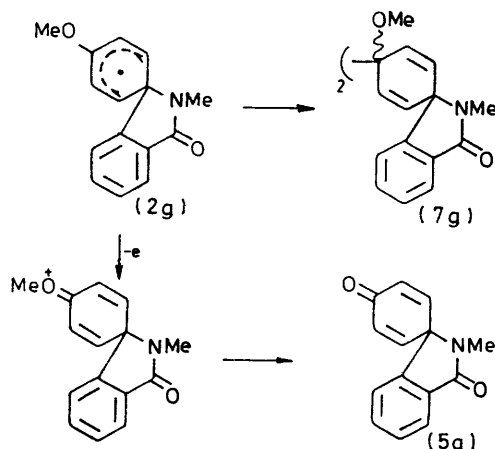
oxidative demethylation in the copper-promoted reaction completely overshadowing any competing dimerisation (*cf.* ref. 16). A similar situation is found in the 2'-methoxy-series, although in this case oxidation appears to be more difficult. In the sodium iodide-induced decomposition a high yield of spirodienyl dimer (7c) is obtained from (1c), whereas in the copper-catalysed reaction both dimer and linear dienone (4; R = Me) are formed unless copper(II) acetate is present during the reaction; in the latter case oxidative demethylation of the spirodienyl intermediate to give (14) appears to be quantitative.

For some closely related reactions it has been suggested that the principal oxidant for the cyclohexadienyl intermediates is unchanged diazonium ion.[18] Although the δ-lactam cyclohexadienyl radicals (3) are apparently oxidised cleanly to phenanthridinones in all the diazonium reactions (the same is true in the aryl iodide photo-

¹⁷ D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 105.
¹⁸ J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186.

lyses), the foregoing observations concerning oxidation of the methoxy-substituted γ-lactam cyclohexadienyl intermediates (which should be particularly susceptible to electron-transfer oxidation) seem difficult to reconcile with a mechanism solely involving oxidation by diazonium ions. On the other hand the electrochemical data [16] are not inconsistent with the occurrence of this reaction in competition with other oxidation steps.

The competition between γ- and δ-lactam formation must clearly be influenced by the position and nature of substituents in the anilide ring, all of which are weakly o/p-directing towards attack by aryl radicals.[19] Typically the γ : δ ratio for cyclisation of the 2-(N-methyl-3-methoxyphenylcarbamoyl)phenyl radical (1e) is appreciably less than unity, whilst that for the corresponding 4-methoxy-system is approximately 2, entirely in accord with this o/p-directing effect of the substituent. A more dramatic effect is found in the cyclisations of those radicals which carry a 2'-substituent. This has previously been attributed simply to steric effects,[20] but such effects are normally small in intermolecular homolytic arylation. Furthermore, as the major reaction path in these instances is γ-lactam cyclisation, rather than hydrogen transfer,* the aryl radicals must be formed in a conformation in which the two aryl groups are *cis*. It seems possible that the preference for γ-lactam cyclisation over and above that which might be anticipated from the weak o/p-directive effects of the substituents may be a consequence of a preferred conformation in which the *ortho*-substituted anilide ring lies perpendicular to the amide unit (12). Therefore attack by the aryl radical, which occurs roughly perpendicular to the face of the anilide ring, occurs most readily at C-1'.
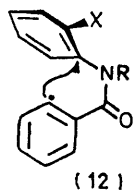

(12)

In the few instances in which quantitative comparisons have been made, no effect of changing the nitrogen substituent from ethyl to methyl has come to light. This is consistent with occurrence of hydrogen transfer only in those radicals that are generated in a conformation in which the aryl groups are *trans*.

One additional conformational factor is of interest in the light of the recent report [21] concerning competition between inter- and intra-molecular reactions of the amide radical (24). Our failure to detect any inter-

* Intramolecular hydrogen transfer appears to be reflected in the formation of dealkylated anilide [such as benzanilide (18) from (1a) or (1b)]. The penultimate column of the Table shows that the extent of this process is consistently low, at least in the photochemical reactions, for which quantitative data are available. Identification of this pathway in earlier work [20] was probably a consequence of the relative ease of isolation of this type of product in particular reactions, rather than of dealkylation becoming a major reaction pathway, although in some instances yields of dealkylated anilide reached *ca.* 10%.

molecular arylation product in the reactions of radicals (1) in benzene, and similar failure to detect more than traces of N-alkylbenzanilides from the reactions of
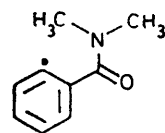
(24)

radicals (1) in acetone, suggest that intermolecular reactions of these radicals with solvent molecules is unimportant. Low yields of aryl iodides are obtained from aryl radicals (1) generated from the diazonium salts in the presence of iodine. We conclude that rotation about the C–CO bond in (1) is rapid compared with any intermolecular reaction with benzene or acetone.
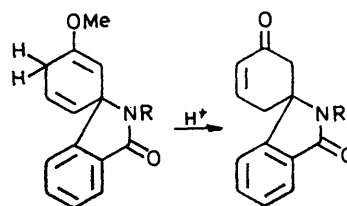
(13)

The formation of the cyclohexenone (13) merits comment. This was first isolated from the photolysis of an aryl iodide,[1] and was postulated to arise by acid-catalysed rearrangement of a 3'-methoxy-diene. However, initial attempts to reproduce this result by use of the hydrogen iodide-catalysed diazonium decomposition gave only trace amounts of the enone. It was eventually appreciated that this difficulty must be a consequence of the capture of the spirodienyl intermediate by iodine formed in the reaction, rather than by hydrogen iodide. To circumvent this problem, the diazonium salt was slowly added to an excess of hydrogen iodide in methylene chloride. Under these conditions, a high yield of the cyclohexenone was obtained, confirming that its formation in the photochemical reaction did not require the intervention of a second quantum of light.

EXPERIMENTAL

The general experimental and analytical procedures have been detailed in Part XXVI.[9]

Diazonium fluoroborates were prepared from the appropriate amino-compounds as described in Parts XXII [12] and XXVII.[17] The salts were washed thoroughly with water, then dried *in vacuo* (P_2O_5) for 24 h.

Decomposition of Diazonium Salts.—(i) *With copper powder in the presence of oxygen.* The diazonium salt was dissolved or suspended in acetone (50 ml per 1—2 g of fluoroborate), and the mixture was stirred while a stream of oxygen was bubbled through. Copper powder was

[19] D. H. Hey, *Adv. Free Radical Chem.*, 1967, **2**, 47; G. H. Williams, *Chem. Soc. Special Publ. No.* 24, 1970, p. 25.
[20] D. H. Hey and D. G. Turpin, *J. Chem. Soc.*, 1954, 2471.
[21] T. Cohen, K. W. Smith, and M. D. Swerdloff, *J. Amer. Chem. Soc.*, 1971, **93**, 4303.

added in small batches (50—100 mg) during *ca.* 2 h. Evolution of nitrogen was noticeably slower than in reactions from which oxygen was excluded, and each reaction was continued until the mixture no longer gave a colour reaction with alkaline β-naphthol. The mixtures were worked up according to the general procedure outlined previously, except that a small sample was examined by g.l.c. prior to column chromatography. The cyclohexadienones were eluted from neutral alumina with mixtures of benzene and methylene chloride. The yields of the principal products are summarised in the Table. Analytical and spectroscopic data for dienones not documented in earlier parts of this series are as follows.

2'-*Methoxy*-2-*methylisoindoline*-1-*spiro*-1'-*cyclohexa*-2',5'-*diene*-3,4'-*dione* (5c), pale yellow prisms (from ethanol), m.p. 232—236° (Found: C, 70·2; H, 5·2; N, 5·4. $C_{15}H_{13}NO_3$ requires C, 70·6; H, 5·1; N, 5·5%), $\nu_{max.}$ 1715 (γ-lactam) and 1665 cm⁻¹ (αβ-unsaturated ketone), τ 1·9—2·8 (4H, m), 3·45 (1H, dd, *J* 9·5 and 1 Hz), 3·7 (1H, d, *J* 9·5 Hz), 4·1 (1H, d, *J* 1 Hz), 6·35 (3H, s, OMe), and 7·05 (3H, s, NMe).

3'-*Methoxy*-2-*methylisoindoline*-1-*spiro*-1'-*cyclohexa*-2',5'-*diene*-3,4'-*dione* (5e), crystals (from ethanol), m.p. 216—218° (Found: C, 70·7; H, 5·25; N, 5·5%), $\nu_{max.}$ 1690 (γ-lactone) and 1675 cm⁻¹ (αβ-unsaturated ketone), τ 1·9—2·9 (4H, m), 3·5 (2H, s), 4·6 (1H, s), 6·35 (3H, s), and 7·0 (3H, s).

2-*Ethyl*-3'-*methoxyisoindoline*-1-*spiro*-1'-*cyclohexa*-2',5'-*diene*-3,4-*dione* (5f), crystals (from ethanol), m.p. 170—171° (Found: C, 71·9; H, 5·7; N, 5·55. $C_{16}H_{15}NO_3$ requires C, 71·3; H, 5·6; N, 5·2%), $\nu_{max.}$ 1700 (γ-lactam) and 1670 cm⁻¹ (αβ-unsaturated ketone); n.m.r. spectrum very similar to that of (5e) except for N-ethyl signal at τ 6·5 (2H) and 8·7 (3H).

1,4-*Dihydro*-2'-*methylnaphthalene*-1-*spiro*-1'-*isoindoline*-3',4-*dione* (5i), prisms (from ethanol), m.p. 178—180° (Found: C, 78·4; H, 4·7; N, 5·4. $C_{18}H_{13}NO_2$ requires C, 78·5; H, 4·7; N, 5·1%), $\nu_{max.}$ 1705 (γ-lactam) and 1670 cm⁻¹ (αβ-unsaturated ketone), τ 1·6—3·2 (8H, m), 3·3 (2H, ABq, *J* 12 Hz), and 7·1 (3H, s, NMe).

1,2-*Dihydro*-2'-*methylnaphthalene*-2-*spiro*-1'-*isoindoline*-1,3'-*dione* (15), pale yellow needles (from ethanol), m.p. 171—173° (Found: C, 78·5; H, 4·3; N, 5·2%), $\nu_{max.}$ 1705 (γ-lactam) and 1680 cm⁻¹ (aryl ketone).

(ii) *With copper powder in acetone in the absence of oxygen.* The general procedure for this type of reaction is described in Part XXVII.[17] However, in the case of the diazonium salt precursor to radical (1c), the normal decomposition procedure was found to give two products not identified in the earlier work, both of which were derived from the γ-lactam intermediate; these were the spirodienyl dimer (7c) and the linear dienone (14; R = Me). Decomposition of the diazonium salt (5 g) by copper (2 g) in acetone was therefore repeated in the usual way, except that copper(II) acetate (2 g) was first added to the solution. Chromatography of the products of this reaction on neutral alumina gave a mixture of 2'-methoxybenzanilide and 4-methoxy-N-methylphenanthridinone (3% by g.l.c.), from which the latter crystallised [needles (from ethanol), m.p. 125° (lit.,[12] 125°)]. Further elution gave the linear dienone (14; R = Me) (2·165 g, 68%) in yellow needles, m.p. 124—126° (from ethanol) (lit.,[22] 126—128°).

[22] D. H. Hey, J. A. Leonard, C. W. Rees, and A. R. Todd, *J. Chem. Soc.* (C), 1967, 1513.

(iii) *With sodium iodide in acetone in the absence of oxygen.* The general procedure is described in Part XXVII.[17]

(iv) *With hydrogen iodide in methylene chloride.* The procedure for this type of reaction is described in Part XXVIII.[23] Attempted decomposition of the diazonium salt (1e) by this method led to a straw-coloured methylene chloride solution which slowly liberated iodine. This solution is considered to have contained spirodienyl iodides (see later); it was not further investigated. In order to isolate the spirocyclohexenone (13; R = Me) from the decomposition of radical (1e), the following procedure was adopted. The diazonium salt corresponding to (1e) (300 mg) was dissolved in methylene chloride (50 ml) and added in a steady stream (*ca.* 5 s) to a well-stirred saturated solution of hydrogen iodide in methylene chloride (200 ml), through which was bubbling a rapid stream of hydrogen iodide. The mixture was worked up at once, following the general procedure,[23] to give a pale yellow methylene chloride solution. The solvent was removed and the residue was dissolved in acetone, to which was added dropwise an aqueous solution of silver nitrate (to hydrolyse any spirodienyl iodides, see later). The small precipitate of silver nitrate was removed, and the solution was then distributed between water and methylene chloride. The methylene chloride solution was washed thoroughly with water, dried, and evaporated. The residue was chromatographed on neutral alumina; elution with methylene chloride then gave the principal products free from cyclohexadienols produced in the foregoing hydrolysis. These products were found to comprise 1-methoxy- and 3-methoxy-N-methylphenanthridinone, and the enone (13)[1] in approximately equal proportions (n.m.r.). The total yield of compound (13) was estimated from this to be *ca.* 25%.

(v) *With sodium iodide in methylene chloride.* The diazonium salts could also be decomposed by treating their solutions in methylene chloride with sodium iodide. The products of this reaction again slowly liberated iodine, and were suspected to be spirocyclohexadienyl iodides. To improve the efficiency of the capture of the spirodienyl radical by iodine, the following general procedure was adopted, in which iodine was added at the outset of the reaction. The diazonium salt was dissolved or suspended in methylene chloride (30—50 ml per g of diazonium salt) containing a little iodine (100 mg per g of salt), and the mixture was stirred under nitrogen. Powdered sodium iodide (1 g per g of salt) was added all at once, and the mixture was stirred until evolution of nitrogen had ceased (2—30 min). The mixture was washed with aqueous sodium thiosulphate solution, and with water, dried, and evaporated under reduced pressure. The products, which slowly liberated iodine, were examined by n.m.r. spectroscopy and immediately used for further reactions. In only one instance was the spirodienyl iodide isolated.

(*a*) The reaction of 2-(N-methyl-N-phenylcarbamoyl)-benzenediazonium fluoroborate under the above conditions gave a mixture of two major products (t.l.c.), of which one had the chromatographic characteristics of N-methylphenanthridinone. The n.m.r. spectrum exhibited singlets at τ 6·25 (N-methylphenanthridinone) and at 6·95 and 7·1 [considered to be due to the N-methyl groups of the stereoisomeric *iodospirodienes* (9a)]. In

[23] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 113.

addition, vinyl proton signals were evident at τ 3·45 and 4·61 (ABq, J $ca.$ 10 Hz) for the major isomer of (9a), and at τ 3·45 and 4·71 for the minor isomer. The doubly allylic protons on C-4' gave rise to overlapping multiplets with small splittings due to the vinyl protons, at τ 4·37. From the N-methyl resonances the ratio of phenanthridinone to iodospirodienes was estimated as 35 : 45, and the two diene isomers were present in the approximate ratio of 2 : 1. The product was dissolved in methanol and treated with methanolic silver nitrate until precipitation of silver iodide was complete. After filtration, the resulting solution was diluted with methylene chloride, and washed with water. The organic layer was dried and evaporated. Examination of the residue by t.l.c., g.l.c., and n.m.r. spectroscopy showed that the N-methylphenanthridinone was now accompanied by a mixture of the stereoisomeric spirodienyl methyl ethers (9a; I replaced by OMe).[24]

Similar results were obtained with the diazonium fluoroborate precursor of (1e); that of (1h) gave instead the dienone (5b).

(b) The reaction of the diazonium salt precursor of (1i) under these conditions gave a mixture which apparently (t.l.c.) contained a single major product, accompanied by a trace of N-methylbenzo[c]phenanthridinone. The i.r. spectrum of the crude product showed $\nu_{max.}$ 1690 cm^{-1} (γ-lactam). On evaporation of the methylene chloride solution to small bulk, a tan solid separated which was removed, washed with methylene chloride, and dried in $vacuo$ to give, as a mixture of stereoisomers, 1,4-$dihydro$-4-$iodo$-2'-$methylnaphthalene$-1-$spiro$-1'-$isoindolin$-3'-one (9i) (pale yellow powder; 61%) (Found: C, 56·6; H, 4·0; N, 3·9. $C_{18}H_{14}NO$ requires C, 55·8; H, 3·6; N, 3·6%), $\nu_{max.}$ 1690 cm^{-1}, τ 1·8—3·3 (8H, m), 3·0—3·6 (2H, m, vinyl CH and ⸬CHI), 4·4br (1H, d, J 9 Hz), and 7·0 and 7·25 (3H, 2 × s, ratio 1 : 3, NMe of two isomers). A sample of the freshly prepared product was suspended in methanol and treated with methanolic silver nitrate as before, to give a product identified (t.l.c.; i.r. and n.m.r. spectra) as a mixture of the stereoisomeric methyl ethers (11).[24] A further sample of the iodo-dienes (9i) (1 g) was dissolved in benzene (300 ml) and the oxygen-free solution was irradiated with light from a medium-pressure mercury arc. Rapid liberation of iodine

occurred; when this was complete (t.l.c.) the mixture was washed with aqueous sodium thiosulphate and water, dried, and evaporated. T.l.c. and i.r. and n.m.r. spectra indicated an essentially quantitative conversion into the spirocyclohexadienyl dimers (7i).[17]

(c) The hydrochloride of 2-(N-methyl-β-naphthylcarbamoyl)aniline (1 g) in aqueous hydrochloric acid (8% w/w; 20 ml) was diazotised at 0° with sodium nitrite (300 mg) in water (5 ml). Sodium fluoroborate (1 g) in water (5 ml) was added, and the yellow diazonium salt which separated was removed, washed with a little cold water, and dissolved in methylene chloride (50 ml). The solution was dried briefly (Na_2SO_4) and filtered, and iodine (100 mg) was added. The mixture was stirred under nitrogen and powdered sodium iodide (1·5 g) was added. Stirring was continued for 10 min, and the mixture was then worked up as already described. The n.m.r. spectrum of the total product was consistent with the formation of the expected N-methylbenzo[a]phenanthridinone and N-methylbenzo[b]phenanthridinone together with two isomeric spirodienyl iodides (16) in the approximate proportions 6 : 2 : 3 : 2. The n.m.r. spectra of the spirodienyl iodides exhibited N-methyl singlets at τ 7·0 and 7·4; other resonances were at 3·05(d), 4·18(d), and 3·9(s), and at 3·22(d), 4·38(d), and 4·01(s) for the two isomers. Details of the reactions of these compounds with silver nitrate will be presented elsewhere.[24]

$Photolysis$ of N-$Ethyl$-2-$iodobenzanilide$ in $Benzene$.—The N-ethyl-2-iodobenzanilide, m.p. 88·5—90°, was prepared, and the photolysis was carried out, exactly as described in Part XXVI [9] for the N-methyl analogue. The products were very similar (see Table). One stereoisomer (the least polar) of the $spirocyclohexadienyl$ $dimer$ (7b) was isolated by careful chromatography; m.p. 224—229° (from ethanol) (Found: C, 79·8; H, 6·3; N, 6·1. $C_{30}H_{28}N_2O_2$ requires C, 80·4; H, 6·25; N, 6·25%).

[24] D. H. Hey, G. H. Jones, and M. J. Perkins, following paper.