Internuclear Cyclisation. Part XXVII.[1, 2] Further Studies on the Aromatisation of Spirocyclohexadienyl Dimers

By **D. H. Hey**, **G. H. Jones**, and **M. J. Perkins**,* Department of Chemistry, King's College, Strand, London WC2R 2LS

The formation and pyrolysis of a series of spirocyclohexadienyl dimers related to the bis-(spirodiene-lactam) (1) has been reinvestigated, and the scope of the reactions has been extended. The pyrolyses give phenanthridinones by a radical mechanism in which ring-expansion involves nitrogen migration and not aryl migration as previously reported. The effects of substituents on the ease of dissociation of the dimers, and on the ease of the nitrogen migration are briefly considered.

In Part XXV[3] the formation of phenanthridinones by pyrolysis of the bis-(spirodiene-lactam) (1) and related compounds was described, and from the results obtained it was inferred that ring-expansion involved migration of the aryl group in the intermediate spirodienyl radical (2). Although not explicitly stated, it was envisaged that this occurred by a one-step aryl shift. An alternative to this would be a mechanism involving ring-opening to (3) and recyclisation. This would be in accord with our recent observation that the 6,6-diphenylcyclohexadienyl radical decomposes by fragmentation rather than by rearrangement [equation (i)].[4] However, new evidence has now come to light which requires that both of these possibilities be rejected.

In the course of further investigation into the formation of phenanthridinones by the pyrolysis of bis-(spirodiene-lactams), some methoxylated analogues of (1) have been studied. For example, pyrolysis of one stereoisomer of the dimer (4: R = Et) at 214° in 1,2,4-trichlorobenzene gave the 3-methoxy-*N*-ethylphenanthridinone (5) as the only observable phenanthridinone in approximately 55% yield. Improved yields were obtained in lower boiling solvents. The formation of the phenanthridinone (5) indicates that rearrangement has taken place by nitrogen migration. Further results obtained with other methoxylated dimers (see below), were consistent in every case with nitrogen migration only.

This new information led to a careful re-examination of the earlier results, which relate to benzologues of the dimer (1), and it has now been found that in all the cases studied the rearrangement of the intermediate spirocyclohexadienyl radical involves nitrogen migration and not migration of the aryl group as previously reported.[3]

The catalytic decomposition of the diazonium fluoroborate prepared from 2-amino-*N*-methyl-*N*-(2-naphthyl)-benzamide gave, by way of the radical (6), the benzophenanthridinones (7) m.p. 120° and (8) m.p. 196° in the approximate proportions of 3 to 1, as well as a mixture of dimeric products considered from spectroscopic evidence (see below) to consist principally of a mixture of stereoisomers of the dimer (9) together with dimers containing the ring-opened structural unit (9a). The combined yield of the two benzophenanthridinones (7) and (8) was approximately twice that of the dimeric product. Pyrolysis of the crude dimer at 214° in trichlorobenzene gave a mixture of benzophenanthridinones (8) (8%) and (10) (27%), which crystallised together.

In similar manner, the catalytic decomposition of the diazonium fluoroborate prepared from 2-amino-*N*-methyl-*N*-(1-naphthyl)benzamide gave, by way of the radical (11), the benzophenanthridinone (10) (1·5%), m.p. 145°, together with a mixture of dimers regarded as stereoisomers of (12) (*ca.* 70%). Pyrolysis of such a mixture in boiling 1,2,4-trichlorobenzene gave the benzophenanthridinone (7) (47%), together with the dialin (13) (47%), which was identified by spectroscopy, elemental analysis, and its chemical reactions.

---

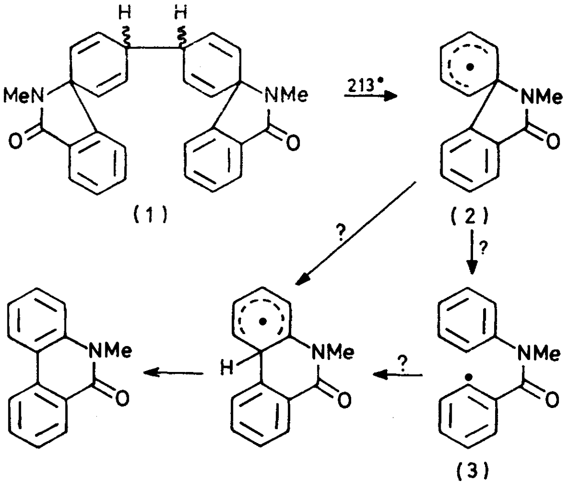
[1] Part XXVI, D. H. Hey, G. H. Jones, and M. J. Perkins, *J. Chem. Soc.* (*C*), 1971, 116.

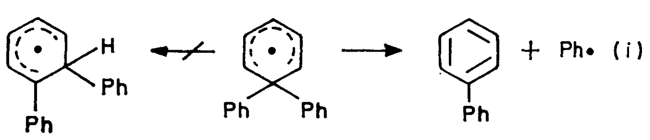
[2] A preliminary account of part of this work has appeared. D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Comm.*, 1970, 1438.

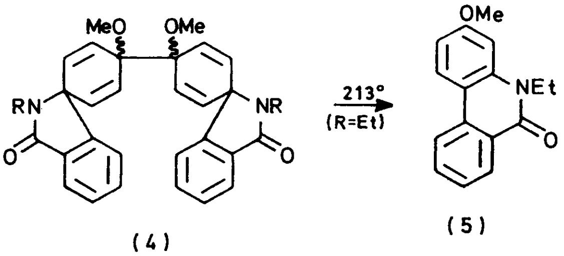
[3] D. M. Collington, D. H. Hey, and C. W. Rees, *J. Chem. Soc.* (*C*), 1968, 1026.

[4] M. J. Perkins and P. Ward, *Tetrahedron Letters*, 1971, 2379; D. J. Atkinson, M. J. Perkins, and P. Ward, *J. Chem. Soc.* (*C*), 1971, 3247.

In an earlier report[5] the copper-catalysed decomposition of the diazonium fluoroborate from 2-amino-*N*-methyl-*N*-(2-naphthyl)benzamide was stated to give a compound m.p. 196° and an unsaturated dimer m.p. 147—150°. Pyrolysis of the dimer was claimed[3] to give the benzophenanthridinone (7) m.p. 120—121°. In similar manner, catalytic decomposition of the diazonium fluoroborate from 2-amino-*N*-methyl-*N*-(1-naphthyl)benzamide was stated[5] to give *N*-(1-naphthyl)-benzamide (6·5%) and, as the major product (55%) a dimer m.p. 172—175° which on pyrolysis[3] was claimed to give the benzophenanthridone (10), m.p. 98—99°. This melting point was in agreement with a value previously noted for this compound,[6] but which is different from the figure given more recently.[7] The earlier results, therefore, require correction.

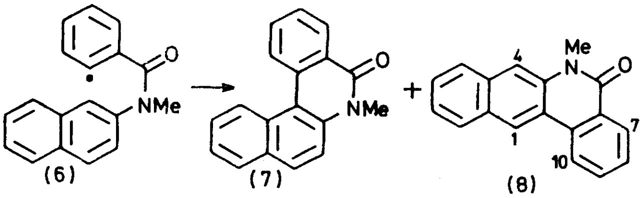


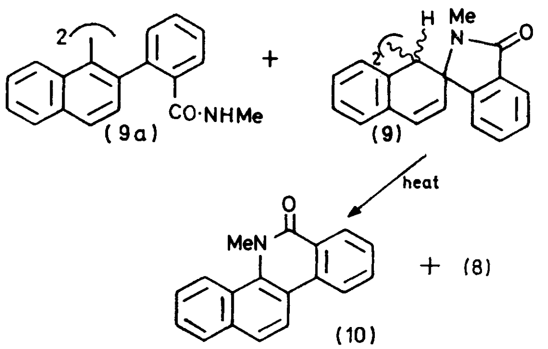


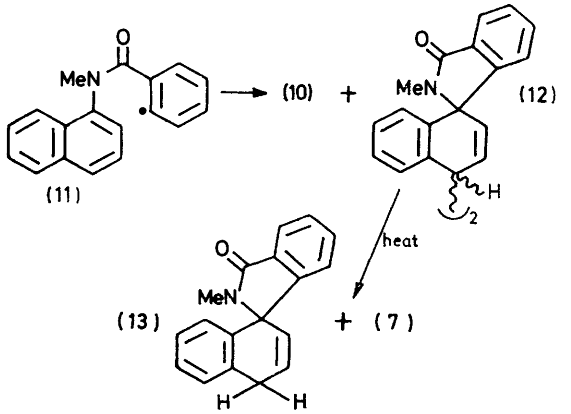


The authentic benzophenanthridones (7), (8), and (10) were characterised following chromatographic isolation, by comparison with recent literature data,[7,8] and by analysis of their n.m.r. spectra. Their yields were estimated by g.l.c. The application of g.l.c. to the reaction mixtures greatly simplified the task of unravelling the errors in the earlier work, to which yet earlier errors and confusions in the literature contributed.

The melting point of benzophenanthridinone (10) now reported is in agreement with that in the recent literature.[7] The failure of the earlier workers to equate the compound m.p. 196° with structure (8) appears to have been consequent upon incorrect identification of a synthesised reference compound, m.p. 173°, as (8).[6,8] Although an independent synthesis of (8) * has not now been undertaken, spectroscopic data (see Experimental section), coupled with the analogy of all the results of the remaining cyclisation and dimer pyrolysis reactions in this series, leaves no doubt as to the correctness of the identification of the product m.p. 196° as (8). The difficulty in earlier work[5] in identifying (7) as the major phenanthridone from (6) was probably a consequence of its high solubility compared with that of







---

* An inconsistency in the earlier work has since come to light.[9]

[5] D. M. Collington, D. H. Hey, C. W. Rees, and E. le R. Bradley, *J. Chem. Soc.* (*C*), 1968, 1021.

[6] D. N. Brown, D. H. Hey, and C. W. Rees, *J. Chem. Soc.*, 1961, 3873.

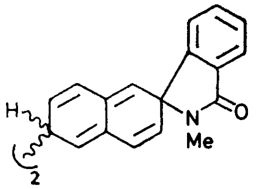
[7] I. Ninomiya, T. Naito, and T. Mori, *Tetrahedron Letters*, 1969, 3643.

[8] B. R. T. Keene and K. Schofield, *J. Chem. Soc.*, 1958, 2609.

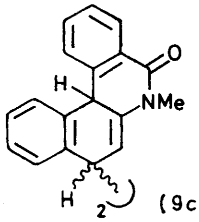
[9] L. H. Klemm and A. Weisert, *J. Heterocyclic Chem.*, 1965, **2**, 15.

(8). Indeed, in the earliest experiments it was overlooked completely. Finally, the previous identification of the pyrolysis product of (9) as (7),[3] was probably due to the fact that (8) and (10) which are actually formed, initially separate together, and the mixture melts at *ca.* 120°; *i.e.* close to the m.p. of (7). The cyclisation of (11) to (10), albeit in small yield, was apparently missed. In addition, it would appear that the isolated[3] pyrolysis product from (12) must have been impure [possibly contaminated with (13)], and, by chance, have melted close to the then recorded,[6] but incorrect, m.p. of (10).

In the earlier report[5] the dimers (12) and (9) were considered to have been obtained structurally pure, with reasonably sharp melting points, in yields of 55 and 18% respectively, but no consideration was given to stereoisomerism. Dimerisation to form (12) can occur in six geometrically distinct ways [two *meso*, and four (±)-pairs]. As it seems likely that these are of comparable energy, an isolated yield of 55% of any one of them seems improbable. In the present work, a chromatographic fractionation yielded an amorphous solid (70%), the n.m.r. spectrum of which was complex in the manner expected for a mixture of stereoisomers, and showed the expected ratio of aromatic : olefinic : allylic : *N*-Me protons of 8 : 2 : 1 : 3. This 'dimer fraction' was used in most pyrolysis experiments. A similar, though still more complex, situation applies in the case of (9). Although n.m.r. data reported[5] for (9) were substantially in accord with the assigned structure, the highly crowded nature of this counsels caution. Two structural alternatives (9b) and (9c), either symmetrically coupled as shown, or unsymmetrically coupled ('9—9b', '9—9c', '9b—9c'), merit consideration. In the present work, the total chromatographic fraction believed to consist of dimeric products was carefully scrutinised for these possibilities. The n.m.r. spectrum was extremely complex, and there seemed little likelihood of isolating any single dimer from the mixture. Integration of the spectrum suggested that structures containing the (9b) grouping were, at most, unimportant. In fact the integral shows an excessively large aromatic signal, which, coupled with infrared absorption in the N-H region, and a broad carbonyl band led to the suggestion that the ring-opened structure (9a) may constitute one half of at least 50% of the dimer molecules. Dimers of the type ('9—9a') would not give phenanthridinones on pyrolysis; this could explain the low yields from the pyrolysis of this dimer.



(9b)



(9c)

In addition to a (9a) component, the possibility of a (9c) component in the dimer fraction was suggested by the detection in the dimer pyrolysate of a minor product (*ca.* 1%), which was not isolated, but which had g.l.c. and the t.l.c. retention characteristics indistinguishable from those of (7). Again, the broad carbonyl band in the i.r. spectrum of the dimer fraction was not inconsistent with the presence of a δ-lactam component such as (9c).

The above conclusions may now be briefly summarised in the following terms. Both (6) and (11) can undergo cyclisation to give the expected phenanthridinones, together with spirodienyl radical dimers. These dimers decompose on heating, and amide nitrogen migrates leading again to phenanthridinones. When aryl radical cyclisation, or nitrogen migration, can give two different phenanthridinones, both are formed, but cyclisation or nitrogen migration to a vacant α-position predominates. In no experiments has evidence been found to indicate the occurrence of cyclisation or migration to a *peri*-position. The formation of (13) and the mechanism of nitrogen migration will be discussed below; the mechanism of nitrogen migration is also considered further in an accompanying paper.[10]

The methoxylated dimers (4) R = Me and R = Et, (16), and (17) were prepared by decomposition of the appropriate methoxy-*N*-alkylbenzanilide-2-diazonium fluoroborates induced by sodium iodide,[2,11] or copper in acetone. The choice of alkyl group was partly dictated by the ease of g.l.c. separation of the isomeric methoxy-*N*-alkylphenanthridinones. The synthetic method with sodium iodide normally gives better yields of dimers than the corresponding copper-catalysed decomposition, possibly because the faster reaction with sodium iodide may give a higher concentration of radicals, and hence favour their destruction by dimerisation.

TABLE 1

Products from the pyrolysis of spirodienyl dimers in boiling 1,2,4-trichlorobenzene

Dimer	Approx. $t_{\frac{1}{2}}$ at 213°	Products Phenanthridinones [%] [c]	Other [%] [c]
(1; R = Me)	5 min	(18) [90]	
(12; R = Me)	7 h	(7) (*N*-methylbenzo[*a*]-phenanthridinone) [47]	(13) [47]
(9; R = Me)	[b]	(10) (*N*-methylbenzo[*c*]-phenanthridinone) [27] (8) (*N*-methylbenzo[*b*]-phenanthridinone) [8]	
(16; R = Me)	1 min	(18) [19]; (19) [23]	(23) [9] [d]
(17; R = Et)	1 h	(20) [80]	
(4; R = Et)	<1 min	(5) [55]	

[a] The boiling point of trichlorobenzene is 213°; reactions were carried out under nitrogen. [b] Difficult to estimate in view of uncertain nature of dimer fraction, probably 5—10 min. [c] 100% = 2 mol/mol of dimer. [d] See Discussion.

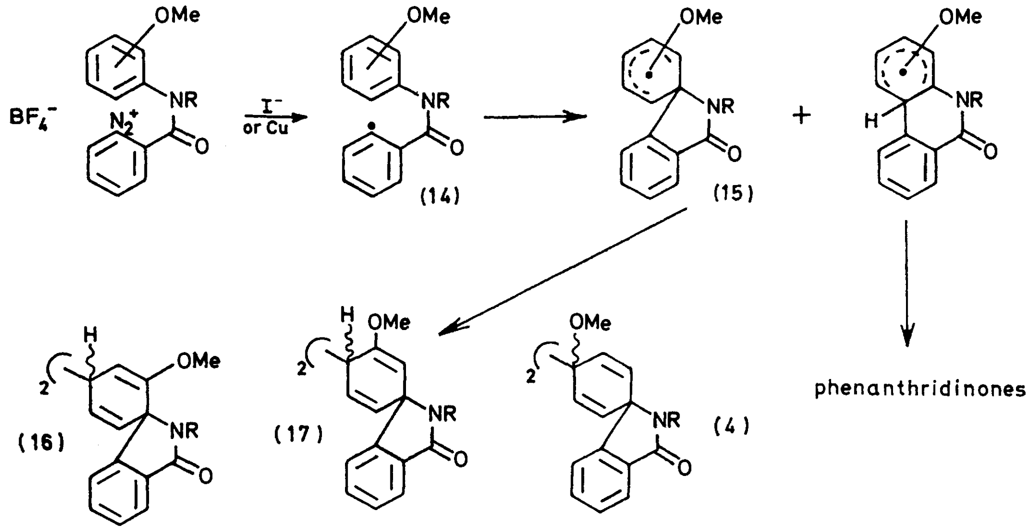
The products of pyrolysis in trichlorobenzene of (16), (17), and (4; R = Et) as well as those of pyrolysis of (9), (12), and the unsubstituted dimer (1), are listed in Table 1, which also gives approximate half-lives for

---

[10] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 118.

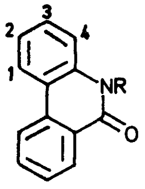
[11] B. Chauncy and E. Gellert, *Austral. J. Chem.*, 1969, **22**, 993.

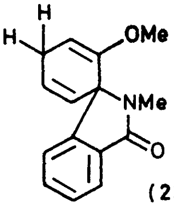
the reactions. The dimers pyrolysed were mixtures of stereoisomers with the exception of (17) and (4), in which cases a single, sharp-melting compound of undefined stereochemistry was employed.



It will be seen that pyrolysis of (16) gives unsubstituted *N*-alkylphenanthridinone as well as the expected 4-methoxy-derivative (19). More surprising, however, is the exclusive production of a 2-methoxyphenanthridinone (20) from the pyrolysis of (17); although the isomeric (21) is stable to the reaction conditions, it could not be detected amongst the products (g.l.c.).

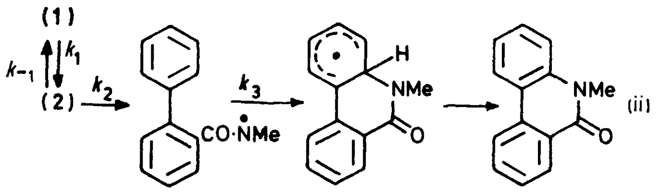
(18) R = Me
(19) R = Me; 1-MeO
(20) R = Et; 2-MeO
(5) R = Et; 3-MeO
(21) R = Et; 4-MeO
(22) R = Me; 3-MeO





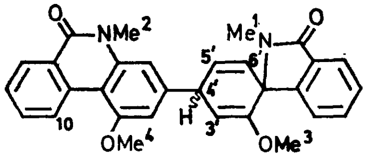
(23)

The most plausible mechanism which can be written for these rearrangements would appear to be one involving rupture of the relatively weak C–N bond in the first-formed spirodienyl radicals [*e.g.* (2)], followed by recyclisation to a δ-lactam structure [equation (ii)], though it is hard to rationalise the selective formation of (20) from (17) on this basis.

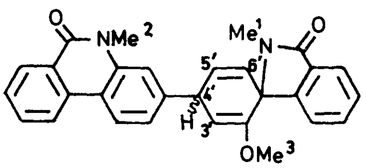


(ii)

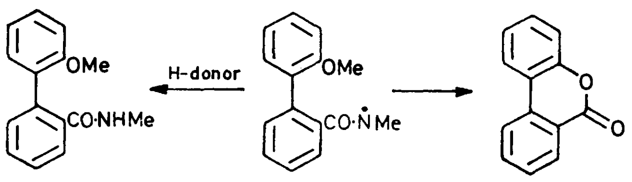
In the pyrolysis of (12), hydrogen transfer from a rearranged to an unrearranged cyclohexadienyl radical accounts for the two observed products (7) and (13). The fate of the supernumerary hydrogens in the pyrolyses of the other dimers is not known. The methoxy-diene (23), formed in low yield from (16), may be a disproportionation product, or it may be the result of hydrogen abstraction by (15: *o*-MeO) from unchanged dimer. Certainly, an appreciable yield (*ca.* 40%) of 'modified dimer' makes up the product balance from this reaction. From spectroscopic evidence, this modified dimer appears to consist predominantly of stereoisomers of (24) and (25) (see Experimental section). When a good hydrogen donor, 9,10-dihydroanthracene, was present during the pyrolysis of (16), this complication was reduced, and the yields of phenanthridinones (18) and (19), as well as that of (23), were increased (see Table 2). In addition, two new products were detected, namely the ring-opened amide (26), and a trace of benzocoumarin (28). The formation of these compounds may be interpreted in terms of a ring-opened amido-radical intermediate (27). Interception



(24)

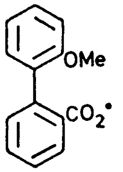


(25)



(26) (27) (28)

by the hydrogen donor can give (26), and cyclisation at the amido-oxygen followed by hydrolysis can give benzocoumarin. It is surprising, however, that the latter compound was never detected as a product of pyrolysis in the absence of hydrogen donor. The displacement of the methoxy-group, both in the formation of (28) and in the formation of the unsubstituted *N*-methylphenanthridinone (18), finds precedent in reactions believed to involve the 2′-methoxybiphenyl-2-carboxyl radical (29);[12] these produce unsubstituted benzocoumarin (28) in high yield, but no methoxybenzocoumarin.



(29)

Neither a spirodienyl radical nor a ring-opened amido-radical was intercepted (to form diene or ring-opened amide respectively) when the pyrolysis of (1) was carried out under similar conditions in the presence of dihydroanthracene. Possibly the partial interception of (27) is a consequence of interference with cyclisation to δ-lactam structures by the 2′-methoxy-group.

TABLE 2

Products from the pyrolysis of spirodienyl dimers in various solvents [a]

Dimer	Solvent (temp. °C)	Approx. $t_{\frac{1}{2}}$	Products Phenanthridinones [%]	 Other [%]
(12; R = Me)	Trichlorobenzene/9,10-DHA [b] (reflux)	<5 min	(7) [5]	(13) [>95]
(16; R = Me)	*p*-Chlorotoluene (162)		(18) [13]; (19) [21]	(23) [13]
(16; R = Me)	*o*-Dichlorobenzene (180)		(18) [16]; (19) [22]	(23) [11]
(16; R = Me)	Chloronaphthalene (255)		(18) [23]; (19) [23]	(23) [5]
(16; R = Me)	9,10-DHA [b,c]		(18) [34]; (19) [34]	(23) [14]; (26) [14]; (28) [0·2]
(16; R = Me)	9,10-DHA [b]/*p*-chlorotoluene (1 : 2) (reflux)		(18) [23]; (19) [38·5]	(23) [25]; (26) [5]; (28) [trace]
(4; R = Et)	*p*-Chlorotoluene (162)	<5 min	(5) [63]	
(4; R = Me)	Chlorobenzene (130)	30 min	(22) [75]	
(4; R = Me)	Benzene/toluene (100)	20 h	(22) [84]	

[a] Reactions at reflux under nitrogen. The data should be read in conjunction with those in Table 1. [b] 9,10-Dihydroanthracene. [c] Dimer mixed with 9,10-DHA [b] under N_2, and mixture heated to boiling and cooled.

The pyrolysis half-lives are probably determined not only by the strength of the bond linking the two cyclohexadienyl units, but also by the ease of C–N bond cleavage in the spirodienyl radical intermediate. Evidence for this comes from observations on the pyrolysis of individual dimer stereoisomers. For instance, the three possible isomers of (1) have been separated and it has been found that some equilibration of these occurs, presumably by a dissociation–recombination mechanism, in competition with rearrangement [*i.e.* in equation (ii), $k_2 \simeq k_{-1}$]. A different situation is found with (12), which normally appears on t.l.c. as three overlapping spots. This can be fractionated chromatographically, and if a fraction containing only one of the three components is heated at 213° for 1 min, an equilibrium mixture of the three is generated, in spite of the 7 h half-life for decomposition (*i.e.* in this case, $k_{-1} \gg k_2$). The evident reluctance of the spirodienyl radical from (12) to undergo rearrangement is clearly associated with the efficient scavenging of rearranged radicals in a hydrogen-transfer step which gives (13). Furthermore, if the pyrolysis of (12) is effected in the presence of 9,10-dihydroanthracene an almost quantitative yield of (13) is rapidly produced. This supports the earlier hypothesis that those spirodienyl radicals which are less prone to rearrange, such as are formed from (16) and (12), can abstract hydrogen from a suitable donor molecule.

The other extreme is encountered with (17), a single isomer of which was used in the pyrolysis experiments. No evidence was found here for the occurrence of equilibration with isomeric dimers in competition with phenanthridinone formation (*i.e.* $k_2 > k_{-1}$).

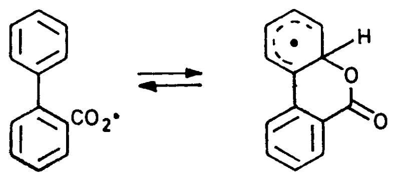
The results of experiments involving dihydroanthracene are summarised in Table 2, together with some observations on the effect on the yields of products of employing solvents of different boiling points for the pyrolyses.

Whilst it seems evident (and reasonable) that the central bond in (4) is relatively weak, and probable that that in (17) is relatively strong, a more detailed appraisal of reaction half-lives in this series would, at the present time, be purely speculative. The results with (16) over a wide temperature range reveal a marked temperature dependence of the relative yields of the two phenanthridinones (18) and (19). There is an increasing proportion of the methoxy-derivative (19) as the reaction temperature is lowered. One factor which may contribute to this is that cyclisation to a δ-lactam intermediate [identified by k_3 in equation (ii)] may be appreciably reversible. Demonstration of this would necessitate small modifications to the above discussion. There is some precedent to be found in the demonstrated reversibility of the reaction (iii).[13]

---

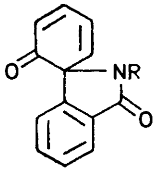
[12] P. M. Brown, J. Russell, R. H. Thomson, and A. G. Wylie, *J. Chem. Soc.* (*C*), 1968, 842; D. I. Davies and C. Waring, *ibid.*, 1967, 1639.

[13] D. B. Denney and P. P. Klemchuk, *J. Amer. Chem. Soc.*, 1958, **80**, 3289; J. Saltiel and H. C. Curtis, *ibid.*, 1971, **93**, 2056.

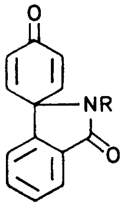


(iii)

A significant feature of the pyrolysis reactions of (16) and (4) is the absence of dienones (30) and (31) from among the products. These normally accompany dimer and phenanthridinones from cyclisation reactions of the aryl radicals (14: *o*- and *p*-OMe),[14] and presumably arise *via* the spirodienyl radicals (15: *o*- and *p*- OMe).

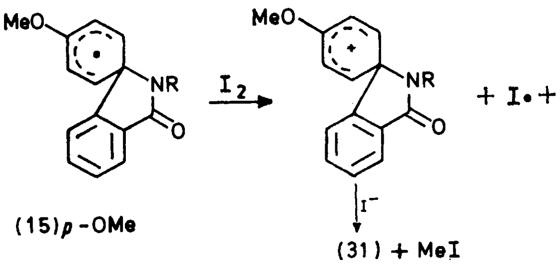


(30)



(31)

This apparent anomaly was investigated further in the case of (4). It was first demonstrated that the *para*-dienone (31) is stable to the pyrolysis conditions, and a pyrolysis experiment was then carried out in the presence of iodine as an added oxidising agent. An excellent yield of (31) (84%) was obtained. The annexed mechanism, in which demethylation is essentially an ionic process instead of a free-radical one, is regarded as a plausible rationalisation. In cyclisation reactions of (14) brought about by copper-catalysed or iodide-catalysed homolysis of a diazonium salt, suitable oxidising agents are formed in the reaction system (cupric copper and iodine respectively).



(15)*p*-OMe

EXPERIMENTAL

Treatment of reaction mixtures, analytical procedures, and instrumentation were as described in Part XXVI.[1]

Diazonium fluoroborates were prepared from the appropriate amino-compounds as described in Part XXII.[14] After washing the salts thoroughly with water, they were dried *in vacuo* over P_2O_5 for 24 h. Decomposition with copper powder followed the general procedure previously reported,[14] except that reactions were conducted in the absence of oxygen, and the yields reported are based on dry diazonium salt instead of amino-compound. The diazonium fluoroborate derived from 2-amino-*N*-methyl-*N*-(2-naphthyl)benzamide could not be stored, and therefore after washing the solid with water it was dissolved in acetone, the solution was dried briefly over magnesium sulphate, filtered, deoxygenated, and then copper powder was added to effect decomposition. Decomposition of diazonium fluoroborates catalysed by sodium iodide was carried out by the following general procedure. The diazonium salt (5 g) was dissolved or suspended in acetone (50 ml) and the mixture was stirred under nitrogen. Sodium iodide (3 g) in acetone (30 ml) was deoxygenated by passage of nitrogen and added in one batch to the stirred solution. Nitrogen evolution, which was copious and instantaneous, was complete within *ca.* 10 s. The product mixture was reduced in bulk by rotary evaporation, dissolved in chloroform, and the chloroform solution was extracted with water, with aqueous thiosulphate, again with water, dried, filtered, and the solvent was removed.

Products from the Decomposition of the Diazonium Salt formed from 2-*Amino*-N-*methyl*-N-(1-*naphthyl*)*benzamide*.—Chromatography of the products formed by copper-catalysed decomposition gave a fraction containing three products (g.l.c.) which were partially separated by fractional crystallisation from ethanol, and were identified as 1-naphthylbenzamide, m.p. and mixed m.p. 161°; *N*-methylbenzo[*c*]phenanthridinone, m.p. 145° (lit.,[7] m.p. 148—149° n.m.r. spectrum identical with that reported previously [7]); and a product m.p. 113—115° believed to be 2-*chloro*-N-*methyl*-N-(1-*naphthyl*)*benzamide* principally on the basis of parent peaks at *m/e* 295 and 297 in the mass spectrum, and a strong fragment peak at *m/e* 260 (*M* – Cl). This compound was not present in the diazonium salt; it presumably arose from the decomposition of diazonium chloride contaminating the fluoroborate. G.l.c. analysis indicated total yields of 5, 1·5, and 5% of these products respectively, based on diazonium salt (calculated as fluoroborate).

A second chromatographic fraction gave crude spirodimer (12) (*ca.* 70%). No single compound could be isolated from this by crystallisation.

When the decomposition was repeated using the sodium iodide procedure, chromatography gave a 71% yield of dimer (12) as a colourless amorphous solid m.p. 150—180° (Found: C, 82·7; H, 5·5; N, 5·4. $C_{36}H_{28}N_2O_2$ requires C, 83·1; H, 5·4; N, 5·4%), $\nu_{max.}$ 1690 cm^{-1} (γ-lactam), τ 1·8—4·7 (8H, m + 2H, m; aromatic + vinyl CH), 5·3 and 5·4 (together 1H, m; aliphatic CH), 7·0—7·45 (3H, 5 × s, N-CH_3 singlets). These figures are entirely consistent with the formulation of the product as a mixture of stereoisomers of (12). It was this material which was employed without further purification in most of the pyrolysis experiments with this dimer. However, t.l.c. revealed fractionation into three major components and repeated column chromatography enabled a fraction to be collected which appeared to comprise only one of these. Its n.m.r. spectrum was considerably simplified, and showed only two *N*-methyl singlets at τ 7·3 and 7·35.

Products from the Decomposition of the Diazonium Salt formed from 2-*Amino*-N-*methyl*-N-(2-*naphthyl*)*benzamide*.—As noted above, the diazonium fluoroborate from this amine was used without prior isolation and drying. The products of a copper-catalysed decomposition gave two major fractions on chromatography. The first was found by g.l.c. to comprise two components in a ratio of *ca.* 3·5 : 1. Crystallisation from ethanol readily afforded a

---

[14] D. H. Hey, C. W. Rees, and A. R. Todd, *J. Chem. Soc.* (*C*), 1967, 1518.

specimen of the minor constituent m.p. 195—198° (Found: C, 83·1; H, 4·75; N, 5·4. $C_{18}H_{13}NO$ requires C, 83·4; H, 5·1; N, 5·4%) (*cf.* unidentified product m.p. 196° of ref. 5), $\nu_{max.}$ 1650 (δ-lactam), and 1625 cm^{-1} (3-substituted *N*-alkylphenanthridinone *), τ 6·5 (3H, s, N·CH_3), 2·8 (1H, s, H-4 †), 2·2—2·75 (6H, m), 2·02 (1H, dd, H-10 †), 1·8 (1H, s, H-1 †), and 1·64 (1H, dd, H-7 †). These spectroscopic data are entirely consistent with formulation of the product as N-*methylbenzo*[b]*phenanthridinone*. With time, the mother liquors deposited crystals, m.p. 120° (after recrystallisation from ethanol), of the major constituent identified as *N*-methylbenzo[*a*]phenanthridinone (lit.,[8] m.p. 120°).

The other major chromatographic fraction, obtained as a pale brown amorphous solid, showed $\nu_{max.}$ 1690 (γ-lactam), 1650 (sh, amide), and 3300 (NH). The n.m.r. spectrum was complex, but the ratio of vinyl protons to aromatic protons was less than that calculated for the spirocyclohexadienyl dimer (9). No single component could be isolated from this mixture by crystallisation. A very similar dimeric product was obtained from a sodium iodide-catalysed decomposition.

Pyrolysis of Spirocyclohexadienyl Dimers.—*Starting materials.* The unsubstituted *N*-methyl spirocyclohexadienyl dimer (1) was a single isomer, m.p. 259—261°, isolated from the photolysis of *N*-methyl-2-iodobenzanilide.[1] The spiro-dimer (17; R = Et) was also a single isomer m.p. 295—297° isolated from the copper-catalysed decomposition of the appropriate diazonium fluoroborate.[14] The spiro-dimer (4, R = Et) 2,2″-*diethyl*-4′,4‴-*dimethoxy*-3,3″-*dioxo*-4′,4‴-*bi*(-*isoindoline*-1-*spiro*-1′-*cyclohexa*-2′,4′-*diene*) was also a single isomer, m.p. 209—210° [(Found: C, 75·6; H, 6·4; N, 5·3. $C_{32}H_{32}N_2O_4$ requires C, 75·3; H, 6·3; N, 5·5%) $\nu_{max.}$ 1695 (γ-lactam); τ 6·4 and 8·7 (2H, q and 3H, t, N-Et), 6·65 (3H, s, O-CH_3), 3·9 (4H, ABq, olefinic H), and 1·9—2·8 (4H, m, aromatic)] isolated from the sodium iodide-catalysed decomposition of the appropriate diazonium fluoroborate. The spiro-dimer (4; R = Me) was a mixture of stereoisomers, m.p. 212—218°, isolated from the photolysis of 2-iodo-4′-methoxy-*N*-methylbenzanilide.[15] The spiro-dimer (16; R = Me), isolated as a mixture of stereoisomers, was an amorphous colourless solid obtained in 74% yield by chromatography of the products of sodium iodide-catalysed decomposition of the appropriate diazonium fluoroborate. The dimer melted in the range 110—130° (Found: C, 74·3; H, 5·6; N, 5·3. $C_{30}H_{28}N_2O_4$ requires C, 75·0; H, 5·8; N, 5·8%); $\nu_{max.}$ 1695 (γ-lactam), and 1650 cm^{-1} (olefinic unsaturation), τ 7·1 (3H, s, N-CH_3), 6·5 and 6·6 (together 3H, 2 × s, 2 × O-CH_3), 6·4 (1H, broad s, allylic H), 4·75 (1H, broad s, olefinic H), 3·7 and 4·6 (2H, ABq, vinyl H), and 2·0—2·9 (4H, m, aromatic H). When this dimer was prepared by the copper-catalysed diazonium decomposition it was difficult to separate from the dienone (30; R = Me).[16] This was a negligible product of the sodium iodide-promoted reaction.

The preparation of the spiro-dimers (9) and (12) used in the pyrolysis experiments has been described above.

Pyrolysis Reactions.—All pyrolyses were carried out under nitrogen. The progress of prolonged reactions was monitored by g.l.c. and/or t.l.c. Product yields were determined by g.l.c. Percentage yields of monomeric products are based on 2 mol/mol of dimer = 100%. Further details of product identification are given below for individual experiments. The methoxyphenanthridinones have been characterised previously[17] with the exceptions of 3-methoxy-*N*-ethylphenanthridinone (see Expt. 7), 1-methoxy-*N*-methylphenanthridinone, m.p. 151—152°,[15] and 3-methoxy-*N*-methylphenanthridinone, m.p. 92—94°.[15]

(1) *Pyrolysis of* (1) *in* 1,2,4-*trichlorobenzene*. A solution of the dimer (1) (m.p. 259—261°) (66 mg) in trichlorobenzene was refluxed (*ca.* 214°) for 3 min, cooled rapidly, and chromatographed to remove solvent. The total products were examined by t.l.c. which showed starting material, *N*-methylphenanthridinone, and, in addition, traces of products with the correct R_F-values for the two stereoisomers of (1) reported previously. Repetition of the above pyrolysis for 1 h gave *N*-methylphenanthridinone (90%) as the only detectable product (*cf.* ref. 3).

(2) *Pyrolysis of* (16; R = Me) *in trichlorobenzene.* A solution of the dimer (120 mg) in trichlorobenzene (2 ml) was refluxed for 30 min, monitoring by t.l.c. after 1 min and 10 min. The reaction appeared to be complete after 1 min. G.l.c. analysis showed the formation of the 2′-methoxyspirodiene (23) (9%), *N*-methylphenanthridinone (19%), and 1-methoxy-*N*-methylphenanthridinone (23%). The remaining products appeared (t.l.c.) to be dimeric. The nature of these ' modified dimers ' is described later. The diene (23) was not isolated from this experiment but it has been isolated (m.p. 85—86°) in a related study, and its characterisation will be described elsewhere.[18]

(3) *Pyrolysis of* (17; R = Et) *in trichlorobenzene.* A solution of the dimer (20 mg) in trichlorobenzene (1 ml) was refluxed for 30 min, and chromatographed to remove solvent. The total product mixture was examined by t.l.c., which revealed only the starting dimer and product phenanthridinone. A solution of the dimer (30·5 mg) in trichlorobenzene (1 ml) was refluxed for 7 h, after which time a single reaction product, 2′-methoxy-*N*-ethylphenanthridinone (80%) was detected. 4-Methoxy-*N*-ethylphenanthridinone was not detected although it was stable to the reaction conditions.

(4) *Pyrolysis of* (4; R = Et) *in trichlorobenzene.* A solution of the dimer (66 mg) in trichlorobenzene (1 ml) was refluxed for 10 min. The reaction appeared to be complete within 2 min (t.l.c.). The only identified product was 3-methoxy-*N*-ethylphenanthridinone (53%). The spirodienone (31; R = Et), although stable to the reaction conditions, could not be detected (g.l.c., t.l.c.).

(5) *Pyrolysis of* (12) *in trichlorobenzene.* A solution of the dimer mixture of m.p. 150—180° (see above) (500 mg) in trichlorobenzene (5 ml), was boiled under reflux for 36 h, after which time t.l.c. indicated little further change was taking place. G.l.c. and t.l.c. showed the presence of two major products. These were separated from the trichlorobenzene by chromatography (combined yield 483 mg). The n.m.r. spectrum of the total product was consistent with its formulation as a 1 : 1 mixture of *N*-methylbenzo-[*a*]phenanthridinone and the dihydronaphthalene derivative (13) (see below). Crystallisation from ethanol gave *N*-methylbenzo[*a*]phenanthridinone, m.p. 119—120° (132 mg), identical with the sample obtained previously. From the alteration in the n.m.r. spectrum of the solute in the mother

---

* We have found a split carbonyl absorption to be a feature of all 3-substituted *N*-alkylphenanthridinones encountered in this work and have elsewhere used this feature diagnostically.[17]

† For numbering, see formula (8).

[15] D. H. Hey, G. H. Jones, and M. J. Perkins, in preparation.

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

[17] See refs. 14 and 16 and earlier papers in this series.

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

liquors, it was estimated that the yield of each product was 47%. The contents of the mother liquors were then chromatographed on a column of alumina which was eluted with methylene chloride. In this way a pure sample of the second product was isolated as a colourless oil which crystallised from benzene–light petroleum as colourless needles, m.p. 132—133°. Spectroscopic and analytical data were consistent with the formulation of this product as *2′-methyl-3′-oxo-*1,4-*dihydronaphthalenespiro-*1-*isoindoline* (13) (Found: C, 82·7; H, 5·6; N, 5·4. $C_{18}H_{15}NO$ requires C, 82·8; H, 5·7; N, 5·4%), $\nu_{max.}$ 1690 cm^{-1} (γ-lactam), τ 1·9—3·5 (8H, m, aromatic H), 3·6 (1H, d of t, vinyl H), 4·55 (1H, d of t, vinyl H), 6·35 (2H, m, benzylic CH_2), and 7·23 (3H, s, N-CH_3).

The spiro-dimer fraction (see details of preparation) (50 mg) was dissolved in boiling trichlorobenzene (1 ml), and the mixture refluxed for 1 min and cooled. The trichlorobenzene was removed by chromatography, and the reaction products were examined by t.l.c.; negligible phenanthridinone formation had occurred, but the chromatogram revealed a mixture of products identical with the synthetic dimer before chromatographic fractionation.

(6) *Pyrolysis of* (9) *in trichlorobenzene.* The crude dimer (700 mg) was dissolved in boiling trichlorobenzene and the mixture was refluxed until no further change in product composition was detected (t.l.c.) (*ca.* 30 min). Chromatography gave a phenanthridinone fraction (298 mg) which crystallised from ethanol as pale yellow needles, m.p. 120—130° (246 mg, 35%). This solid was shown by n.m.r. and g.l.c. to be a mixture of *N*-methylbenzo[*c*]phenanthridinone and *N*-methylbenzo[*b*]phenanthridinone in a ratio of *ca.* 3·3 : 1. Examination of the mother liquors from the crystallisation by g.l.c. revealed the presence of the same two isomers in comparable proportions, together with a trace of a product having the same retention characteristics as *N*-methylbenzo[*a*]phenanthridinone (*ca.* 1%).

(7) *Pyrolysis of* (4, R = Et) *in* p-*chlorotoluene.* A solution of the dimer (51 mg) in *p*-chlorotoluene (1 ml) (b.p. 162°) was refluxed for 2 h, after which time no dimer remained. G.l.c. indicated the formation of *3-methoxy-*N-*ethylphenanthridinone* (63%); this was isolated by column chromatography as a colourless oil which crystallised from ethanol–light petroleum, m.p. 86·5—87·5° (Found: C, 75·5; H, 5·9; N, 5·7. $C_{16}H_{15}NO_2$ requires C, 75·9; H, 5·9; N, 5·5%), $\nu_{max.}$ 1650 (γ-lactam) and 1615 cm^{-1} (3-substituted *N*-alkylphenanthridinone). The product was identical with one of the phenanthridinones isolated from the copper-catalysed decomposition of *N*-ethyl-3′-methoxybenzanilide-2-diazonium fluoroborate.[15] The structure was further supported by the n.m.r. spectrum which showed a highly perturbed ABX pattern for 1-H, 2-H, and 4-H. 1-H Appeared at τ 1·95, while 2-H and 3-H were almost coincident at τ 3·2. The pattern was approximated by computer simulation with $J_{1,2}$ = 9 Hz and $J_{2,4}$ = 2 Hz.

(8) *Pyrolysis of* (4, R = Me) *in chlorobenzene.* A solution of the dimer (33 mg) in chlorobenzene (1 ml) was refluxed overnight, after which t.l.c. showed that the dimer had completely decomposed. The yield of 3-methoxy-*N*-methylphenanthridinone (g.l.c.) was 75%. In a repetition of this experiment, heating was discontinued after 2 h. Solvent was removed, and a solution of the residual oil in 20% aqueous sulphuric acid was boiled under reflux overnight.[19] The mixture was cooled, extracted with chloroform, and the extract was examined by t.l.c. and g.l.c. No evidence could be found for the formation of benzocoumarins.*

(9) *Pyrolysis of* (4, R = Me) *in benzene-toluene.* A solution of the dimer (42 mg) in benzene-toluene (4 ml; b.p. 100°) was refluxed until the dimer had completely decomposed (5 days). The yield of 3-methoxy-*N*-methylphenanthridinone was 84%.

(10) *Pyrolysis of the dimer* (16, R = Me). This was investigated in several solvents with b.p. in the range 130—250°. With the exception of the reaction in ethylene glycol, the ratio of monomeric products to chemically modified dimeric material (' modified dimers ', see below) was *ca.* 1 : 1. The results of these reactions, in each of which *ca.* 30 mg of dimer and *ca.* 1 ml of solvent were employed, are summarised in Table 2. Reaction times were: α-chloronaphthalene, solution rapidly heated to boiling and cooled at once; *o*-dichlorobenzene, 2 h; *p*-chlorotoluene, 15 h; chlorobenzene, 250 h. A reaction in ethylene glycol (b.p. 195°) for 1 h gave (g.l.c.) 1-methoxy-*N*-methylphenanthridinone (11%) and *N*-methylphenanthridinone (25%), but no detectable diene (23). In a larger scale reaction, the dimer (1 g) and *o*-dichlorobenzene (5 ml) were boiled under reflux for 2 h, solvent was removed, and the products were carefully chromatographed in order to fractionate the dimeric product. A major fraction (*ca.* 250 mg), obtained as an amorphous pale yellow solid, has been tentatively identified as a 1 : 1 mixture of the half-rearranged dimers (24) and (25); $\nu_{max.}$ 1690 (γ-lactam), 1650 (δ-lactam), and 1610 cm^{-1} (3-substituted *N*-alkylphenanthridinone), τ 0·8 (0·5H, d, H-10), 1·5—2·8 (*ca.* 9H, m), 3·7 (1H, broad d, 5′-H), 4·65 (2H, m, 3′-H and 6′-H), 5·45 (1H, broad s, 4′-H), 5·9 (1½H, 2s, $O-Me^4$), 6·2 (3H, 2s, $N-Me^2$), 6·6 (3H, s, $O-Me^3$), 7·0 (3H, 2s, N-Me′). An additional product in a further dimer fraction has been tentatively identified (t.l.c. comparison with authentic material [18]) as 3,3′-bi-*N*-methylphenanthridinone.

(11) *Pyrolysis of* (16, R = Me) *in* 9,10-*dihydroanthracene.* The dimer (208 mg) and 9,10-dihydroanthracene (1 g) were heated at 130° until the mixture became homogeneous. The mixture was then rapidly heated to boiling point (*ca.* 5 s), and at once cooled to room temperature. No dimeric products were detected by t.l.c. After chromatographic removal of hydrocarbon, examination of the total reaction product both by g.l.c. and by n.m.r. revealed it to be predominantly a mixture of 1-methoxy-*N*-methylphenanthridinone (34%), *N*-methylphenanthridinone (34%), diene (23) (14%), and 2′-methoxy-*N*-methylbiphenyl-2-carboxamide. A trace of benzocoumarin (<0·5%) was detected by g.l.c.; this was isolated by repetitive chromatography, and its identity established by comparison of its i.r. spectrum with that of an authentic sample.

The pyrolysis of (16, R = Me) (1·5 g) in the presence of 9,10-dihydroanthracene (6 g) was repeated in solution in *p*-chlorotoluene (10 ml). The mixture was refluxed for 20 h, after which analysis (g.l.c., n.m.r.) indicated the formation of 1-methoxy-*N*-methylphenanthridinone (38·5%), *N*-methylphenanthridinone (23·5%), diene (23) (25%), 2′-methoxy-*N*-methylbiphenyl-2-carboxamide (5%), and a trace of benzocoumarin. Chromatography on alumina gave a fraction containing the diene (23), and the biphenylcarboxamide (together 465 mg). This mixture

---

* We are grateful to Professor R. H. Thomson for a reference sample of 7-methoxybenzocoumarin.

[19] C. J. M. Stirling, *J. Chem. Soc.*, 1960, 255.

(300 mg) in benzene (10 ml) was added to a solution of potassium t-butoxide (300 mg) in t-butyl alcohol (10 ml). The combined solutions were boiled briefly, cooled, and diluted with benzene; the solution was washed with water. The benzene solution was dried ($MgSO_4$) and the solvent removed. A trace of the 2′-methoxy-derivative [14] of the diene (31) was detected in the product (g.l.c.). This was removed by borohydride reduction in boiling ethanol, and subsequent chromatography of the products on a column of alumina; the major fraction, a colourless oil which crystallised from ethanol–light petroleum, m.p. 113—115°, was identified as *2′-methoxy-N-methylbiphenyl-2-carboxamide* [Found: *M*, 241·1101 (m.s.). $C_{15}H_{15}NO_2$ requires $M = 241{\cdot}1103$], $\nu_{max.}$ 3300 and 1630 (ArCONHR); τ 2·2—3·3 (8H, m), 4·6 (1H, broad s, N-H), 6·3 (3H, s, O-CH_3), and 7·4 (3H, d, NHCH_3).

(12) *Pyrolysis of the dimer* (12) *with dihydroanthracene.* A solution of the dimer (100 mg) and 9,10-dihydroanthracene (500 mg) in trichlorobenzene (1 ml) was refluxed for 10 min. T.l.c. showed decomposition to be complete, and two products were detected, *N*-methylbenzo[*a*]phenanthridinone (*ca.* 4—5%) and the dihydronaphthalene (13) (95—96%).

(13) *Pyrolysis of the dimer* (1) *with dihydroanthracene.* The dimer (30 mg) and 9,10-dihydroanthracene were heated together at 210° for 30 min. Only one product, *N*-methylphenanthridinone, was detected by g.l.c. and t.l.c.

(14) *Pyrolysis of the dimer* (4, R = Et) *in the presence of iodine.* A solution of the dimer (35 mg) and iodine (23 mg) in trichlorobenzene (1 ml) was refluxed for 1 min. The only identifiable product (t.l.c., g.l.c.) was the dienone (31, R = Et) (84%).

We are grateful to the S.R.C. for the award of a studentship (G. H. J.), and to King's College, London for financial assistance.

[1/1564 *Received, August* 26*th*, 1971]