43. *Internuclear Cyclisation. Part XVI.* Abnormal Reactions of Diazonium Salts from* N-*Alkyl-2-amino-2′- and -4′-methoxybenzanilides. A New Dienone–Phenol Rearrangement.*

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Thermal decomposition of an aqueous solution of the diazonium sulphate from 2-amino-*N*-ethyl-4′-methoxybenzanilide (I) did not give the normal product of ring-closure, 10-ethyl-3-methoxyphenanthridone, but the spirodienone (III). This results from attack at the nuclear carbon atom *para* to the methoxyl group which also carries the *N*-ethyl group, and loss of the methyl from the methoxyl group. A similar reaction occurred with the corresponding *N*-methyl compound and with the 2′-methoxy-isomer of (I). The dienone (III), though remarkably stable to acid, underwent the dienone–phenol rearrangement to give 10-ethyl-3-hydroxyphenanthridone (IV), and was reduced to the dienol (VII). This dienol was rearranged by acid to 10-ethylphenanthridone (VI) and by alkali to *N*-ethyl-4′-hydroxybiphenyl 2-carboxyamide (VIII). Independent syntheses of these products of rearrangement are described and reaction mechanisms proposed.

In the extension of the Pschorr phenanthrene synthesis for the preparation of phenanthridones anomalous reactions have already been reported in the attempted preparation of 1-substituted 10-methylphenanthridones[1] and in the preparation of 10-phenylphenanthridones.[2] A further anomalous reaction has now been investigated which occurs in the attempted preparation of 1- and 3-methoxy-10-alkylphenanthridones.

It has already been reported[3] that 3-substituted 10-methylphenanthridones can be prepared in the normal manner from 4′-substituted 2-amino-*N*-methylbenzanilides $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4R\text{-}p$ where R is Me, Br, Cl, or NO_2. When the reaction was applied to 2-amino-4′-methoxy-*N*-methylbenzanilide a product was obtained which consistently gave an analytical result agreeing with a molecular formula with one carbon atom and two hydrogen atoms less than are required by the expected 3-methoxy-10-methylphenanthridone. After completion of these experiments it was reported by Govindachari and Arumugam[4] that 2-amino-*N*-ethyl-4′-methoxybenzanilide could be converted into 3-methoxy-10-ethylphenanthridone, although in a later communication[5] these authors, on the basis of the ultraviolet spectrum, stated that the product of this reaction could not be a derivative of phenanthridone. No alternative structure was put forward. In an attempt to explain these reactions further work has now been carried out on reactions with 2-amino-*N*-ethyl-2′-methoxybenzanilide, 2-amino-*N*-ethyl-4′-methoxybenzanilide (I), and 2-amino-4′-methoxy-*N*-methylbenzanilide.

The amines, 2-amino-*N*-ethyl-2′- and -4′-methoxybenzanilide, prepared as described by Govindachari and Arumugam,[4] were diazotised and decomposed thermally in aqueous acid. Purification of the products by chromatography yielded, together with the corresponding phenols, a single pure compound in each case, with melting points in agreement with those reported[4] but with differences in the ultraviolet absorption spectra.

Since the product, m. p. 137—138°, from 2-amino-*N*-ethyl-4′-methoxybenzanilide (I), was available in larger quantity further investigation centred upon this compound. The infrared spectrum showed peaks at 1668 and 1692 cm.$^{-1}$, which indicated the possible presence of a carbonyl group in addition to the expected amide-carbonyl function. This was confirmed by the formation of a dinitrophenylhydrazone and an oxime. Elementary

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* Part XV, *J.*, 1959, 4110.

[1] Hey and Turpin, *J.*, 1954, 2471.

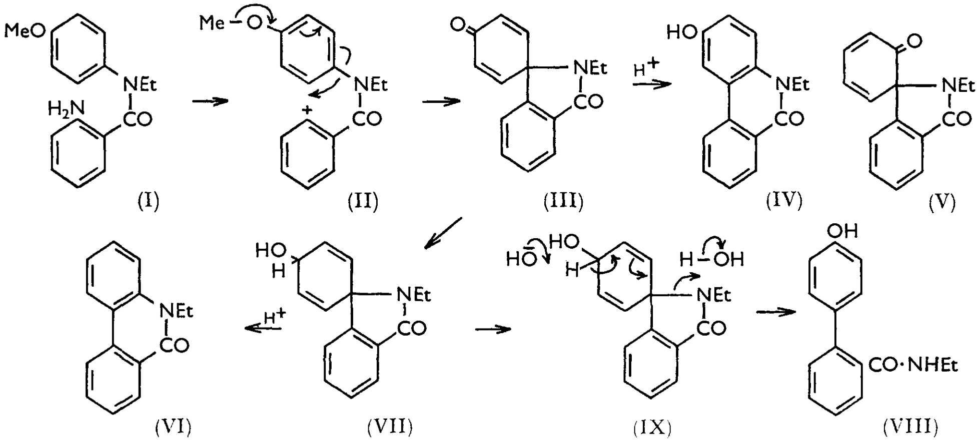
[2] Hey and Moynehan, *J.*, 1959, 1563.

[3] Heacock and Hey, *J.*, 1952, 4059; 1953, 3.

[4] Govindachari and Arumugam, *J. Sci. Ind. Res. India*, 1954, **13**, 694.

[5] Govindachari and Arumugam, *J. Sci. Ind. Res. India*, 1955, **14**, 250.

analysis and molecular-weight determination on the compound and its derivatives were consistent with a molecular formula $C_{15}H_{13}O_2N$, indicating the loss of a carbon atom from the original amine. That the *N*-ethyl group was not involved in this abnormal reaction was shown by the entirely analogous behaviour of the corresponding *N*-methyl compound. 4′-Methoxy-2-nitrobenzanilide was prepared from *o*-nitrobenzoyl chloride and *p*-anisidine and methylated with dimethyl sulphate, and the product was reduced catalytically to 2-amino-4′-methoxy-*N*-methylbenzanilide (I; Me instead of Et). Thermal decomposition of an aqueous solution of the corresponding diazonium sulphate gave a product, m. p. 217—218°, which exhibited very similar ultraviolet and infrared absorption to the *N*-ethyl compound, m. p. 137—138°, and similarly formed a 2,4-dinitrophenylhydrazone and had a molecular formula, $C_{14}H_{11}O_2N$, corresponding to the loss of one carbon atom. The strong absorption band at 1668 cm.$^{-1}$ due to the carbonyl group in these two products is in very close agreement with that attributed to the cross-conjugated carbonyl group of the cyclohexadienone system in, for example, steroidal dienones (1666—1663 cm.$^{-1}$),[6] geodin (1665 cm.$^{-1}$) and erdin (1667 cm.$^{-1}$),[7] and picrolichenic acid and its derivatives (1670—1665 cm.$^{-1}$).[8] Further, the ketone, on quantitative hydrogenation in ethanol over Adams catalyst, reacted with 1·95 mol. of hydrogen to yield a saturated ketone, m. p. 150°, with the carbonyl absorption shifted to 1717 cm.$^{-1}$ (saturated six-membered cyclic ketone). On the basis of these observations and the results, described below, of reactions carried out on these compounds, it is proposed that the product from (I) is 2-ethylisoindoline-1-spiro-1′-cyclohexadiene-3,4′-dione (III), and that from the isomeric *o*-methoxy-compound has the corresponding *o*-quinonoid structure (V). The latter product showed a broad maximum in the ultraviolet spectrum at 335 mμ (log ε 3·8) and a peak in the infrared spectrum at 1678 cm.$^{-1}$ characteristic of linearly conjugated cyclohexadienones.[6,8] The dienone (III) would result from electrophilic attack by the carbonium ion, formed from the diazonium ion by loss of nitrogen, at the carbon atom *para* to the methoxyl group, as shown in (II), the methyl group being lost, presumably as methanol. The alternative free-radical mechanism is perhaps less likely under the present conditions of thermal decomposition in aqueous acid; decomposition of the diazonium borofluoride by copper powder in acetone, conditions known to favour a radical mechanism, yields different products which will be described later.



Treatment of the dienone (III) with aqueous alkali yielded highly coloured decomposition products. Attempted reduction of it by the Wolff–Kishner method caused a breakdown of the molecule and the only product isolated was biphenyl-2-carboxylic acid. This

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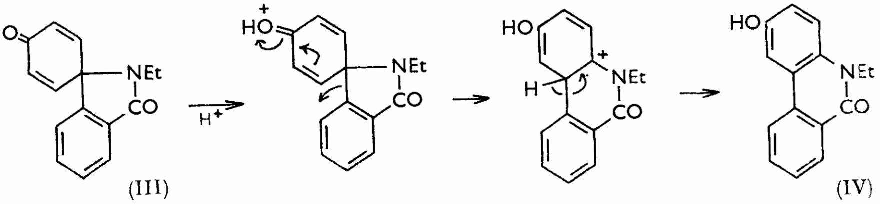
[6] Jones, Humphries, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 958.
[7] Barton and Scott, *J.*, 1958, 1767.
[8] Wachtmeister, *Acta Chem. Scand.*, 1958, **12**, 147.

observation provided the first evidence of the existence of a bond between the two benzene rings. The dienone (III) was stable to prolonged boiling with concentrated hydrochloric acid, but 100% phosphoric acid at 170° isomerised it to a phenol, m. p. 260°, identified as 10-ethyl-3-hydroxyphenanthridone (IV), an independent synthesis of which is described below. Thus the spiran (III) has undergone the dienone–phenol rearrangement as illustrated. This is thought to be the first example of the dienone–phenol rearrangement involving a nitrogen-heterocyclic ring. The striking stability of the dienone (III) to acid is noteworthy; the compound was also stable to acetic anhydride containing sulphuric acid at room temperature, the usual conditions for this rearrangement,[9] but it rearranged when heated in this medium at 107° for 2 hr., to give 3-acetoxy-10-ethylphenanthridone. Reduction of the dienone (III) with sodium borohydride in methanol gave the alcohol (VII), m. p. 170—178°, which may be a mixture of stereoisomers. When heated with hydrochloric acid this alcohol underwent the dienol–benzene rearrangement,[10] analogous to the dienone–phenol rearrangement of (III), to give 10-ethylphenanthridone (VI). The alcohol (VII) was isomerised by sodium hydroxide to a phenol, m. p. 184—185°, which yielded a diacetyl derivative. This product has been identified as *N*-ethyl-4′-hydroxybiphenyl-2-carboxyamide (IX) by mixed-melting-point determinations and infrared comparison with the independently synthesised product and its diacetyl derivative. Thus the rearrangement shown in (VIII) has occurred. 4′-Hydroxybiphenyl-2-carboxylic acid was prepared by heating fluorene-2-sulphonic acid with potassium hydroxide in diphenyl ether in a modification of Huntress and Seikel's method [11] and converted into its ethylamide *via* the acid chloride.



(III) (IV)

3-Nitrophenanthridone [12] was methylated, to yield 10-methyl-3-nitrophenanthridone identical with an authentic specimen,[3] thus confirming the position of the nitro-group. Diethyl sulphate converted 3-nitrophenanthridone into 10-ethyl-3-nitrophenanthridone, m. p. 216°, and an isomer, m. p. 159·5—161°, whose melting point was unaltered on crystallisation from ethanol, benzene, or light petroleum. This product was shown not to be 10-ethyl-1-nitrophenanthridone which would have been formed from any 1-nitro-isomer in the starting material. The *O*-ethyl compound, 9-ethoxy-3-nitrophenanthridine was synthesised from the 9-chloro-compound and sodium ethoxide and found to have m. p. 180—180·5°. The unknown product, m. p. 159·5—161°, was then subjected to chromatography on alumina which separated it into two compounds identical with 9-ethoxy-3-nitrophenanthridine and 10-ethyl-3-nitrophenanthridone respectively. The formation of a relatively large amount (27%) of the *O*-alkyl derivative with diethyl sulphate in alkaline-aqueous acetone, conditions which normally lead almost exclusively to *N*-alkylation, must presumably be attributed to electron-withdrawal from the amide-nitrogen atom by the *p*-nitro-group. Assignment of the *O*-ethyl and *N*-ethyl structure severally to these isomers was confirmed by their ultraviolet and infrared spectra. 10-Ethyl-3-nitrophenanthridone was reduced catalytically to the amine which was diazotised in sulphuric acid and converted into 10-ethyl-3-hydroxyphenanthridone (IV).

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[9] Woodward and Singh, *J. Amer. Chem. Soc.*, 1950, **72**, 494.
[10] Gentle, Moss, Hertzog, and Hershberg, *J. Amer. Chem. Soc.*, 1958, **80**, 3702.
[11] Huntress and Seikel, *J. Amer. Chem. Soc.*, 1939, **61**, 816.
[12] Caldwell and Walls, *J.*, 1952, 2163.

EXPERIMENTAL

Ultraviolet spectra were determined for ethanol solutions, and infrared spectra for Nujol mulls.

2-Amino-*N*-ethyl-2′-methoxybenzanilide and 2-amino-*N*-ethyl-4′-methoxybenzanilide were prepared as described by Govindachari and Arumugam.[4] The former was obtained in plates, m. p. 99—101°, from aqueous methanol (Found: C, 71·2; H, 6·5. Calc. for $C_{16}H_{18}N_2O_2$: C, 71·1; H, 6·7%) and gave a benzoyl derivative, m. p. 133°; Govindachari and Arumugam [4] described this base as a viscous oil, which gave a benzoyl derivative, m. p. 133°. The second anilide was obtained in prisms, m. p. 101—102° (from ethanol) (Found: C, 71·2; H, 6·6%), from the corresponding 2-nitro-compound, which separated from ethanol in pale green needles, m. p. 74—75° (Found: C, 63·8; H, 5·3. Calc. for $C_{16}H_{16}N_2O_4$: C, 64·0; H, 5·3%). Govindachari and Arumugam [4] reported m. p. 102° for the base and m. p. 66° for the nitro-compound.

4′-Methoxy-2-nitrobenzanilide.—*o*-Nitrobenzoyl chloride (17 g.) in ether (50 ml.) was added dropwise to *p*-anisidine (10 g.) in a mixture of pyridine (15 ml.) and ether (50 ml.), and the mixture was boiled under reflux for 1 hr. The ether was removed and the residue poured into water. Crystallisation of the precipitated solid from ethanol gave *4′-methoxy-2-nitrobenzanilide* (18·5 g.) as yellow needles, m. p. 168—169° (Found: C, 61·9; H, 4·2. $C_{14}H_{12}N_2O_4$ requires C, 61·8; H, 4·4%).

*2-Amino-4′-methoxy-*N*-methylbenzanilide.*—4′-Methoxy-2-nitrobenzanilide (12 g.) in acetone (150 ml.) and 10% aqueous sodium hydroxide (150 ml.) was boiled under reflux and dimethyl sulphate (20 ml.) was added dropwise. The solution was boiled for 15 min. and then poured into water. The precipitate crystallised from ethanol, to give *4′-methoxy-*N*-methyl-2-nitrobenzanilide* (11·8 g.) as pale yellow needles, m. p. 144—146° (Found: C, 63·5; H, 5·0. $C_{15}H_{14}N_2O_4$ requires C, 62·9; H, 4·9%). A solution of this nitro-compound (4 g.) in benzene (100 ml.) with Raney nickel (4 g.) was hydrogenated at room temperature and pressure. Filtration, removal of the solvent, and recrystallisation of the residue from ethanol gave *2-amino-4′-methoxy-*N*-methylbenzanilide* (2·8 g.) in needles, m. p. 105—107° (Found: C, 70·0; H, 6·1. $C_{15}H_{16}N_2O_2$ requires C, 70·3; H, 6·2%).

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-*N*-ethyl-2′-methoxybenzanilide.*—The amine (2·7 g.), suspended in 5% sulphuric acid (100 ml.), was diazotised at 0° with aqueous sodium nitrite (0·8 g. in 10 ml.). After being stirred at 0° for 1 hr. the mixture was gradually warmed to 70° and kept at that temperature for 1 hr. The mixture was then extracted with chloroform, and the extract was washed with aqueous sodium hydroxide and dried (Na_2SO_4). Removal of the solvent left a brown oil, which was dissolved in benzene–light petroleum and adsorbed on alumina (80 g.). Elution with benzene–light petroleum (800 ml.) gave gums (0·61 g.). Elution with benzene (1200 ml.) gave a brown solid gum (0·38 g.), which on crystallisation from light petroleum gave *2-ethylisoindoline-1-spiro-1′-cyclohexadiene-2′,3-dione* (V) (0·22 g.) in pale yellow needles, m. p. 117—118° (Found: C, 74·9; H, 5·1. $C_{15}H_{13}NO_2$ requires C, 75·3; H, 5·4%). Govindachari and Arumugam [4] obtained a compound, m. p. 117°, from a similar reaction. Further elution with benzene–ether, ether, and ethanol gave only tars (0·94 g.). The alkaline washings gave a yellow oil (0·17 g.).

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-*N*-ethyl-4′-methoxybenzanilide* (I).—The amine (3 g.) was diazotised and decomposed as described for the previous experiment. The product in benzene was adsorbed on alumina (80 g.). Elution with benzene–light petroleum (1 : 1, 200 ml.; and 2 : 1, 500 ml.) gave gums (0·15 g.). Elution with benzene (1 l.) and benzene–ether (2 : 1; 300 ml.) gave a yellow solid, which crystallised from light petroleum, to give *2-ethylisoindoline-1-spiro-1′-cyclohexadiene-3,4′-dione* (III) (1·45 g.) in needles, m. p. 137—138° (Found: C, 75·4; H, 5·3; N, 5·8; O, 13·5%; *M*, 208. $C_{15}H_{13}NO_2$ requires C, 75·3; H, 5·4; N, 5·9; O, 13·4%; *M*, 239). Govindachari and Arumugam [4] obtained a compound, m. p. 138°, in smaller yield from a similar reaction. The *2,4-dinitrophenylhydrazone* separated from ethyl acetate in orange-red needles, m. p. 219—222° (Found: C, 59·8; H, 4·3%; *M*, 412. $C_{21}H_{17}N_5O_5$ requires C, 60·1; H, 4·1%; *M*, 419). The *oxime* separated from ethanol in prisms, m. p. 257° (decomp.) (Found: C, 70·0; H, 5·5. $C_{15}H_{14}N_2O_2$ requires C, 70·8; H, 5·5%). Elution with methanol gave a tar (0·08 g.). The alkaline washings, on acidification, gave *N-ethyl-2-hydroxy-4′-methoxybenzanilide* (0·5 g.), which separated from aqueous ethanol in needles, m. p. 133—134° (Found: C, 71·0; H, 6·5. $C_{16}H_{17}NO_3$ requires C, 70·8; H, 6·3%).

Decomposition of the Diazonium Sulphate prepared from 2-*Amino*-4′-*methoxy*-N-*methylbenzanilide*.—The amine (2 g.) was diazotised and decomposed, as described above for the *N*-ethyl compounds, and the product, in benzene, was adsorbed on alumina (80 g.). Elution with benzene (300 ml.) gave brown tars; more benzene (800 ml.) and benzene–ether (1 : 1; 600 ml.) gave a white solid which crystallised from ethanol to give 2-*methylisoindoline*-1-*spiro*-1′-*cyclohexadiene*-3,4′-*dione* (0·7 g.) in prisms, m. p. 217—218° (Found: C, 74·2; H, 4·9; N, 6·05. $C_{14}H_{11}NO_2$ requires C, 74·6; H, 4·9; N, 6·2%). The 2,4-*dinitrophenylhydrazone* crystallised from ethyl acetate in orange-red needles, m. p. 234—235° (Found: C, 58·7; H, 3·4; N, 17·3. $C_{20}H_{15}N_5O_5$ requires C, 59·2; H, 3·7; N, 17·3%). Elution with ether and methanol gave tars (0·13 g.). Acidification of the alkaline washings gave 2-*hydroxy*-4′-*methoxy*-N-*methylbenzanilide* (0·32 g.), which crystallised from aqueous ethanol in pale fawn plates, m. p. 152—153° (Found: C, 69·6; H, 5·8. $C_{15}H_{15}NO_3$ requires C, 70·0; H, 5·8%).

Reactions of 2-*Ethylisoindoline*-1-*spiro*-1′-*cyclohexadiene*-3,4′-*dione* (III).—(a) *Decomposition of the hydrazone.* The dienone (0·15 g.) was subjected to the Huang-Minlon modification of the Wolff–Kishner reduction.[13] The alkaline reaction mixture, on dilution with water and extraction with ether, gave only a yellow gum. The alkaline solution was acidified and extracted with ether. Concentration of the dried (Na_2SO_4) extract gave a solid, which crystallised from aqueous ethanol to give biphenyl-2-carboxylic acid (0·05 g.), m. p. and mixed m. p. 112—114°.

(b) *Reaction with phosphoric acid.* The dienone (0·2 g.), in 100% phosphoric acid (5 g.), was heated to 170° for 2 hr. The solid which was precipitated on addition of water crystallised from ethanol, to give 3-*hydroxy*-10-*ethylphenanthridone* (0·16 g.) in prisms, m. p. and mixed m. p. 260° (Found: C, 75·4; H, 5·5; N, 6·1. $C_{15}H_{13}NO_2$ requires C, 75·3; H, 5·4; N, 5·9%), $\lambda_{\max.}$ 232, 239, 266, and 346 mμ (log ε 4·63, 4·61, 4·20, and 3·92). When this compound was left in acetic anhydride containing a few drops of concentrated sulphuric acid the *acetyl derivative* was obtained which crystallised from aqueous ethanol in needles, m. p. and mixed m. p. 150° (Found: C, 72·6; H, 5·3. $C_{17}H_{15}NO_3$ requires C, 72·6; H, 5·3%).

(c) *Reaction with acetic anhydride and sulphuric acid.* The dienone (0·052 g.) in acetic anhydride (3 ml.) was added to acetic anhydride (3 ml.) containing sulphuric acid (0·08 g.), and the mixture heated at 107° for 2 hr. and then poured into water (20 ml.). The 3-acetoxy-10-ethylphenanthridone (0·022 g.) which separated had m. p. and mixed m. p. 151°. More of this acetyl derivative (0·018 g.) was isolated from the aqueous solution, after neutralisation, by ether-extraction. When the dienone was treated similarly at 100° for 30 min., 23% was recovered, and after 22 hr. at room temperature 92% was recovered.

(d) *Action of sodium borohydride.* Sodium borohydride (0·1 g.) in methanol (15 ml.) was added dropwise to the dienone (0·2 g.) in methanol (20 ml.), and the mixture kept at room temperature for 2 hr. Water (25 ml.) was added and the solution saturated with potassium carbonate and extracted with ether. Evaporation of the dried (Na_2SO_4) extract and recrystallisation of the residue from aqueous ethanol and repeatedly from benzene gave 2-*ethyl*-4′-*hydroxyisoindoline*-1-*spiro*-1′-*cyclohexadien*-3-*one* (VII) (0·17 g.) in prisms, m. p. 170—178° (Found: C, 75·0; H, 6·2; N, 6·1. $C_{15}H_{15}NO_2$ requires C, 74·7; H, 6·2; N, 5·8%).

(e) *Hydrogenation.* The dienone (0·0955 g.) in ethanol (10 ml.), containing Adams catalyst (0·092 g.) and saturated with hydrogen, absorbed hydrogen (19·5 ml., 1·95 mol.) in 6 hr. The solution was filtered and evaporated and the residue crystallised from benzene–light petroleum, to give 2-*ethylisoindoline*-1-*spiro*-1′-*cyclohexane*-3,4′-*dione* (0·074 g.) in prisms, m. p. 149—150° (Found: C, 74·6; H, 7·5. $C_{15}H_{17}NO_2$ requires C, 74·1; H, 7·0%). This reduction product gave a positive test with the 2,4-dinitrophenylhydrazine reagent.

Reactions of 2-*Ethyl*-4′-*hydroxyisoindoline*-1-*spiro*-1′-*cyclohexadien*-3-*one* (VII).—(a) *Action of hydrochloric acid.* The dienol (0·2 g.) in concentrated hydrochloric acid (20 ml.) and ethanol (5 ml.) was boiled under reflux for 6 hr., poured into water, and extracted with chloroform. The extract was dried (Na_2SO_4) and the solvent removed. Crystallisation of the residue from light petroleum gave 10-ethylphenanthridone (0·16 g.), m. p. and mixed m. p. with an authentic specimen prepared by the method of Graebe and Wander,[14] 99—100° (lit.,[4,14] m. p. 89°).

(b) *Action of sodium hydroxide.* The dienol (0·2 g.) in a mixture of 10% aqueous sodium hydroxide (20 ml.) and ethanol (3 ml.) was boiled under reflux for 2 hr. The solution was acidified with hydrochloric acid and extracted with chloroform. The dried (Na_2SO_4) extract

[13] Huang-Minlon, *J. Amer. Chem. Soc.*, 1948, **70**, 2802.

[14] Graebe and Wander, *Annalen*, 1893, **276**, 245.

was evaporated and crystallisation of the residue from aqueous ethanol gave N-*ethyl*-4′-*hydroxybiphenyl*-2-*carboxyamide* (0·16 g.) in plates, m. p. and mixed m. p. 184—185° (Found: C, 74·5; H, 6·4; N, 5·6. $C_{15}H_{15}NO_2$ requires C, 74·7; H, 6·2; N, 5·8%), $\lambda_{max.}$ 209 and 262 mμ (log ε 4·25 and 3·93). When this amide was heated in acetic anhydride containing a few drops of sulphuric acid on a water-bath for 30 min. a *diacetyl derivative* was formed, which crystallised from aqueous ethanol in plates, m. p. and mixed m. p. 103—104° (Found: C, 69·6; H, 5·8; N, 4·5. $C_{19}H_{19}NO_4$ requires C, 70·1; H, 5·8; N, 4·3%).

3-Nitrophenanthridone [12] was methylated with dimethyl sulphate in alkaline aqueous acetone to give 10-methyl-3-nitrophenanthridone, m. p. and mixed m. p. with an authentic specimen,[3] 253°.

Reaction of 3-*Nitrophenanthridone with Diethyl Sulphate.*—3-Nitrophenanthridone [12] (4 g.) in acetone (100 ml.) and 10% aqueous sodium hydroxide (50 ml.) was boiled under reflux and diethyl sulphate (6·7 ml.) was added dropwise. The solution was boiled for 25 min., cooled, and poured into water. The yellow precipitate was recrystallised successively from benzene, ethanol, and light petroleum (b. p. 100—120°), to give 10-*ethyl*-3-*nitrophenanthridone* (2·13 g.) as a pale yellow powder, m. p. 216° (Found: C, 66·8; H, 4·4; N, 10·4. $C_{15}H_{12}N_2O_3$ requires C, 67·2; H, 4·5; N, 10·4%), $\lambda_{max.}$ 226, 252, 263, and 341 mμ (log ε 4·41, 4·22, 4·21, and 3·96 respectively). The benzene mother-liquor, on concentration, gave a yellow powder (1·72 g.), m. p. 159·5—161° (Found: C, 67·0; H, 4·5; N, 10·5. Calc. for $C_{15}H_{12}N_2O_3$: C, 67·2; H, 4·5; N, 10·4%), $\lambda_{max.}$ 226, 232, 246, and 324 mμ (log ε 4·34, 4·35, 4·35, and 4·04 mμ respectively), whose m. p. was unaltered on crystallisation from ethanol or benzene and undepressed when mixed with 10-ethyl-3-nitrophenanthridone. This product (0·64 g.) in benzene was adsorbed on alumina and eluted with benzene (200 ml.) which gave a yellow solid (0·38 g.), m. p. and mixed m. p. with 9-ethoxy-3-nitrophenanthridine, 181°. Elution with benzene–ethanol (4 : 1; 300 ml.) gave a yellow solid (0·25 g.), m. p. and mixed m. p. with 10-ethyl-3-nitrophenanthridone, 216°.

9-*Ethoxy*-3-*nitrophenanthridine.*—3-Nitrophenanthridone (0·58 g.), phosphorus pentachloride (0·54 g.), and phosphoryl chloride (6 ml.) were heated at 130° for 5 hr. The mixture was poured on ice, and the solid which separated crystallised from benzene in needles of 9-*chloro*-3-*nitrophenanthridine* (0·49 g.), m. p. 251° (Found: C, 60·4; H, 2·8. $C_{13}H_7ClN_2O_2$ requires C, 60·1; H, 2·7%). A suspension of this chloro-compound (0·2 g.) in ethanol (40 ml.) was added to sodium ethoxide (from sodium, 0·24 g.) in ethanol (10 ml.), and the mixture boiled under reflux for 4 hr. The solution was concentrated, water was added, the mixture was extracted with ether, and the extracts were dried ($MgSO_4$). Removal of the ether gave 9-*ethoxy*-3-*nitrophenanthridine* (0·17 g.) which crystallised from ethanol (charcoal) in pale yellow needles, m. p. 180—180·5° (Found: C, 66·9; H, 4·7; N, 10·2. $C_{15}H_{12}N_2O_3$ requires C, 67·2; H, 4·5; N, 10·4%).

3-*Amino*-10-*ethylphenanthridone.*—10-Ethyl-3-nitrophenanthridone (0·83 g.) in ethanol (350 ml.) containing 10% palladised charcoal (0·1 g.) was shaken with hydrogen, uptake of which was complete in 2 hr. The *amine*, obtained in quantitative yield, crystallised from benzene–light petroleum (b. p. 60—80°) and then had m. p. 165·5° (Found: C, 74·9; H, 5·9; N, 11·9. $C_{15}H_{14}N_2O$ requires C, 75·6; H, 5·9; N, 11·8%).

10-*Ethyl*-3-*hydroxyphenanthridone.*—3-Amino-10-ethylphenanthridone (0·5 g.) in water (40 ml.) containing sulphuric acid (5 ml.) was diazotised at 0° with aqueous sodium nitrite (0·5 g. in 10 ml.) and stirred at 0° for 30 min. Water (25 ml.) was added, and the solution was gradually heated to 100°, kept at that temperature for 2 hr., made alkaline, filtered, and acidified. The orange precipitate crystallised from aqueous ethanol (charcoal) in pale orange prisms, m. p. and mixed m. p. 260° with the dienone–phenol rearrangement product described above. The infrared spectra of these two samples were identical. The acetyl derivative had m. p. and mixed m. p. 150°.

N-*Ethyl*-4′-*hydroxybiphenyl*-2-*carboxyamide.*—A suspension of sodium fluorene-2-sulphonate [15] (5 g.) in diphenyl ether (60 ml.) was added to a vigorously stirred emulsion of potassium hydroxide (12 g.) in hot diphenyl ether (70 ml.). After 4 hours' heating at 180° with stirring, the mixture was cooled and extracted with water (100 ml.), and the aqueous solution was acidified. The dark brown precipitate crystallised from water (charcoal) in pale yellow needles of 4′-hydroxybiphenyl-2-carboxylic acid (13%), m. p. 205·5°. The infrared absorption bands

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[15] Wedekind and Stüsser, *Ber.*, 1923, **56**, 1561.

at 759 (1,2-disubstituted benzene) and 830 cm.$^{-1}$ (1,4-disubstituted benzene) confirm the structure of this acid.

This acid (0·4 g.) was boiled under reflux with thionyl chloride (1 ml.) for 40 min. and excess of thionyl chloride was then removed by distillation with benzene. 33% Aqueous ethylamine (4 ml.) at 0° was added to the residue dissolved in acetone (2 ml.) at 0°, and the mixture was stirred for 30 min. The brown oil which separated crystallised from aqueous ethanol and then from ethanol–benzene in large prisms of the amide, m. p. and mixed m. p. 185° with the product of alkaline hydrolysis of the dienol (VII). These two specimens had identical infrared spectra. The diacetyl derivatives had m. p. and mixed m. p. 102—103°.

10-*Ethyl*-1-*nitrophenanthridone*.—1-Nitrophenanthridone [12] was ethylated with diethyl sulphate in the usual way, to give 10-*ethyl*-1-*nitrophenanthridone* which, crystallised from ethanol, had m. p. 127° (Found: C, 67·9; H, 4·6; N, 10·3. $C_{15}H_{12}N_2O_3$ requires C, 67·2; H, 4·5; N, 10·4%).

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